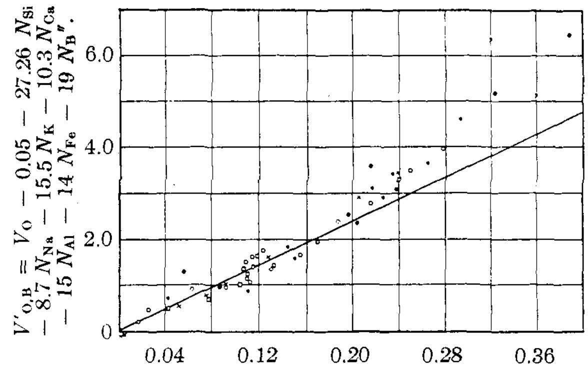
THE STRUCTURE AND PROPERTIES OF GLASSES CONTAINING BORON

Sir:

In a series of papers to be published in the *Journal of the Optical Society of America*, a large amount of evidence is presented to show that the volume, the refraction, and the dispersion of that amount of a silicate glass which contains one gram atom of oxygen are simple additive functions of the ratios (N_M) of the numbers of atoms of the "metallic" elements to the number of atoms of oxygen, in accordance with the equations

$$V_0 = k + b_{Si} + c_{Si}\, N_{Si} + \Sigma' c_M\, N_M$$
$$(n_\lambda - 1) V_0 = R_{0,\lambda} = \Sigma a_{M,\lambda}\, N_M$$
$$(n_{\lambda_1} - n_{\lambda_2}) V_0 = D_{0,\lambda_1\lambda_2} = \Sigma(a_{M,\lambda_1} - a_{M,\lambda_2}) N_M$$

In general, the a_M and c_M constants do not vary with the composition. The constants b_{Si} and c_{Si}, however, are different for different ranges of N_{Si}. The constant k is small, or zero, and seems to depend on the laboratory in which the data originate, presumably on the annealing technique.



$$N_B' = \begin{cases} N_B, \text{ for } (N_{Si} + N_B) < 0.50 \\ 2\text{-}4N_{Si}\text{-}3N_B, \text{ for } (N_{Si} + N_B) > 0.50 \end{cases}$$

Fig. 1.—Data by Turner and co-workers, $(N_{Si} + N_B) > 0.435$: ○, Na_2O–B_2O_3; ●, Na_2O–B_2O_3–SiO_2; □, Na_2O–B_2O_3–SiO_2(–CaO–Al_2O_3–Fe_2O_3); ×, Na_2O–K_2O–CaO–B_2O_3–SiO_2(–Al_2O_3–Fe_2O_3).

Boron-containing glasses do not obey these simple equations without modification. The contribution of the boron to the volume (or the refraction or the dispersion) depends not only on N_B but also on N_{Si}. From our present knowledge of atomic and ionic radii and of the crystal structures of boron-containing compounds, we should expect that in glasses in which both N_{Si} and N_B are small (*i. e.*, in which oxygen atoms are present in relatively large proportions), most or all of the boron atoms would be surrounded tetrahedrally by four oxygen atoms. On the other hand, with large N_{Si} and N_B we should expect some of the boron atoms to be surrounded by but 3 close oxygen neighbors.

A computation of the relative amounts of B′ (with 4 oxygen neighbors) and B″ (with 3) is possible on the basis of the following assumptions. (1) If $(N_{Si} + N_B)$ is less than one-half, every boron atom is surrounded by 4 oxygens; (2) if $(N_{Si} + N_B)$ is greater than one-half, every oxygen atom has two silicon or boron neighbors. Assuming also (3) that the values of b_{Si} and c_{Si} depend on the range of $(N_{Si} + N_B)$, rather than on N_{Si} alone, $c_{B'}$, $c_{B''}$, $a_{B'}$ and $a_{B''}$ values have been deduced which give fair agreement with experiment, much better than is obtained on the assumption that the boron atoms are all alike, as regards their effect on the volume and refraction of glasses.

There is some indication that the actual number of B′ atoms is somewhat greater than that calculated, especially for $(N_{Si} + N_B)$ near 0.50, with N_B large compared with N_{Si}. This would account for the large deviations from the straight line of the points on the right-hand side of the accompanying figure. The discrepancy might be expected to be less, the better the annealing.

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THE APPARENT MOLECULAR SHAPE AND MOLECULAR WEIGHT OF PROTEINS, FROM VISCOSITY AND DIFFUSION MEASUREMENTS

Sir:

As a part of an investigation of the molecular shape and weight of native and denatured proteins, we have carried out viscosity and diffusion measurements of some undenatured proteins, under carefully controlled experimental conditions. Our viscosity measurements were confined to low protein concentrations, *i. e.*, between 1 and 15 mg. per cc. The specific viscosities of the proteins investigated are independent of the velocity gradient and linear with respect to the protein concentrations up to about 8 mg. per cc. The diffusion measurements were carried out as described previously.[1,2] The apparent shapes of the protein molecules, assuming negligible hydration, were calculated from their specific viscosities with the equation derived by Simha,[3] without the approximation given previously.[3]

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[1] Neurath and Saum, *J. Biol. Chem.*, **128**, 437 (1939).

[2] Neurath and Cooper, *ibid.*, in press (1940).

[3] Simha, *J. Phys. Chem.*, **44**, 25 (1940).

Substituting the values for the axial ratio for prolate (b/a) and oblate (a/b) ellipsoids into Perrin's diffusion equations,[4] we have calculated the dissymmetry constants f/f_0 for the shapes of prolate and oblate ellipsoids. From these and the diffusion constant, D, the molecular weight, M, has been calculated and compared with the values for f/f_0 and M, as found by sedimentation and diffusion measurements.[5,6] Rotatory diffusion constants have been computed from the axial ratios and the calculated molecular weights by the Gans equation.[7] The amount of hydration has been estimated from the viscosity data on the assumption of spherical shape.[8]

For crystalline lactoglobulin, for instance, the following has been found: $b/a = 4.9$ and $a/b = 7.6$, for prolate and oblate ellipsoids. The molecular weight, calculated from the axial ratios and D, was 43,300 and 33,700 as compared with 41,500 from sedimentation and diffusion data. Rotatory diffusion constants, D_r, were 2.8 and 3.8×10^6 for these two models. 93% hydration had to be assumed in accounting for the specific viscosity. For crystalline, carbohydrate-free serum albumin the values were 5.0 and 7.8 for the axial ratios, and 71,000 and 55,700 for M, as compared with 70,00 from sedimentation data; 1.3 and 2.9×10^6 for D_r, and 97% hydration. For serum glycoid, obtained by repeated fractional precipitation with 2.5 M ammonium sulfate at pH 5.2, the values were: 5.3 and 8.2 for the axial ratios, 85,000 and 66,200 for M, 1.3 and 2.3×10^6 for D_r, and 105% hydration. Similar data also have been obtained for crystalline pepsin and for three euglobulin-free horse pseudoglobulin fractions, GI, GII and GIII, precipitable by 1.36, 1.6 and 2.1 M ammonium sulfate, respectively, at pH 5.2. The axial ratios for GI, GII and GIII were, respectively, 7.7, 7.2 and 6.8 for prolate ellipsoids and 12.6, 11.6 and 10.6 for oblate ellipsoids. The calculated molecular weights were about 200,000, 150,000 and 200,000 for prolate and 150,000, 120,000 and 150,000 for oblate ellipsoids.

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(4) Perrin, *J. phys. Radium*, **7**, 1 (1936).

(5) Svedberg and Pedersen, "The Ultracentrifuge," Oxford University Press, New York, N. Y., 1940.

(6) Polson, *Kolloid Z.*, **87**, 149 (1939).

(7) Gans, *Ann. Physik*, **86**, 628 (1928).

(8) Kraemer and Sears, *J. Rheol.*, **1**, 667 (1930).

CATALYTIC HYDROGENATION WITH DEUTERIUM

Sir:

When maleic acid is catalytically hydrogenated by shaking with active palladium or platinum in a system initially containing ordinary water and deuterium gas, the hydrogen atoms of the succinate ion formed have a deuterium concentration from three to five times higher than that of the liquid phase. If the reduction is carried out in heavy water by passing through a stream of ordinary hydrogen, the resulting compound contains practically no deuterium. Whatever the mechanism of the reduction may be, the hydrogen at the catalyst surface used for the hydrogenation has not been in equilibrium with the entire liquid phase; the reduction is faster than the exchange between the hydrogen atoms of gas and water.

When α-keto glutaric acid was reduced with ordinary hydrogen in an ammoniacal solution of 6.7 atom per cent. heavy water with active palladium, the glutamic acid formed had the composition $C_5H_{8.963}D_{0.037}NO_4$. The barium succinate obtained after degradation of this glutamic acid with chloramine T had the composition $C_4H_{3.964}D_{0.036}O_4Ba$. As none of the deuterium was lost during degradation, it could not have been attached to the α carbon atom of the glutamic acid. Most probably it was at the β carbon atom.[1] This reduction was also faster than the exchange.

If the reaction is carried out with normal water and deuterium gas, a glutamic acid of different isotope composition results. 0.020 mole of α-keto glutaric acid was dissolved in 2.25 moles of water containing 0.060 mole of ammonia. The solution was shaken for six hours with active palladium in an atmosphere of deuterium gas. At the end of this time the water contained 0.53 atom per cent. deuterium, while the glutamic acid contained 15.4 atom per cent. deuterium. The empirical formula of the glutamic acid was therefore $C_5H_{7.61}D_{1.39}NO_4$. On refluxing this glutamic acid in normal water with 20% hydrochloric acid for five days no change in deuterium concentration occurred. The barium succinate obtained after degradation of the glutamic acid had the formula $C_4H_{2.87}D_{1.13}O_4Ba$. From these figures it can be calculated, assuming that no loss of deuterium had occurred during the degradation, that the α hydrogen atoms contained 26 and the β hydrogen atoms 56 atom per cent. deuterium, respectively. That the α position contains a high

(1) Ratner, Rittenberg and Schoenheimer, *J. Biol. Chem.*, in press.