calculated by one of us.[5] A recalculation using new constants and slightly different structural parameters has been made; the two calculations agree to 0.1 cal./deg./mole. The constants used were 0°C. = 273.16°K., R = 1.9871 cal./deg./mole, $k = 1.3805 \times 10^{-16}$ erg/sec./molecule, $N = 6.023 \times 10^{23}$, $h = 6.624 \times 10^{-27}$ erg sec. The frequencies used were[6] 707, 341, 644(2), 274(2) cm.$^{-1}$. The moments of inertia were calculated from the results of a recent reinvestigation of the structure by electron diffraction.[7] The symmetry is C_{3v}, the As-F distance is 1.73 Å., and the F-As-F angle is 96.5 ± 2°. The results are summarized in Table VIII and compared with the calorimetric value of the entropy.

TABLE VIII

THE ENTROPY OF ARSENIC TRIFLUORIDE FROM MOLECULAR AND CALORIMETRIC DATA

	Spectroscopic entropy cal./deg./mole	Calorimetric entropy cal./deg./mole
Translational and rotational entropy	63.517	
Vibrational entropy	5.263	
Entropy at 1 atm. press. and 292.50°K.	68.78	
Entropy at 141.6 mm. press. and 292.50°K.	72.12±0.10	72.09±0.15
Entropy at 1 atm. press. and 298.16°K.	69.08±0.10	69.05±0.15

The calculated value should be very accurate; an error of 2° in the F-As-F angle makes an error of only 0.02 cal./deg./mole in the entropy; and an error of 0.02 Å. in the As-F distance corresponds to an error of 0.07 cal./deg./mole. The frequencies were measured with the liquid and may be shifted a few wave numbers in the gas, but the error should be less than 0.10 cal./deg./mole.

The excellent agreement between the calculated and observed entropies indicates that the entropy of crystalline arsenic trifluoride approaches zero at 0°K.

Summary

The heat capacity of arsenic trifluoride has been measured from 13 to 290°K. The melting point is 260.21 ± 0.02°K. with a heat of fusion of 2486 ±3 cal./mole. The heat of vaporization is 8566 ±8 cal./mole at 292.50°K. and 142.6 mm. The vapor pressure from 28 to 140 mm. of Hg is given by the equation $\log_{10}p = 61.3797 = (4149.78/T) - 18{,}2640 \log_{10}T$, where p is in intern. mm. of Hg.

The molal entropy from calorimetric data at 142.6 mm. pressure and 292.50°K. is 72.09 ± 0.15 cal./deg., compared with the value calculated from molecular data for the same conditions of 72.12 ± 0.10 cal./deg. The molal entropy at 1 atm. and 298.16°K. is 69.07 ± 0.10 cal./deg.

The strong luminescence noted when solid arsenic trifluoride is warmed or cooled near liquid air temperature is not associated with a change in phase.

PASADENA, CALIF. RECEIVED AUGUST 5, 1941

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(5) Yost, *Proc. of the Ind. Acad. of Sci.*, **VIII**, 333 (1938).

(6) Howard and Wilson, *J. Chem. Phys.*, **2**, 630 (1934).

(7) Private communication from Dr. Verner Schomaker.

[CONTRIBUTION FROM NEWCOMB COLLEGE, TULANE UNIVERSITY]

An X-Ray Study of the Structure of Polyvinyl Alcohol*

BY ROSE C. L. MOONEY

An X-ray fiber diagram of polyvinyl alcohol, $(\text{—}CH_2CHOH\text{—})_n$, on which some fifteen reflections were recorded, was published by Halle and Hoffmann in 1935.[1] The extent of the work was a measurement of the periodicity along the fiber axis, given as 2.57 Å., and the calculation of interplanar spacings. In a fibrous substance such as this, "crystalline" orientation exists only along the fiber axis. Consequently, the amount of obtainable data, consisting, in general, of the equivalent of a rotation about a single axis, falls far short of that required for the best use of the X-ray methods. Usually, the determination of atomic positions is extremely difficult if not altogether impossible. Nevertheless, the vinyl alcohol fiber seemed to present an unusually favorable case for structure analysis, inasmuch as well oriented samples can be obtained, the fiber periodicity is short, and the chemical composition known and simple.

Experimental Data.—Two types of photographs were taken: one the usual fiber diagram, for which a beam of

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* Reported at Washington meeting of American Physical Society, April, 1941.

(1) Halle and Hoffmann, *Naturwiss.*, **45**, 770 (1935).

Cu K radiation, filtered through nickel, was passed perpendicular to the fiber axis, or at an angle with it, and was registered on a cylindrical film; the other, a Weissenberg photograph, in which the spots were drawn out into parallel lines which were quite sharp and very much more convenient for the precise measurement of positions and the comparison of intensities than the more or less fuzzy spots of the fiber diagram.

The intensities of reflections were evaluated visually by comparison with a calibrated intensity scale. Several sets of independent comparisons were made from photographs taken with different exposure times, in order to arrive at a set of numerical values which, though entirely arbitrary, furnish a reasonably good relative scale of observed intensities. These values, corrected by the polarization Lorentz factor, and expressed as F rather than F^2, appear in Table I as experimental observations.

Cell Size and Density.—The cell spacing along the fiber axis, measured directly from the layer line separation, is 2.52 Å. to within 1%. This is the distance between 1,3 carbons in the planar zigzag chain configuration. It follows that the glycol units are in the 1,3 positions rather than in the 1,2 arrangement, which would require a periodicity one and a half times as great. This arrangement of the glycol groups on alternate carbon atoms has been demonstrated by chemical methods,[2] but the X-ray fiber diagram gives at once a simple and direct confirmation.

The periodicities in the directions other than the fiber axis cannot be directly obtained, but a simple orthogonal reciprocal lattice net is readily derived from measurement of the equatorial reflections. All of the reflections can be referred to a cell of the dimensions: $a = 7.82$, $b = 2.52$ (fiber axis), $c = 5.60$ Å. It is not possible from these measurements to determine whether the angles between the axes differ from 90°.

On the basis of the reported density, 1.293 g./cc., the number of "molecules" in the unit cell is 1.97. Assuming that the cell contains two chain units, —CH_2CHOH—, the calculated density is 1.31 g./cc. Therefore, the number of atoms for which positions must be found is only six: four carbons and two oxygens. Since the glycol carbons cannot be considered equivalent to the other two, the structure must be based on three sets of two-fold positions, involving three parameters each.

Space Group and Parameters.—Inspection of the X-ray data (Table I, columns 1 and 2), shows that, though all reflections can be referred to the chosen cell, the overlapping of spectra causes uncertainty in a number of indices. (This has been indicated in the table by bracketing the possible indices of a given observation.) Considering only observations which are uniquely indexed, it is found that there are no typical absences in planes *hkl*, *h0l* and *hk0*; that 011, 012 and 013 are absent, which may or may not be a space group vanishing, and that 0*k*0 is of course unobserved.

It is obvious that there are far too few observations to permit a space group determination based on absent reflections; indeed, due to the random orientation of the crystallites, not even a distinction between the orthorhombic and monoclinic systems has been possible. However, it has been shown that there are two chain units in the cell, which, from the evidence of the 2.52 Å. periodicity along the fiber axis, must belong to different long chain molecules. Furthermore, from this same evidence, the configuration of these molecules must be that of a zigzag planar carbon chain with 1,3 glycol arrangement. Finally, steric conditions indicate that oxygens cannot be coplanar, and are probably separated by half the fiber periodicity.

In the light of these considerations, all of the monoclinic and orthorhombic space groups of sufficiently low symmetry were carefully reviewed, and systematically eliminated, until only two types of arrangement (for suitable choice of our axes), remained as possibilities. These arrangements,[3] both monoclinic, were C_s^2— Pc, with positions $xyz;\ x,\bar{y},\frac{1}{2}+z;$ and C_2^2— P_1^2, with positions $xyz;\ \bar{x},\frac{1}{2}+y,\bar{z}$.

Now a model of the vinyl alcohol chain was set up analytically, assuming that the C–C distance in the zigzag chain is 1.54 Å., that the C–O distance is 1.43, and that the bond angles are tetrahedral. This model was tested in a systematic manner for both space group arrangements. The testing consisted in calculating the structure amplitudes of the simple planes whose indices were trustworthy, for all orientations of the chain about the b axis in steps of 15°, and for 7.5° translations along the x and along the y axis. The results showed that satisfactory agreement could be obtained for C_2^2, but not for C_s^2. The space group symmetry must then be the former, which, for values of $^1/_4$ and $^3/_4$ for the y parameters, reduces to the special positions of

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[2] Marvel and Denoon, THIS JOURNAL, **60**, 1045 (1938).

[3] "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935.

C_{2h}^2— $P2_1m$ with all of the atoms in the mirror planes. The structure amplitude expression, for each pair of geometrically equivalent atoms, is conveniently given as

$$F = 2f \cos 2\pi(hx + lz) \cos 2\pi ky, \text{ when } k \text{ is even, and}$$
$$F = -2f \sin 2\pi(hx + lz) \sin 2\pi ky, \text{ when } k \text{ is odd}$$

The symbol, f, represents the atomic scattering factor, obtained from the usual tables.[3]

This space group does not explain, at first glance, the observed absences of planes $0kl$ where k is odd. However, in calculating the amplitudes, it must be remembered that the fiber diagram is essentially a complete rotation pattern, so that the number of planes coöperating in the formation of a given reflection must be taken into account. Furthermore, either because the monoclinic angle is nearly 90°, or because the chains run equally probably in either direction with reference to the fiber axis, planes of the type hkl are experimentally indistinguishable from planes of the type $\bar{h}kl$, though their intensities cannot be the same. If, for convenience in calculating, the viewpoint of approximately equal numbers of oppositely directed chains is adopted, it follows that four quasi-equivalent points are simultaneously involved in the production of a given intensity as observed; namely, xyz; $\bar{x},y + \frac{1}{2},\bar{z}$; and also $\bar{x}yz$, $x,y + \frac{1}{2},\bar{z}$. Therefore, the summation for the structure amplitude must include terms for all four points. These, combined trigonometrically, give the expressions

$$F = 4f \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz, \text{ for } k \text{ even, and}$$
$$F = -4f \sin 2\pi hx \sin 2\pi ky \cos 2\pi lz, \text{ for } k \text{ odd}$$

which explain the vanishing of planes $0kl$ where k is odd.

The parameters which give the most satisfactory agreement appear in Table I. The structure amplitudes calculated from these parameters are given in Table II. In general, the values are large for planes of high intensity, and low for weak ones. There are too few dependable X-ray data to warrant any attempt at greater precision; no effort was made to correct discrepancies by small parameter shifts, or by slight deformations of the alcohol chain. Since there has been a rather thorough testing of possibilities, and since, due to the small number of atoms involved, each atom has an appreciable effect on the amplitude, it seems safe to say that the parameters give the vinyl alcohol structure to a first approximation.

TABLE I

PARAMETERS

	$2\pi x$	$2\pi y$	$2\pi z$
Carbon$_1$	56.6°	270°	59°
Carbon$_2$	97.6	90	59
Oxygen	134.9	90	135

TABLE II

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

(Bracketed indices are experimentally indistinguishable)

Reflections Index	Reflections Sin θ/λ	F Values Obs.	F Values Calcd.	Reflections Index	Reflections Sin θ/λ	F Values Obs.	F Values Calcd.
100	0.064	21	−41	401	0.271	30	60
001	.089	17	−10	003	.273	30	18
101	.110	100	95	103	.275	30	−71
200	.128	47	−55	112	.275	10	3
201	.156	30	−49	310	.276	10	−12
002	.179	32	−30	311	.295	49	64
102	.190	20	12	212	.297	49	−25
300	.192	20	21	203	.297	12	−60
110	.208	38	−42	402	.310	12	− 3
301	.212	30	−68	500	.320	18	17
011	.218	0	0	303	.330	18	55
202	.219	19	34	501	.333	18	−40
111	.227	60	46	410	.324	12	−26
210	.236	60	84	312	.329	12	−21
211	.253	20	−33	013	.333	0	0
400	.256	28	−38	113	.340	10	42
012	.267	0	0	004	.358	10	50

Figure 1 shows a projection of the structure on a plane perpendicular to the fiber axis. The circles, in order of size, represent oxygen, carbon and hydrogen. The last, of course, make no appreciable contribution to structure amplitude. The positions have been assumed on the basis that the hydrogens attached to carbon are at tetrahedral angles, at a C–H distance of 1.08, and are lying in the reflection planes; and that the hydroxyl hydrogens are somewhere on the line joining two oxygens of adjacent chains. The center of this line is $\frac{1}{2},0,\frac{1}{2}$. The filled and open circles distinguish between atoms lying in different planes, 1.26 Å. apart. The hydroxyl H is shown by a dotted circle.

Discussion of the Structure.—As has been shown, the positions of the carbons and oxygens in the cell have been determined by X-rays, under the restricting condition that they must be part of a conventional planar zigzag carbon chain running parallel to the fiber axis. However, the direct evidence for this assumption is the observed fiber periodicity. Again because of this periodicity, the short 2.52 Å. distance must be accepted as the separation between successive oxygens in a given chain. No assumptions have been made concerning the relationship between the two

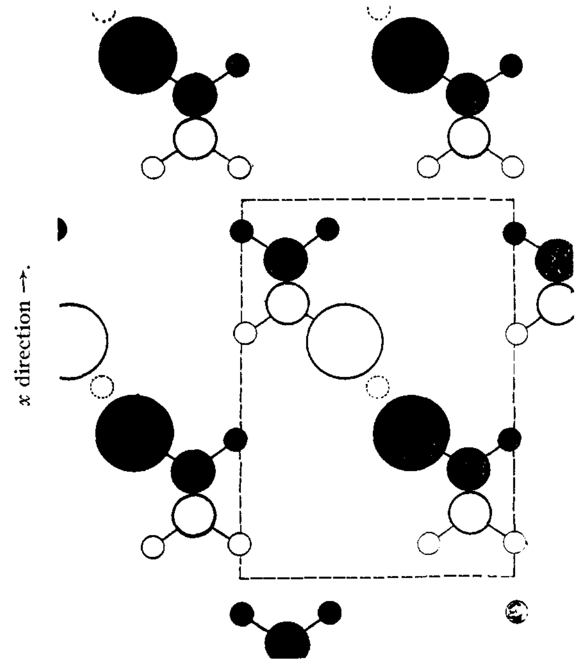


Fig. 1.—Structure of polyvinyl alcohol projected on the plane perpendicular to the fiber axis. The circles, in descending order of size, represent oxygen, carbon and hydrogen. The filled and empty circles distinguish between atoms lying in alternate planes, 1.26 Å. apart. The hydroxyl hydrogens are shown by the dotted circle.

chains in the unit cell. Therefore, the orientation of the two chains and the distances found between their atoms form part of the experimental results of the structure determination. The distances between any oxygen and its two nearest neighbors on the opposite chain is 2.72 Å. This, as well as the small separation between successive oxygens on the same chain, must be attributed to some sort of conjugation, due to the formation of hydrogen bonds between the chains. The actual positions of the hydrogens forming such bonds are not subject to direct experimental proof by means of X-rays. Only their effect on interatomic distances gives evidence of their whereabouts. Since unbonded oxygens are expected to be at least 3.5 Å. apart, the two short O-O distances in the structure require explanation. The assumption that the hydrogens are lying between successive oxygens in the same chain would not explain the 2.72 Å. separation between oxygens of adjacent chains, and would give a hydrogen bond distance somewhat shorter than is usual in alcohols. On the other hand, the assumption that each hydrogen occupies a position on the line joining two oxygens of neighboring chains gives a hydrogen bond distance in agreement with that found in crystalline alcohols, namely, 2.72 Å.; while the close approach of successive oxygens on the same chain might well be due to the stabilizing influence of the two hydrogen bonds attached to each oxygen. This is therefore chosen as the more reasonable arrangement. The configuration is illustrated in Fig. 2, which shows the paired vinyl alcohol chain projected on the 101 plane. The O-H . . . O-H . . . zigzag lying in this plane, together with the carbon zigzag, forms a puckered net, each mesh consisting of three carbons and three H-bonded oxygens. The angle between the C-O and the O-H . . O bond directions is about 167°. The methylene groups of associated chains are more than 5.5 Å. apart, as are also the oxygens of non-associated chains. The average distance between methylene groups in adjacent cells is 4.3 Å., with individual values ranging from 3.5 to 5 Å., though these cannot be taken too seriously in the case of randomly oriented fibers.

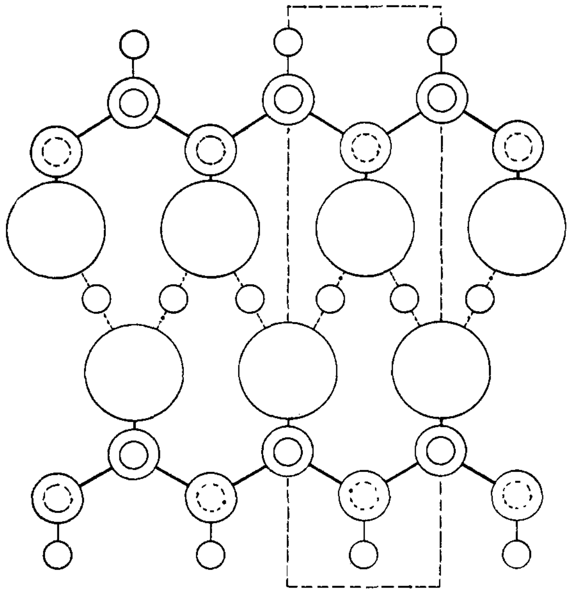


Fig. 2.—Polyvinyl alcohol chains projected on the 101 plane. The circles, in descending order of size, represent oxygen, carbon and hydrogen. The dotted and solid circles distinguish between hydrogens on alternate sides of the chains.

In brief, the structure of polyvinyl alcohol, as determined from X-ray diffraction, consists of pairs of long-chain molecules, held together by hydrogen bonds. These double chains all lie along the fiber axis, but in random orientation about it, and either parallel or antiparallel to it. Each chain has a zigzag carbon planar configuration, with glycol units in the 1,3-positions.

Thanks are due to Dr. Cutler West, who drew attention to the fact that this particular fiber, because of the short fiber periodicity, might be sufficiently simple for an attempt at complete structure analysis; and who very kindly supplied the samples from which the X-ray data were obtained.

Summary

The structure of polyvinyl alcohol has been determined from a study of its X-ray fiber diagram. The experimental data consist of photographs taken with copper radiation filtered through nickel. The reflections, about thirty in number, were indexed with reference to a pseudo-orthorhombic cell of the following dimensions: $a = 7.82$, $b = 2.52$, $c = 5.60$ Å. The periodicity along the fiber axis, namely, 2.52 Å., points to a planar zigzag configuration for the carbon chain, with glycols in the 1,3 positions. There are two chain segments, —CH_2CHOH—, in the unit cell, giving a calculated density of 1.31. The reported value is 1.293. The symmetry is C_{2h}^2—$P2_1m$ with the carbons and oxygens lying in planes of symmetry. Positions for these atoms have been found such that the calculated intensities give satisfactory agreement with the limited number of observed intensities. The structure consists of long chain molecules so oriented that pairs of chains are linked through hydroxyl bonds.

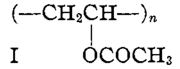
NEW ORLEANS, LOUISIANA RECEIVED JULY 26, 1941

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

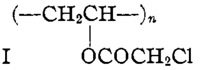
Electrical Properties of Solids. XI. Polyvinyl Acetate and Polyvinyl Chloroacetate*

BY DARWIN J. MEAD AND RAYMOND M. FUOSS

I. Introduction.—A number of the papers of this series have dealt with a polar polymer of very simple structure, polyvinyl chloride, in which the dipoles are attached directly to the carbon atoms which make up the chain. In this paper we shall present the results of an experimental study of two polymers, polyvinyl acetate (I) and polyvinyl chloroacetate (II), in which the

I 

$(\text{—}CH_2\underset{OCOCH_3}{\underset{|}{C}H}\text{—})_n$

II 

$(\text{—}CH_2\underset{OCOCH_2Cl}{\underset{|}{C}H}\text{—})_n$

polar groups are attached to the chain carbons by flexible ester-oxygen hinges.

Qualitatively, one can make several predictions concerning their electrical properties. First, granting that the extremely broad absorption of polyvinyl chloride is caused by a distribution of relaxation times characteristic of the polymeric chain, we expect that the absorption peak for the acetates will be much sharper than for the chloride, because the flexibility of the oxygen bond places a rotational degree of freedom between the chain and the dipole. Consequently the orientation of the acetate dipoles is much less influenced by the convolutions of the chain than that of the chloride dipoles. Second, the off-chain dipoles in I and II are restricted to the chain by the bond as far as relative translational motion is concerned and therefore we expect less association and hence a higher static dielectric constant in the polymers than in the corresponding monomers. Third, since the resultant —$COCH_2Cl$ dipole is stronger than the —$COCH_3$ dipole, and possesses an additional degree of rotational freedom, the static dielectric constant should be greater for the chloroacetate, and it should give a sharper absorption curve. Data presented here confirm these predictions.

Two samples of polyvinyl acetate were studied; their weight average molecular weights, as determined by their intrinsic viscosities, were in the ratio 2.2:1. The one with the lower degree of polymerization had, at a given temperature, its maximum absorption at a frequency 2.2 times that for the maximum in the sample of higher molecular weight. The distribution of relaxation times,[1] although much sharper than that for the (—CH_2CHCl—)$_n$ polymers, is therefore still about a most probable value which is proportional to the number of monomer units in the polymer.[2] Since the acetates were unfractionated, we conclude further that the reciprocal of the frequency

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* Presented September 10, 1941, at the Atlantic City meeting of the American Chemical Society.

[1] Fuoss and Kirkwood, THIS JOURNAL, **63**, 385 (1941).

[2] Kirkwood and Fuoss, *J. Chem. Phys.*, **9**, 329 (1941).