acid solutions. The properties of the mixtures resulting from suspending (or dissolving) the black precipitate in water, concentrated sulfuric, nitric or perchloric acid were studied in a qualitative way. The solution was found to be one of the most active and powerful oxidizing agents known. Thus it rapidly oxidizes chlorides with liberation of chlorine; chromic salt to chromate; manganous salt to permanganate and manganese dioxide, and ammonia to nitrogen. The substance is not a peroxide of the hydrogen peroxide type, since the solution gives no color with titanium salt; it resembles rather the oxides of trivalent cobalt, thallium and gold.

Representative values of the rate constants are 0.333 at 25° and 0.765 at 35°, the unit of time being the minute and concentrations being expressed in moles per liter of solution. From these values the temperature coefficient of the reaction is found to be 2.30.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 82]

CONFIRMATION OF THE PRESENCE OF A NON-TETRAHEDRAL CARBON ATOM IN CRYSTALS OF PENTA-ERYTHRITOL

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The crystal structure of penta-erythritol, $C(CH_2OH)_4$, has recently been investigated by Mark and Weissenberg,[2] using the rotating crystal method. Their conclusions may be summarized as follows. The structure possesses ditetragonal pyramidal symmetry, the space group being C_{4v}^9. The lattice is body centered. The unit cell, containing two molecules, has the dimensions $a_0 = 6.16$ Å. and $c_0 = 8.76$ Å. The symmetry of the position occupied by the central carbon atom of each molecule is that of the point group C_{4v}; the four surrounding carbon atoms must therefore be structurally equivalent and all in the same plane, at the corners of a square, although not necessarily in the same plane as the central atom. Similarly, all four oxygen atoms of each molecule are equivalent and coplanar.

It seemed to us that these results, indicating that the carbon atom in aliphatic organic compounds is not always tetrahedral in shape, are of such importance as to deserve verification, especially in view of the fact that similar methods had yielded[3] a structure of tin tetra-iodide which have been shown by Laue photographic data obtained in this Laboratory[4] to be incorrect. We have therefore investigated the structure of penta-

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[2] Mark and Weissenberg, *Z. Physik*, **17**, 301 (1923).

[3] Mark and Weissenberg, *ibid.*, **16**, 1 (1923).

[4] Dickinson, THIS JOURNAL, **45**, 958 (1923).

erythritol, using not only spectral data obtained in a manner similar to those of Mark and Weissenberg, but also Laue photographic data. Our results completely verify the conclusions reached by these investigators.

The spectral data obtained by us give the same values of d/n for (001) and (100) as obtained by Mark and Weissenberg. The Laue data, summarized in Table I, further show that a unit with $a_0 = 6.16$ Å. and $c_0 = 8.76$ Å. satisfactorily accounts for the observed reflections, since the values of $n\lambda$'s calculated on the basis of this unit show the absence of wave lengths shorter than 0.24 Å., the minimum value present in the incident radiation. A Coolidge tube with a tungsten anticathode, operated at a peak voltage of 52 kv., was used throughout this investigation.

TABLE I

LAUE PHOTOGRAPHIC DATA FROM PENTA-ERYTHRITOL

Incident beam of X-rays about 3° from normal to (001)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity[a]	hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity[a]
$1\bar{4}1$	1.48	0.46	0.6	532	1.03	0.47	1.5
411	1.48	.46	1.6	$\bar{5}11$	1.02	.39	*a*
331	1.43	.48	*a*	$\bar{7}12$	0.854	.29	0.1
421	1.36	.42	*a*	$\bar{1}72$	.854	.39	.5
$\bar{4}31$	1.22	.42	0.6	563	.825	.45	.45
$\bar{4}\bar{3}1$	1.22	.33	.8	$6\bar{5}3$	.825	.34	.05
$\bar{5}01$	1.22	.38	.3	$7\bar{2}3$	.813	.39	.08
061	1.20	.31	*a*	743	.740	.37	.10
$\bar{5}\bar{2}1$	1.12	.37	.4	$8\bar{3}5$	.710	.46	1.0
521	1.12	.31	.5	1257	.443	.33	v. f.
161	1.04	.30	.25				

[a] *a* signifies absent.

The absence of reflection in the first order from planes with two odd and one even indices, and with one odd and two even indices [such as (331), (421), (061) and ($\bar{5}$11)], although they were in a position to reflect the incident beam of X-rays, requires the underlying lattice to be the body-centered tetragonal one. The only space groups based on this lattice and possessing the observed crystal symmetry are C_{4v}^9, C_{4v}^{10}, C_{4v}^{11}, and C_{4v}^{12}.[5] The space groups C_{4v}^{10}, C_{4v}^{11} and C_{4v}^{12} do not admit of an arrangement of 10 carbon atoms in the unit.

In an arrangement arising from C_{4v}^9 two carbon atoms must be equivalent and possess the symmetry of the point group C_{4v}, thus necessitating the presence of a four-fold axis about these atoms, and consequently a non-tetrahedral arrangement. If the logical assumption is made that the two $C(CH_2OH)_4$ in the unit act as structural entities, that is, as molecules, the analysis given below leads to a possible atomic arrangement.

If we place the origin (000) of our system of coördinates at the center

[5] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Inst. Pub.*, No. 318, 1922, p. 85.

of one of the two central carbon atoms in a unit, the other must be[5] at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The eight equivalent carbon atoms within the unit may be in either of the positions designated (c) and (d) by Wyckoff:

(c) uuv; $\bar{u}\bar{u}v$; $u+\frac{1}{2}, \frac{1}{2}-u, v+\frac{1}{2}$; $u+\frac{1}{2}, u+\frac{1}{2}, v+\frac{1}{2}$;
$\bar{u}\bar{u}v$; $\bar{u}uv$; $\frac{1}{2}-u, u+\frac{1}{2}, v+\frac{1}{2}$; $\frac{1}{2}-u, \frac{1}{2}-u, v+\frac{1}{2}$;
(d) uOv; Ouv; $\frac{1}{2}, u+\frac{1}{2}, v+\frac{1}{2}$; $u+\frac{1}{2}, \frac{1}{2}, v+\frac{1}{2}$;
$\bar{u}Ov$; $O\bar{u}v$; $\frac{1}{2}, \frac{1}{2}-u, v+\frac{1}{2}$; $\frac{1}{2}-u, \frac{1}{2}, v+\frac{1}{2}$.

Similarly, the eight equivalent oxygen atoms may be either in (c) or in (d). The position of the 24 hydrogen atoms need not necessarily conform to the space-group criteria,[6] but presumably eight atoms are in positions (c) or (d), and 16 in the general positions

(e) xyz; $\bar{y}xz$; $\bar{x}\bar{y}z$; $y\bar{x}z$;
yxz; $x\bar{y}z$; $\bar{y}\bar{x}z$; $\bar{x}yz$;
$x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$; $\frac{1}{2}-y, x+\frac{1}{2}, z+\frac{1}{2}$; $\frac{1}{2}-x, \frac{1}{2}-y, z+\frac{1}{2}$; $y+\frac{1}{2}, \frac{1}{2}-x, z+\frac{1}{2}$;
$y+\frac{1}{2}, x+\frac{1}{2}, z+\frac{1}{2}$; $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; $\frac{1}{2}-y, \frac{1}{2}-x, z+\frac{1}{2}$; $\frac{1}{2}-x, y+\frac{1}{2}, z+\frac{1}{2}$.

In order to maintain CH_2OH groups it is necessary that the eight equivalent carbon atoms, the eight equivalent oxygen atoms and the eight

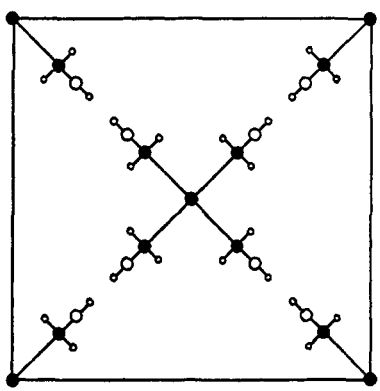

Fig. 1.—Illustrating, in plan, the type of arrangement of atomic centers within the unit of $C(CH_2OH)_4$, if the 8 equivalent atoms of C, of O and of H are all in positions (c) of C_{4v}^9. Large dots represent C, large circles O, and small circles H atoms.

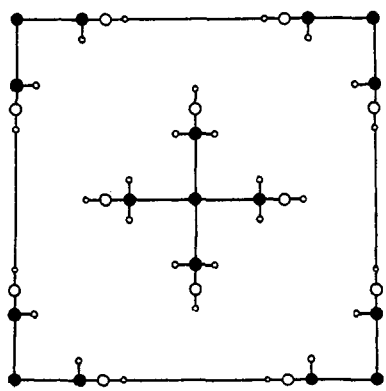

Fig. 2.—The same as in Fig. 1, assuming the 8 equivalent atoms of C, of O and of H to be all in positions (d) of C_{4v}^9.

equivalent hydrogen atoms all occupy positions (c) (with different values of the parameters) or positions (d). The data obtained were not sufficient to decide between these two molecular orientations (shown in Figs. 1 and 2), nor to determine any of the parameter values.

It should be noted that it is only the central atom of each molecule which cannot be tetrahedral. However, the tetrahedral arrangement may

[6] Wyckoff, *Z. Kryst.*, **57**, 595 (1923). Also, *Am. J. Sci.*, **5**, 209 (1923).

perhaps be the stable one in solution or in the liquid state; for the intermolecular forces operating during the process of crystallization may be sufficient to turn all the CH_2OH groups in the same direction and so transform the tetrahedral arrangement into the one actually found. It is of interest, however, that recent investigations[7] on thin films of the tetrapalmitate of penta-erythritol also indicate a square arrangement rather than a tetrahedral one of the CH_2OR groups around the central carbon atom of each molecule.

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Summary

Additional data confirming the crystal structure of penta-erythritol, $C(CH_2OH)_4$, as previously reported by Mark and Weissenberg, have been obtained. These data verify the non-tetrahedral arrangement of atoms about the central carbon atom of the molecule.

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NOTES

The Hydrolysis of Sulfur Monochloride.—In the discussion of the products resulting from the hydrolytic decomposition of sulfur monochloride the current standard textbooks of chemistry give the reaction[1] as

$$2S_2Cl_2 + 3H_2O = 2S + 4HCl + H_2S_2O_3 \quad (1)$$

A simple qualitative examination, however, shows immediately the presence of hydrogen sulfide in the vapors issuing from the reaction flask and in the alkaline solution in which those vapors are fixed. In view of this fact, therefore, the primary reaction must be represented by the equation

$$S_2Cl_2 + 2H_2O = 2HCl + H_2S + SO_2 \quad (2)$$

which obviously is followed by the reactions usually given but which are, nevertheless, distinctly secondary.

A search of the literature shows that Carius[2] was apparently the first and only investigator to note the presence of hydrogen sulfide. Using the notation of his day he wrote "the action of 'half sulfurchloride' on water is analogous to that on alcohol.

$$(\ominus H)_2 + Cl_2SS = (ClH)_2 + S \ominus" \quad (3)$$

His results have evidently been overlooked for the period of nearly three-quarters of a century since they were published.

[7] Adams and Dyer, *Proc. Roy. Soc.* (*London*), **106A**, 706 (1924).

[1] For example, see Mellor, "Modern Inorganic Chemistry," Longmans and Co., **1925**, p. 500.

[2] Carius, *Ann.*, **106**, 291–336 (1858); *Pharm. Centrallbl.*, **1858**, 545.