

At low frequencies $\alpha/v^2 \approx 2\mu_m/c.v_m = A$, say. Kneser's equation can then be put in the form

$$1/\alpha = 1/A(1/v^2 + 1/v_m^2),$$

and may be tested by plotting $1/\alpha$ against $1/v^2$. This plot yields the best values of A and v_m to fit the experimental points; from the plot we find $A = 12,000 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$ and $v_m = 2.0 \times 10^6 \text{ c.p.s.}$ These constants can be used to calculate the theoretical variation of α/v , which is proportional to μ . In Fig. 2 the expected variation of α/v as a function of $\log v$ is represented by the solid line, and the points are observed values of α/v , after subtraction of the absorption corresponding to $\alpha/v^2 = 155 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$. The agreement with theory is good and suggests that the extra absorption is correctly ascribed to some phenomenon with a relaxation time of $5 \times 10^{-7} \text{ sec.}$

The process responsible for the absorption in this case is very probably the chemical equilibrium between the dimer and the monomer of acetic acid. The rate of this reaction, and consequently v_m , should increase rapidly with temperature. Experiments to find the temperature dependence of v_m are in progress.

Kneser's relation (11) also enables an estimate to be made of the total change in velocity to be expected corresponding to the fall in α/v^2 . For

$$\frac{\Delta c}{c} \approx \frac{\mu_m}{\pi} = \frac{\alpha c v_m}{\pi v_m^2} = A \cdot \frac{c v_m}{2\pi}$$

Using the values of A and v_m quoted above, and putting $c \approx 1 \times 10^5 \text{ cm. sec.}^{-1}$, we find

$$\frac{\Delta c}{c} \approx 4 \times 10^{-3}.$$

It seems likely that such a small change in velocity will be hard to find, due to the heavy absorption in the frequency-range concerned. The 1 per cent dispersion reported by Spakowski⁹ between 0.2 and 3 Mc./s. appears to be roughly confirmed.

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Crystal Structure of B-Starch from X-Ray Fibre Diagrams

In recent papers¹, Kreger has published fibre data from the B(tuber)-modification of starch. Though his technique is new and interesting, Kreger's results mainly confirm data which were published some years ago². Apparently the earlier fibre diagrams were more highly orientated than Kreger's, since the fibre spacing ($10.6 \pm 0.1 \text{ kX.}$) could be obtained unambiguously from these diagrams. More recently, both B and A (cereal-type) fibres have been prepared by new techniques with truly extraordinary orienta-

tions³. The fibre spacing of the A-modification (10.5 kX.) is substantially equal to that of the B-modification, a result not unexpected, since Bear and French established a very close relationship between these modifications of starch⁴.

From the fibre diagrams a unit cell and rough structure for the B-modification of starch have been proposed². The orthorhombic unit, $a = 16.0$, b (fibre) = 10.6 , $c = 9.1 \text{ kX.}$, is essentially the same as suggested in Kreger's first paper. More recently, Kreger has criticized this unit on the grounds that it leads to an X-ray density (1.60) no greater than the observed density of starch under water (1.60 – 1.63)¹. The X-ray density was calculated assuming that the hydration of B-starch amounts to one water molecule per glucose residue.

The degree of hydration assumed by Kreger is apparently about right for the A modification of starch; but there is considerable reason for believing that the ideal hydration of the B-modification is higher. Thus, air-dried corn starch and the cereal starches contain about 10 per cent moisture, while tapioca, potato and other tuber starches normally contain about 15–20 per cent (between $1\frac{1}{2}$ – 2 water molecules per glucose residue⁵). Moreover, it has been noted that the tuber starches especially yield much sharper X-ray diagrams when thoroughly wet with water⁴, indicating that a very high degree of hydration is ideal for the crystalline portions of B-starch. It seems not unreasonable that at the ideal composition of the B-modification there are as many as two water molecules per glucose residue. In this case, the X-ray density would be 1.67 , certainly high enough for a carbohydrate and in very satisfactory agreement with observed densities of starch under water (1.60 – 1.63)¹.

The difficulty in understanding the fibre spacing of starch, noted by Kreger¹, has been discussed before². However, the lower fibre spacing found from space models is sensitive to angles in the glucose ring and in the glucosidic bond, and the proposed structure cannot be eliminated by considerations of only those models which have tetrahedral or other idealized angles.

In considering the possibility of an error in the suggested unit cell for B-starch, it seems well to point out that the difficulties in interpretation of fibre diagrams usually arise from screw axes or centring which eliminate the first-order spacings of the non-fibre axes. The B-modification of starch, in the present interpretation, has a screw axis only along the fibre axis, the spacing of which is not in doubt. The a-axis of the proposed unit cell is just the Bragg spacing of the lowest-order reflexion on the equator of the fibre diagram. This leaves no further room for manipulation of lattice parameters from fibre data for an orthorhombic unit, and makes it nearly certain that no simpler unit for the B-modification can be found.

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