activity of the gas at time, t, to that at equilibrium. The rate of the exchange reaction is proportional[3] to $a\ d \log (1 - F)/dt$, where a represents the quantity of hydrogen gas.

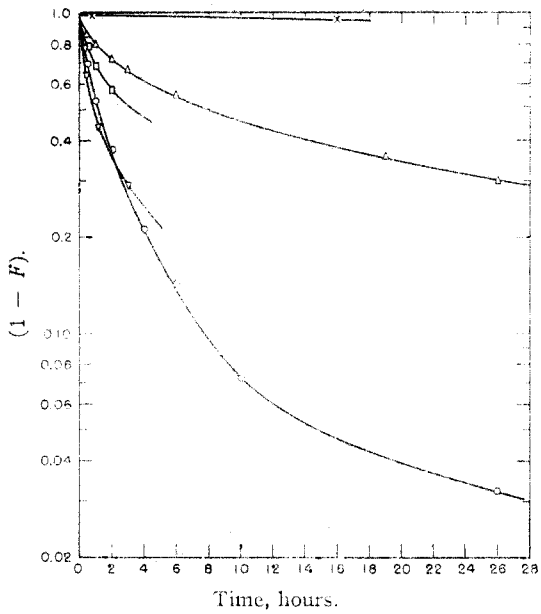


Fig. 1.—Rate of exchange of 1835 millimoles of lithium hydride with hydrogen gas in a one-liter flask; temp., mg. atoms of H_2; x, 25°, 5.5; △, 170°, 36.5; ⊡, 170°, 6.7; ▽, 170°, 2.25; ⊙, 200°, 38.2. F is the fraction of equilibrium concentration of tritium in the gas.

The non-linearity of these plots, judged by the criteria[3,4] of Zimens, indicates that the rate of exchange is controlled by a diffusion process within the solid. This conclusion is substantiated by our observation that the rate of formation of HD in a mixture of H_2 and D_2 in contact with lithium hydride at 40° is tenfold faster than the rate of exchange with the solid. The increase in exchange rate with hydrogen pressure at constant temperature rules out diffusion of hydride ions as the rate-controlling process but would be consistent with a mechanism involving diffusion of hydrogen molecules, possibly as H_3^- ions.

Equilibration experiments at 200°C. gave a value 3.7 for the equilibrium constant, $K = (HT)(LiH)/(H_2)(LiT)$, in agreement with a value 3.66 calculated from the published partition functions[5] for the various isotopic species.

The availability of lithium hydride-t has made possible the preparation[6] of lithium aluminum hydride-t, from which a wide variety of tritium labeled organic compounds can be prepared in high yields.[7] As an example, ethanol-1-t has been obtained in a radiochemical yield of 80% by reduction of ethyl acetate.

An attempt to prepare lithium aluminum hydride-t by the direct exchange of commercial lithium aluminum hydride with a hydrogen-tritium mixture at 100° was unsuccessful.

Acknowledgments.—We are indebted to Dr. B. Weinstock for the mass-spectrometric deuterium analyses, and to Prof. W. G. Brown for many helpful suggestions.

CHEMISTRY DIVISION KENNETH E. WILZBACH
ARGONNE NATIONAL LABORATORY
CHICAGO, ILLINOIS LOUIS KAPLAN

RECEIVED NOVEMBER 10, 1950

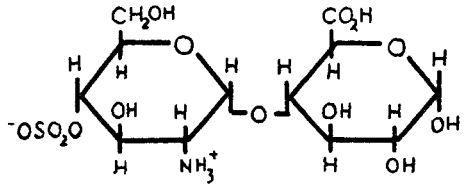
(3) Norris, *J. Phys. Colloid. Chem.*, **54**, 777 (1950).
(4) Zimens, *Arkiv. Kemi, Mineral., Geol.*, **A20**, No. 18 (1945).
(5) Urey, *J. Chem. Soc.*, 562 (1947).
(6) Finholt, Bond and Schlesinger, THIS JOURNAL, **69**, 1199 (1947).
(7) W. G. Brown in R. Adams, "Organic Reactions," Vol. VI, in press.

THE STRUCTURE OF HEPARIN[1]

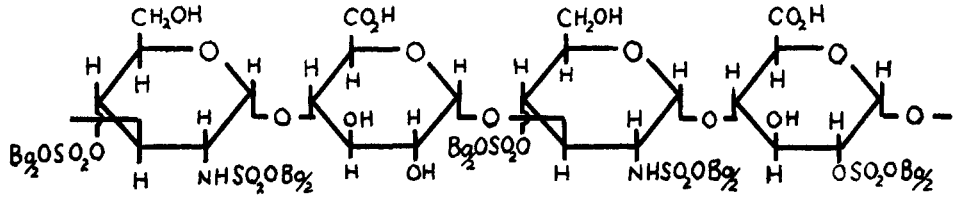
Sir:

Benzidine-purified heparin fractionated from water as its neutral barium salt yields in its lesser-soluble fraction a product which, as the sodium salt, is homogeneous by electrophoresis (mol. wt. by diffusion *ca.* 20,000) and by the Craig countercurrent technic; anticoagulant potency *ca.* 700 Roche ACU/mg. Its crystalline barium acid salt shows essentially the analysis previously reported[2] with the N:S = 2:5 (per tetrasaccharide unit) established. Periodate titer shows the presence of 1.0 α-glycol group per tetrasaccharide unit. Desulfated, acetylated heparin[3] (somewhat degraded), characterized as the amorphous sodium acid salt of $[\alpha]^{24}D$ +16.5° ($CHCl_3$), gives with barium methoxide *N*-acetyl desulfated heparin whose amorphous barium salt, $[\alpha]^{25}D$ +76° (water), consumed 1.0 mole of periodate per disaccharide unit (extrapolated, 3 to 6°, initial *p*H 4.5) without formation of formaldehyde or formic acid and with destruction of the hexuronic acid portion only. Partial acid hydrolysis (*c* 2, 0.5 *N* sulfuric acid, eighteen hours reflux) gave an amorphous reducing disaccharide, $[\alpha]^{22}D$ +79° (water), isolated through its amorphous cupric salt. This, designated heparosinsulfuric acid, contained one sulfate ester group, hexosamine and hexuronic acid with C-1 of the latter free (yellow precipitate with barytes[4]). Periodate assay performed under conditions minimizing formate ester hydrolysis[5] (initial pH 6.8) showed oxidant consumption of 3.0 moles (per mole) with the formation of 1.0 mole of formic acid and no formaldehyde and with the destruction of both the hexosamine and hexuronic acid portions (negative color tests). Amorphous *N*-acetylheparosinsulfuric acid was prepared with silver acetate and acetic anhydride in methanol; periodate assay (moles per mole);

(1) Supported by fellowship funds granted by The Ohio State University Research Foundation to the University for aid in fundamental research.
(2) M. L. Wolfrom, D. I. Weisblat, J. V. Karabinos, W. H. McNeely and J. McLean, THIS JOURNAL, **65**, 2077 (1943).
(3) M. L. Wolfrom and R. Montgomery, *ibid.*, **72**, 2861 (1950).
(4) P. A. Levene and C. C. Christman, *J. Biol. Chem.*, **122**, 204 (1937).
(5) K. Meyer and P. Rathgeb, *Helv. Chim. Acta*, **32**, 1102 (1949).



I



II

oxidant, 2; HCO_2H, 1; HCHO, 0; hexuronic acid (only) destroyed.

Favoring pyranoid rings, the above data indicate I as highly probable for heparosinsulfuric acid and II for barium acid heparinate. The amino groups in II are shown sulfated in view of the work of Jorpes and co-workers.[6] The strongly positive rotations of heparin and its derivatives make the α-D-linkages probable. The O-sulfate placement in the D-glucuronic acid component is limited to one of the four secondary hydroxyl groups. Alkali-treated heparin shows by periodate 2 α-glycol groups per tetrasaccharide unit. The inactivation of heparin by mild acidity with no sulfate loss and with the appearance of a free amino group[2,7] may be caused by sulfate migration from N to O (probably C-3 of the uronic acid), a postulation which will require additional experimental evidence.

(6) J. E. Jorpes, H. Boström and V. Mutt, *J. Biol. Chem.*, **183**, 607 (1950).

(7) M. L. Wolfrom and W. H. McNeely, THIS JOURNAL, **67**, 748 (1945).

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

M. L. WOLFROM
REX MONTGOMERY
J. V. KARABINOS
P. RATHGEB

RECEIVED OCTOBER 23, 1950

BOOK REVIEWS

Advances in Colloid Science. Volume III. Edited by H. MARK, Polymer Research Institute, Polytechnic Institute of Brooklyn, Brooklyn, New York and E. J. W. VERWEY, N. V. Philips Gloeilampenfabricken, Eindhoven, Holland. Interscience Publishers, Inc., 99 Livingston Street, Brooklyn 2, N. Y., 1950. xi + 384 pp. 16 × 23.5 cm. Price, $7.50.

This is the third volume of a series started in 1942. Inasmuch as the second volume appeared in 1946, the successive volumes have been published at four-year intervals. This perhaps constitutes about the right interval of time for the evaluation and recording of the major advances in a continuously expanding science. In the Preface of Volume I the editors expressed the hope that "Advances in Colloid Science could cover world wide developments." Owing to major disorganization, international in scope, the hope expressed could not be entirely fulfilled in any of the volumes to date. In the present volume, however, a gain in that direction has been made, for at least one-half of the contributors are from countries outside of the United States. As in the earlier volumes, the authors were selected because of their favorable reputation and close identification with the field in question. This volume consists of eight sections, the general contents of which are indicated below.

In the first section, "Atomic Forces and Adsorption" by J. H. deBoer, is given a masterful and well integrated presentation of fundamental concepts and theories relating to adsorption. This timely contribution should serve as a stimulating and helpful guide to the very great number of persons who are now working in the field of adsorption.

The second section, "Surface Chemistry and Colloids" by A. E. Alexander, treats of surface properties and of surface films as related to various colloidal systems. These topics are given detailed treatment with special consideration given to the application of surface chemistry to systems of proteins, polymers, foams, emulsions and pastes as well as to different biological systems. This contribution serves to bring out the importance of interfacial studies and the need of further researches pertaining to them.

A specialized treatment of "Quantitative Interpretation of the Electrophoretic Velocity of Colloids" by J. Th. G. Overbeck, emphasizes the important part that electrophoretic experiments have played in the development of colloid science. The author discusses the early work and the classical concepts of electrophoretic velocity as also the fundamental theories with formulations which must be considered. He believes that the inclusion of the "relaxation effect" in the theory of electrophoresis has strengthened the basis for estimating the Zeta potential from electrophoretic mobility. He emphasizes that more and better experimental data are needed and mentions types of investigations that should be productive of useful data.

A fairly short section on "Lyogels" by E. A. Hauser and D. S. LeBeau gives the various theories which have been presented for lyogel structure. A lyogel is defined by the authors as "a colloid semisolid system rich in liquid, its disperse phase characterized by a strong adsorptive capacity for the dispersion medium (solution). The liquid phase, which can be colloidal sol itself, must solvate but not dissolve the gel-forming colloid." It is gratifying to