$$N_2 = \tfrac{1}{2}\left[1 + \frac{H_1 - H_2}{Wab} + \frac{CR}{Wab}\,T\right] \quad . \quad . \quad . \quad (1)$$

$$\mathrm{Ln}\,P = \frac{A}{RT} + D \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$N_2 \sim A^1 \mathrm{ln}\,P + C^1 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where H_1 and H_2 are the latent heats of vaporization of the pure components 1 and 2 respectively, Wab is the mixing energy, P is the total pressure of the azeotropic system, A, C, D, A^1 and C^1 are constants for a given system which can be identified with other more complex functions of thermodynamic quantities.

It appears that there is a broad class of azeotropes the behaviour of which is described by equations 1–3. It is convenient to describe these as *normal azeotropes*.

A fuller treatment of the subject will be published elsewhere.

We are indebted to Dr. R. P. Linstead, director of the Chemical Research Laboratory, for permission to publish this note.

<div align="right">

E. A. COULSON
E. F. G. HERINGTON

</div>

Chemical Research Laboratory,
Teddington, Middlesex.
July 6.

[1] Redlich and Schutz, *J. Amer. Chem. Soc.*, **66**, 1001 (1944).
[2] Kireev, *Acta Physicochimica U.R.S.S.*, **14**, 371 (1941).
[3] Fowler and Guggenheim, "Statistical Thermodynamics" (1939).

Movement of a Thin Plate in Non-Newtonian Liquids

VISCOSITY (or consistency) results obtained with spheres falling through non-Newtonian liquids, unlike results with Newtonian liquids, appear to be difficult of interpretation mainly because the rate of fall is largely dependent on the depth of the sphere in the liquid. Facsimile tracings on a rotating drum (Fig. 1a) obtained with a $\frac{3}{4}$-in. diameter steel ball, carrying a fine rigid stem with pen attached, falling through a lime-base grease in a tall beaker approximately 19 cm. high and 9 cm. diameter, indicate that the rate of fall in the upper region of the grease can be many times that in the lower, and it is possible for the ball to remain suspended. Similar results were obtained with paints (100 gm. zinc-chromate in 100 c.c. linseed oil) using a 1-cm. diameter steel ball attached to a fine thread passing over a 'frictionless' pulley and counterpoised by a known weight (Fig. 1b).
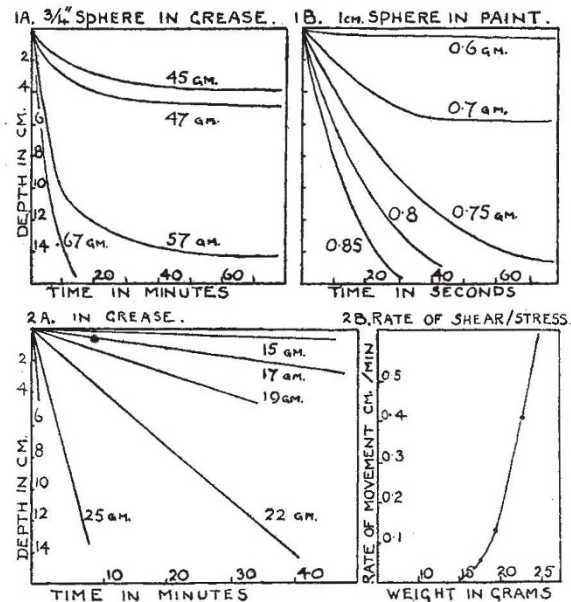
The complexity of the fall behaviour is explicable on the assumption that greater energy is required to displace the system at greater depths because of the rigidity of the system.

A thin plate, such as a thin double-edge razor blade or a glass microscope coverslip, should be largely free from this volume displacement difficulty. When the plate was drawn edge on through the grease by means of a fine thread passing over the pulley, with constant counterpoise, the rate of movement through the bulk of the material was practically constant, and by using different weights as counterpoises it is possible to determine the yield value of the grease (Fig. 2).

Measurements of the rate of withdrawal of a plate from pitch using a clearance of 2 mm. from each of the walls were made by Nutting[1]. Dudeski in 1926, working with a larger vessel, determined the apparent viscosity of a sample of asphalt as 10^{11} poises. More recently, Veiler and Rehbinder[2] have measured the resistance of thin plates, $50\,\mu$ in thickness, and of total area 15–111 sq. cm. of copper and aluminium foil and mica of rough surface, in clay suspensions. The container with suspension was placed on a falling platform, $3\cdot3\,\mu/\mathrm{sec.}$, and the pull on the plate measured on a quartz spring to which the plate was attached by a quartz thread : a micrograph scale was used. Veiler and Rehbinder found with the different plates an ultimate shearing stress of 10·60–10·94 dynes/sq. cm. for a clay suspension. Dumanski, using the same method with gelatin solutions, established the invariability of the shear modulus within a broad range of plate areas and for various container dimensions.

Using an immersed rectangular microscope coverslip, 24 mm. by 32 mm., suspended by a fine quartz thread from a glass or quartz fibre beam, fixed at one end, and observing the depression of the free end of the beam (or rise when the movement of the liquid is stopped), when the level of the liquid is allowed to fall by running the liquid out from the bottom of the vessel, it is easy to demonstrate the viscous drag on a plate by a liquid such as water, with a viscosity as low as a centipoise ; and to show the drag to be proportional to the rate of flow. With non-Newtonian liquids their peculiar rheological properties can be demonstrated by this method.

<div align="right">E. W. J. MARDLES</div>

Royal Aircraft Establishment,
Farnborough.

[1] *Proc. Amer. Soc. Test. Mat.*, **21**, 1162 (1921).
[2] *Doklady, URSS.*, **49**, 345 (1945).

X-Ray Fibre Pattern of Part of a Single Starch Grain : Powder Photographs of Potato, Wheat and Arrowroot (*Maranta*) Starch

ATTEMPTS to elucidate the crystal structure of native starch by means of X-ray diffraction have hitherto failed on account of difficulties due to the small size of the starch grains and their radially arranged crystallites. These circumstances have made it impossible to obtain the so-called fibre pattern of native starch, which is necessary in calculating the net parameters in substances of high polymer nature like this and which has led to a clear picture of the structures of the two related substances, cellulose and chitin.

During recent years we have developed a new micro-method for X-ray diffraction investigation of biological objects[1], which has now enabled us to obtain a fibre pattern of a part of a single starch grain. We used the large starch grains of *Phajus grandifolius*. Before discussing the fibre pattern we will give a description of the powder pattern of *Phajus* starch.

The powder diagram of *Phajus* starch resembles the diagram of potato starch. So we have to do with a B pattern, according to the nomenclature introduced by Katz[2] for the various types of starch patterns. In order to compare both diagrams more exactly, we also made diagrams of potato starch. It then appeared that these latter showed a number of reflexions not mentioned by Katz, nor by other authors (references to non-Continental literature were made up to 1940).

By using a narrow X-ray beam and preventing desiccation of the starch during exposure, it became evident, from the diagrams thus obtained, that reflexion 2 of Katz[3,2] splits up into three weak reflexions, $2a$, $2b$ and $2c$, corresponding respectively to lattice plane distances of 8·8 A., 7·8 A. and 7·1 A. Reflexion $6a$ of Katz splits up into $6a^1$ and $6a^2$, corresponding to $d = 4\cdot11$ A. and $d = 4\cdot02$ A. Finally, reflexion 8 splits up into $8a$ and $8b$ with $d = 2\cdot99$ A. and $d = 2\cdot86$ A. For the lattice plane distance belonging to reflexion 1 we deduced 15·5 A. instead of 15·9 A. as given by Katz. Various other reflexions also showed differences in this respect, but smaller.

Wheat and *Maranta* starch gave powder diagrams showing similar new details, which will be dealt with elsewhere.

Now the powder diagram of *Phajus* starch appeared to differ from that of potato starch only in that reflexions $2c$ and $6a^1$ are missing.

In the fibre pattern obtained from the single grain, all reflexions of the powder pattern are found ; with the exception of 7 and $8a$, they show clear maxima, which make it possible to distinguish four layer lines. The direction of the fibre axis is nearly perpendicular to the layers of the starch grain. When calculating the identity period in the direction of the fibre axis from the maxima we find distances varying from 9·2 to 10·3 A., with a mean value of 9·9 A. $\pm$ 0·3 A. If we assume straight-chain molecules, parallel to the fibre axis, and assume the period to range over two glucose groups, as is the case in cellulose and chitin, we might expect for this period a distance of $c.$ 10·4 A.

It further appears in the fibre pattern that the strong reflexions corresponding to $d = 15\cdot5$ A. and $d = 5\cdot15$ A. and a less strong reflexion with $d = 4\cdot52$ A. (reflexions 1, 4 and 5 of Katz) show maxima at the equator. According to this we can assign these reflexions the indices (001), (003) and (200) respectively. Assuming a primitive orthorhombic cell, this would lead to unit cell dimensions : $a = 9\cdot04$ A. and $c = 15\cdot50$ A. in the (0k0) plane. We will suppose the period in the b-axis to be 10·4 A. as in cellulose and chitin.

Starting from this elementary cell, indexing of all other reflexions appeared to be possible without any difficulty. The differences between calculated and observed values of d generally do not amount to more than 0·5 per cent, except in reflexion $2a$, where the difference is 2 per cent. Supposing the cell contains eight glucose units and eight molecules of water, the density calculated from this unit cell would be 1·63 ; omitting the water the density would be 1·47.

The density of starch, as determined with a pycnometer, is given by H. Rodewald[4]. Starch, dried in a stream of hydrogen at 100° C., has a density of 1·49 when determined under chloroform or petroleum ether (1·43 if dried very thoroughly) and a density of 1·60–1·63 when determined under water at 20° C.

Hence there is a remarkable correspondence between X-ray densities and pycnometric densities of dry and wet starch. We should, however, be cautious in using this as an argument for the exactness of the above dimensions of the unit cell. The X-ray density must be related to monocrystals, and if indeed the starch grain were a monocrystal the numbers found might be considered as a proof. The main component of starch, however, is considered to be a network of primary valency chains, which are linked in crystalline micells in which water is bound in the lattice[5]. These micells alone are responsible for the X-ray density found above.