degree of accuracy. In the cases of krypton and xenon the calculated and experimental (density) values are discrepant and, as pointed out by Aston, new determinations of the densities and compressibilities of these gases should be made.

THE CRYSTAL STRUCTURE OF SOME FORMS OF GLUCOSE. A PRELIMINARY PAPER

BY O. L. SPONSLER AND W. H. DORE

In anticipation of throwing more light upon the atomic arrangement of the cellulose unit, several crystalline forms of glucose have been under investigation. The structural relationship between cellulose and the beta modification of the amylene oxidic ring form of glucose has been pointed out by the authors.[1] In order to gain a clearer conception of cellulose it has seemed desirable to determine the structure of the crystals of the beta form and also of other forms of glucose. The present report deals with some preliminary results on the alpha and the beta forms of d-glucose ($C_6H_{12}O_6$) and on the alpha glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$).

The first two forms were prepared[2] by the method of Hudson and Dale[3] and the monohydrate by that of Hudson and Yanovsky.[4] The fine crystals so obtained were examined by the powder method of x-ray crystal analysis. Radiation from a molybdenum target Coolidge tube was employed for obtaining the diffraction patterns. The existence of crystallographic data for the two alpha forms made it possible to determine the lattice dimensions and to assign space groups to these forms. The absence of similar data for beta glucose precluded those deductions regarding its structure, but the diffraction patterns made it evident that the alpha and beta forms have different crystal structures.

After this paper was written Hengstenberg and Mark[5] reported a lattice for "d-glucose" without stating whether the alpha or beta form was used. They employed a single crystal rotation method. The agreement of their data with those appearing in this paper, together with the method they used for preparing their material, makes it clear that they were working with alpha d-glucose.

[1] Sponsler and Dore, "Fourth Colloid Symposium Monograph," The Chemical Catalog Co., New York, 1926, pp. 174–202; Meyer and Mark, *Ber.*, 61, 593–614 (1928).

[2] The thanks of the authors are due to Mr. T. C. Broyer, of the Plant Nutrition Laboratory, for preparing these two forms.

[3] Hudson and Dale, THIS JOURNAL, 39, 320 (1917).

[4] Hudson and Yanovsky, *ibid.*, 39, 1013 (1917).

[5] Hengstenberg and Mark, *Z. Krist.*, 72, 301 (1929).

Alpha *d*-Glucose.—Taking Bödecker's[6] value of 1.5384 for the specific gravity, 180 for the molecular weight and Avogadro's constant as 6.062×10^{23}, the molecular volume of alpha *d*-glucose is

$$\frac{180}{1.54} \times \frac{1}{6.062 \times 10^{23}} = 193 \times 10^{-24} = 193 \text{ cu. Å.}$$

Groth[7] described *d*-glucose as orthorhombic bisphenoidal with axial ratios: $a : b : c = 0.794 : 1.000 : 0.335$. The determination of these ratios by Becke[8] was made on material which, from the method of its preparation, was clearly the alpha modification.

Assuming four asymmetric molecules in the elementary cell (the minimum for the rhombic bisphenoidal class), the volume is 4×193 or 772 cu. Å., corresponding to cell dimensions: $a = 10.45$ Å., $b = 14.85$ Å., $c =$

TABLE I

INTERPLANAR SPACINGS FOR ANHYDROUS ALPHA *d*-GLUCOSE

Observed spacing	Relative intensities	Calculated spacings and indices	
..	......	14.85	(010)
..	......	10.45	(100)
8.65	V. v. weak	8.55	(110)
7.44	V. weak	7.43	(020)
6.07	Mod.	6.05	(120)
5.23	Mod.	5.23	(200)
..	......	4.97	(001)
4.72	V. strong	4.72	(011)
4.48	Tr.	4.49–7	(101)(130)
4.31	V. v. strong	4.30	(111)
3.87	V. weak	3.84	(121)
3.60	Tr.	3.60	(201), 3.59 (230)
3.51	Mod.	3.51	(031), 3.50 (211)(140)(300)
3.34	Tr.	3.33	(131)
3.16	V. strong	3.15	(320)
2.98	Tr.	2.98	(041), 2.97 (050)
2.88	Weak	2.91	(231), 2.86–5 (141)(330)(301)(150)
2.60	Weak	2.61–59	(400)(241)(250)
2.48	V. strong	2.48	(002)(420)
2.28	Tr.	2.30–28 / 2.31–28	(122)(411)(251) / (401)(350)(341)
2.25	V. strong	2.24–26	(202)(260)(350)(341)
2.06	Mod.	2.06	(042)
1.95	Weak	1.96–7	(441)(270)(242)
1.81	Weak	1.81	(402)(460)
1.68	V. v. weak	1.68	(461)(352)
1.59	V. weak	1.60	(123), 1.58 (203)
1.34	V. weak	1.34	(670)
1.29	V. weak	1.29	(810)(820)

[6] Bödecker, *Ann.*, 117, 111 (1861).

[7] Groth, "Physikalische Krystallographie," 1910, Vol. III, p. 437.

[8] Becke, *Z. Kryst. Mineral*, 20, 297 (1892).

4.97 Å.   Interplanar spacings calculated to these dimensions are compared with the observed spacings in Table I.   The axial values are represented by the half values in the column of observed spacings; lines for the full values are absent from the diffraction pattern.

	Calcd.	Obsd.
$a =$	10.45	5.23
$b =$	14.85	7.44
$c =$	4.97	2.48

Of the nine possible space groups[9] included in the rhombic bisphenoidal class, only one, V^4 (or Q^4), fits the data presented.   In that group four asymmetric molecules are required; and the face planes are interleaved so that only their half values will appear in the diffraction pattern.

TABLE II

INTERPLANAR SPACINGS FOR ALPHA d-GLUCOSE MONOHYDRATE

Observed spacing	Relative intensities	Calculated spacing and indices
9.70	Mod.	9.50 (001)
7.00	Strong	6.88 (101)
6.00	V. weak	5.99 (101)
$\left\{\begin{array}{c} 4.52 \\ 4.30 \end{array}\right\}$	V. v. strong	4.45 (102) 4.31 (200)
4.10	V. v. weak	4.05 (111)
3.85	V. strong	3.87 (111)
3.50	Weak	3.44 (202)
3.30	V. v. weak	3.33 (112), 3.27 (210)
$\left\{\begin{array}{c} 3.20 \\ 3.10 \end{array}\right\}$	Strong	3.20 (211), 3.17 (003) 3.12 (103), 3.11 (112)
3.00	V. v. weak	3.00 (211)(202)
2.85	Mod.	2.87 (300), 2.84 (212)(103)
2.63	Weak	2.66 (301)
2.50	Strong	2.51 (020), 2.50 (310)
2.42	Mod.	2.41 (120)
2.24	V. weak	2.22 (104)
2.17	Strong	2.18 (122), 2.17 (220)(401), 2.16 (400)(014)
2.04	V. weak	2.04 (401), 2.02 (222)
1.99	Mod.	2.00 (303), 1.99 (410)(222), 1.98
1.90	V. v. weak	1.90 (005), 1.89 (320)
1.85	Mod.	1.86 (402)
1.72	V. v. weak	1.72 (500)(404)(024)
1.65	V. weak	1.65 (130)
1.59	V. weak	1.60 (422), 1.58 (006)
1.52	V. v. weak	1.52 (025)
1.39	V. v. weak	1.39 (603)
1.32	V. v. weak	1.32 (430)
1.28	V. v. weak	1.29 (333)(022)(424)
1.21	V. v. weak	1.21 (240)
1.17	V. v. weak	1.18 (242), 1.16 (242)
1.14	V. v. weak	1.15 (340)(036)

[9] Astbury and Yardley, *Phil. Trans. Roy. Soc. London,* **224A**, 221 (1924)

Alpha *d*-Glucose Monohydrate.—Taking Bödecker's value of 1.5714 for the specific gravity and 198 for the molecular weight, the molecular volume of alpha glucose monohydrate is

$$\frac{198}{1.5714} \times \frac{1}{6.062 \times 10^{23}} = 207.9 \times 10^{-24} \text{ or } 207.9 \text{ cu. Å.}$$

Groth[7] describes alpha glucose monohydrate as monoclinic sphenoidal with axial ratios: $a:b:c = 1.735:1:1.908$, with the angle between inclined axes, $\beta = 97°59'$. An elementary cell containing two molecules as a minimum has dimensions: $a = 8.72$ Å. $b = 5.03$ Å., and $c = 9.59$ Å., $\beta = 97°59'$, when based on the volume and axial ratios given. A comparison of the interplanar spacings from those dimensions and from the x-ray data is presented in Table II. From crystallographic data the crystal is shown to be monoclinic; from chemical data the molecule is known to be asymmetric. In the absence of x-ray data from a single crystal, those two considerations would place the structure in space group C_2^2. That space group[9] demands two molecules per unit cell and requires that the (010) spacing be halved. Our interpretation is in agreement with both requirements.

TABLE III

INTERPLANAR SPACINGS FOR BETA *d*-GLUCOSE AND ALPHA *d*-GLUCOSE OBSERVED VALUES

Beta *d*-glucose		Alpha *d*-glucose	
Å. units	Intensity	Å. units	Intensity
{ 5.47 }[a]	V. v. st.[a]	8.65	V. v. w.
{ 5.27 }		7.44	V. w.
4.63	V. v. st.	6.07	M.
4.34	V. st.	5.23	M.
4.11	W.	4.72	V. st.
{ 3.86 }	V. v. w.	4.48	V. v. w.
{ 3.81 }	V. v. st.	4.31	V. v. st.
3.62	M.	3.87	V. w.
3.35	M.	3.60	V. v. w.
3.17	St.	3.51	M.
2.83	V. st.	3.34	V. v. w.
2.78	V. v. w.	3.16	V. st.
{ 2.48 }	W.	2.98	V. v. w.
{ 2.45 }		2.88	W.
{ 2.30 }	W.	2.60	W.
{ 2.27 }		2.48	V. st.
{ 2.14 }	W.	2.28	V. v. w.
{ 2.09 }		2.25	V. st.
1.85	V. w.	2.06	M.
1.78	W.	1.95	W.
1.68	V. w.	1.81	W.
1.56	V. v. w.	1.68	V. v. w.
		1.59	V. w.
		1.34	V. w.
		1.29	V. w.

[a] Bracketed figures indicate outer limits of a broad band which may represent a composite of several lines. V. = Very. W. = Weak. St. = Strong. M. = Medium.

Beta d-Glucose.—The powder data for beta glucose are not capable of interpretation without the support of crystallographic data, but the observed interplanar spacings are here placed on record in Table III in order to point out a difference between the crystals of the beta and alpha forms.

Summary

The crystal structures of three forms of glucose (alpha and beta anhydrous glucose and alpha glucose monohydrate) have been studied by the x-ray powder method. The interplanar. spacings of the three forms are given. The data for anhydrous alpha glucose correspond to an orthorhombic unit cell having dimensions: $a = 10.45$ Å., $b = 14.85$ Å., $c = 4.97$ Å., and meet the requirements of space group V^4. The data for alpha glucose monohydrate agree with the requirements of a monoclinic unit cell having dimensions: $a = 8.72$ Å., $b = 5.03$ Å., $c = 9.59$ Å., $\beta = 97°59'$ and correspond to space group c_2^2.

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OXIDATION-REDUCTION POTENTIALS.
IV. THE DETERMINATION FROM EQUILIBRIUM DATA.
B. FERRIC-FERROUS ELECTRODE

BY STEPHEN POPOFF, VERNON B. FLEHARTY AND EDWIN L. HANSON

The determinations of oxidation–reduction potentials from equilibrium data are considered to be more reliable[1] than those from e. m. f. measurements because in the former one attains true equilibrium, while in the latter one cannot always be certain that an inert electrode will always record the true potential, especially in dilute solutions. E. m. f. measurements are further complicated by liquid junction potentials, which cannot, theoretically at least, always be entirely eliminated. In equilibrium data it is also possible to work with the more dilute solutions in which the principle of ionic strength can be considered to hold—thus the activity coefficients of the ions can be calculated from the limiting case of the Debye–Hückel equation.

When metallic mercury comes in contact with ferric perchlorate solution, the following reaction takes place

$$2Fe(ClO_4)_3 + 2Hg \rightleftharpoons 2Fe(ClO_4)_2 + Hg_2(ClO_4)_2$$
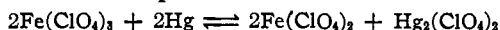
This reaction is of special interest because, at equilibrium, the substances are present in comparable amounts which can be suitably analyzed. It is therefore possible to determine the equilibrium constant by purely

[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 411.