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.

concentration of deuterium is in accord with the experiments with maleic acid, and the same mechanism may be responsible. Such high deuterium concentration in the β position is most striking, as the keto–enol mechanism would tend to introduce normal hydrogen from the water into this position. The β hydrogen atoms of the dissolved keto glutaric acid seem to have exchanged with the deuterium of the gas phase.

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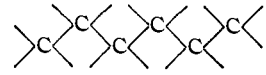
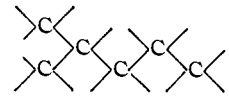
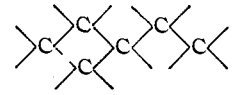
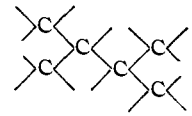
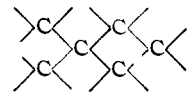
ENERGIES OF ISOMERIZATION OF THE FIVE HEXANES

Sir:

Data obtained in this Laboratory on the heats of combustion of each of the five isomeric hexanes[1] lead to the values given in Table I for the energies of isomerization at 25°, for both the liquid and the gaseous states, expressed in terms of the relative energy content referred to normal hexane as zero, with each substance in its thermodynamic standard state.

TABLE I

RELATIVE ENERGY CONTENTS OF THE FIVE HEXANES AT 25°

Isomer	Skeleton structure	Relative energy content[a] $E°$ (isomer) $- E°$ (n-hexane) Liquid, kcal./mole	Gas, kcal./mole
n-Hexane		0	0
2-Methylpentane		−1335 ± 160	−1748 ± 200
3-Methylpentane		− 754 ± 160	−1069 ± 200
2,3-Dimethylbutane		−1964 ± 160	−2546 ± 200
2,2-Dimethylbutane		−3446 ± 160	−4375 ± 200

[a] See footnotes *a* and *b* of Table II.

These data (see column 1 of Table II for the same quantities converted to 0°K.) indicate that (1) as was expected on the basis of the data previously reported for the butanes[2] and the pentanes,[3,4] there are important differences in the energy contents of these isomers; (2) contrary to what might have been expected on the basis of the values previously reported for normal butane and 2-methylpropane (isobutane) and for normal pentane and 2-methylbutane, there is a significant difference in energy content between 2-methylpentane and 3-methylpentane; (3) the difference in energy content between normal hexane and 2,3-methylbutane is roughly the sum of the differences in energy content between normal hexane and 2-methylpentane and between normal hexane and 3-methylpentane; (4) the difference in energy content between normal hexane and 2,2-dimethylbutane is roughly the same as that between normal pentane and 2,2-dimethylpropane (tetramethylmethane or neopentane).

When combined with the appropriate values of $H - H_0°$ and of $(H_0° - F°)/T$ as calculated by Pitzer,[5] these data yield the thermodynamic values given in Table II. Columns 2, 3, 4, and 5 give, for 0, 298, 600, and 1000°K., values for $H°$ (isomer) $- H°$ (n-hexane), which is the increment in heat content for the reaction, $n\text{-}C_6H_{14} = i\text{-}C_6H_{14}$; columns 6, 7, and 8 give, for 298, 600, and 1000°K., values for $F°/T$(isomer) $- F°/T$ (n-hexane), which when multiplied by

(1) E. J. R. Prosen and F. D. Rossini, forthcoming paper in *J. Research Natl. Bur. Standards.*

(2) F. D. Rossini, *J. Research Natl. Bur. Standards*, **15**, 357 (1935).

(3) F. D. Rossini, *ibid.*, **13**, 21 (1934).

(4) J. W. Knowlton and F. D. Rossini, *ibid.*, **22**, 415 (1939).

(5) K. S. Pitzer, *Chem. Rev.*, **27**, August (1940).