

Fig. 1.—Chromatography of a beef oxycellulose eluate ACTH preparation on Amberlite XE-97 resin. The sample (420 mg.) in 25 ml. pH 8.85 buffer (0.1 M sodium carbonatebicarbonate) was applied to a column 68 cm. high in a tube 3.4 cm. in diameter. The rate of flow was 22.5 ml./cm.<sup>2</sup>/ hour. The volume collected per tube was 10 ml. Recovery of solids in the active peaks was: A<sub>1</sub>, 20 mg.; A<sub>2</sub>, 13.5 mg.

factor of one-third to one-fourth. Correspondingly, the weight yields of the purified fractions from our columns are lower for beef than for pork.

In studying the behavior of beef oxycellulose eluate materials on the XE-97 columns, it was found that the pH conditions previously used by us for pork fractions<sup>9</sup> were unsuitable. No retarded peaks were observed at pH 8.5 and little activity was recovered. However, as the pH of the buffer was raised, retarded peaks appeared. Resolution of the peaks and recoveries of activity reached maximum values at pH 8.85. Figure 1 shows a curve obtained under the best conditions. The two active peaks appear to correspond to those obtained by Dixon and Stack-Dunne<sup>10</sup> for pork materials.

Preliminary physical and chemical studies have been made on material recovered from the  $A_1$  peak. In order to minimize contamination from the  $A_2$ peak, only the second half of the  $A_1$  peak was used (marked in Fig. 1). The ultraviolet absorption curve of this material was identical with that obtained with corticotropin-A. In 0.1 N hydrochloric acid a maximum was obtained at 275 m $\mu$ and a minimum at 250 m $\mu$ . The best preparations

(9) W. F. White and W. L. Fierce, THIS JOURNAL, 75, 245 (1953).
(10) H. B. F. Dixon and M. P. Stack-Dunne, *Biochem. J.*, 61, 483 (1955).

from both species show a 275/250 ratio of 2.2. Paper chromatography of an acid hydrolysate of the bovine product give an amino acid pattern similar to that obtained from corticotropin-A: cystine, threonine and isoleucine are absent, while arginine, histidine, lysine, tyrosine, phenylalanine, methionine, serine, leucine, valine, glycine, glutamic acid, aspartic acid, alanine and proline are present. The presence of tryptophan, suggested by the ultra-violet absorption curve, was confirmed by its appearance on chromatograms of an aminopeptidase digest. An N-terminal determination by the dinitrofluorobenzene method showed only serine,11 and aminopeptidase gave an amino acid release pattern identical with that obtained with corticotropin-A.<sup>12</sup> Treatment of the bovine product with carboxypeptidase also duplicated the result obtained with corticotropin-A.13

Further studies concerning the relationship between the purified bovine product and corticotropin-A are in progress.

(11) As in the case of corticotropin-A, the purified beef preparation gave a yield of DNP-serine corresponding to only 15-20% of the amount calculated on the basis of a molecular weight in the range of 5000. The low yield appears to be due to the proximity of the tyrosine residue, since both synthetic seryltyrosine and synthetic seryltyrosylserylmethionylglutamic acid (both peptides courtesy of Dr. K. Hofmann, University of Pittsburgh) also give low yields of DNP-serine. (12) W. F. White, THIS JOURNAL, **77**, 4691 (1955).

(13) W. F. White, *ibid.*, **75**, 4877 (1953).

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## DEGRADATION OF GLYCOGEN TO ISOMALTOTRIOSE

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It has generally been considered that the  $\alpha$ -D- $(1 \rightarrow 4)$  and  $\alpha$ -D- $(1 \rightarrow 6)$  linkages occur in glycogen in a ratio of approximately twelve to one.

Glycogen (130 g., Pfanstiehl) was subjected to acid hydrolysis under conditions which would reduce "reversion" to a negligible amount, and the resulting hydrolyzate was subjected successively to chromatographic separation on a carbon column, on filter paper, and to paper electrophoresis. This resulted in a yield of 300 mg. of amorphous material,  $[\alpha]^{23}D + 128^{\circ}$  (c 3.5, water). The material was chromatographically homogeneous, moving on paper at a rate slightly slower than panose (4- $\alpha$ -isomalto pyranosyl-D-glucose) but much more rapidly than panose on paper electrophoresis using borate buffer at pH 10. A similar fast moving spot has been noted<sup>1</sup> in the hydrolyzate of yeast glycogen but was not further investigated.

A molecular weight determination on the amorphous, fully acetylated reduction product (alditol) of the isolated material indicated a trisaccharide structure. The reduced trisaccharide was subjected to partial hydrolysis and in the hydrolyzate, D-glucose, D-glucitol and isomaltose (or isomaltitol) were identified by paper chromatography and isomaltose and D-glucose by paper electrophoresis. The acetylated hydrolysis products were then sep-

(1) S. Peat, W. J. Whelan and T. E. Edwards, J. Chem. Soc., 355 (1955).

arated by silicate column chromatography and identified, by melting point and X-ray powder diffraction patterns, as the crystalline, fully acetylated derivatives of isomaltitol,<sup>2</sup>  $\beta$ -isomaltose,<sup>3</sup> D-glucose and D-glucitol. These data identify

(2) M. L. Wolfrom, A. Thompson, A. N. O'Neill and T. T. Galkowski, THIS JOURNAL, 74, 1062 (1952).

(3) M. L. Wolfrom, L. W. Georges and I. L. Miller, *ibid.*, **59**, 473 (1947); **71**, 125 (1949).

the trisaccharide as isomaltotriose<sup>4</sup> and indicate that a part of the  $\alpha$ -D- $(1 \rightarrow 6)$  glycosyl linkages exist in adjacent units in glycogen.

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(4) Allene Jeanes, C. A. Wilham, R. W. Jones, H. M. Tsuchiya and C. E. Rist, *ibid.*,  $75,\,5911$  (1953).

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## BOOK REVIEWS

Introduction to Thermodynamics of Irreversible Processes. By I. PRIGOGINE, D. Sc., Professor, Faculty of Science, University of Brussels, Brussels, Belgium. Charles C. Thomas, Publisher, 301–327 East Lawrence Avenue, Springfield, Illinois. 1955. ix + 155 pp. 14  $\times$  22 cm. Price, \$4.75

This monograph belongs to a series entitled "American Lectures in Biochemistry and Biophysics" edited by Dr. W. Bladergroen of Delft, the Netherlands, for Sandoz Ltd. of Basle, Switzerland. Having been published simultaneously in the U. S. A. by Charles C. Thomas, in Great Britain by Blackwell Scientific Publications (Oxford), in Canada by the Ryerson Press (Toronto), and its author being on the staff of the University of Brussels, Belgium, this work has a strong international flavor. It is a welcome addition to the still limited "digested" sources of information on the recent developments in the thermodynamics of irreversible processes and it will, in particular, be of definite help to the readers of the author's previous "Etude Thermodynamique des Phénomènes Irréversibles" (Desoer, Liège, Belgium, 1947). Professor Prigogine has been one of the main contributors to this field. As a member of De Donder's school of thermodynamics (see a review by F. O. Koenig, THIS JOURNAL, 77, 6718 (1955)) he brought into complete harmony De Donder's affinity theory and the developments based upon Onsager's linear phenomenological laws and reciprocity relations. From there Professor Prigogine moved on toward a series of brilliant contributions of his own.

The first three chapters constitute a clear condensation of the fundamentals of thermodynamics in the De Donder form, the second principle being presented as that of "entropy production." The section of Chapter III on entropy production due to heat flow, to chemical and electrochemical reactions in closed, open and continuous systems, and the considerations on internal degrees of freedom furnish the transition toward the presentation, in the remaining three chapters, of a detailed study of the general properties of, and relations between rates and affinities, of the linear phenomenological laws, of Onsager's reciprocity relations, etc. Chapter V contains treatments of several important particular cases: chemical reactions near equilibrium, electrokinetic effects and Saxen's relation (the proof of which constitutes one of the main achievements of the thermodynamics of irreversible processes), thermomolecular pressure difference and thermomechanical effect, etc. Chapter VI gives a thorough treatment of stationary non-equilibrium states, of states of minimum entropy production, of stationary state coupling, and finishes with two pages of remarks on applications in biology, a section one would wish to see greatly expanded by someone in the near future. An appendix on non-linear problems, a list of sixty-three references to the literature of the subject (some of them including several titles), a three-page list of notations and a two-page subject index conclude this monograph.

Professors Prigogine and Defay have announced, sometime ago already, a more detailed treatment of irreversible processes in a third and last volume of their "Chemical Thermodynamics." Many workers in a large variety of fields will be waiting with impatience for its publication. In the meantime, the present small volume provides a very readable and clear survey of these fascinating developments.

DEPARTMENT OF CHEMISTRY UNIVERSITY OF OREGON PIERRE VAN RYSSELBERGHE EUGENE, OREGON

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Gmelins Handbuch der Anorganischen Chemie. Edited by E. H. ERICH PIETSCH. Verlag Chemie, G. m. b. H., Weinheim/Bergstr., Germany. 17.5  $\times$  25.5 cm.

This review covers four portions of the 8th Edition, all in the now-familiar style and plan of organization, as follows:

1. Selen, Teil A. System-Nummer 10. xvii + 184 pp. Price \$26.64. No. 3 of Part A of the volume on Selenium. Completes Part A. Covers the literature through 1952 on selenium rectifiers (107 pages) and photoelectric cells (75 pages).

pages).
2. Boron, System-Nummer 13. vii + 253 pp. Price
\$34.80 in cloth, \$33.60 in wrappers. This is the complete volume on Boron. Fifty-eight pages deal with occurrences, 38 with preparation and properties of the element and analytical methods, 117 with compounds of boron with elements of "system-numbers" 1-12. The literature is covered through 1949.

of "system-numbers 1-12. The increases 1-12 through 1949. 3. Gold, Part 2. System-Nummer 62. v + 306 pp. Price \$40.32. No. 2 of the volume on Gold. Covers the literature through 1949 on occurrences (178 pp.), ore reduction and extraction (57 pp.), preparation and purification of the metal (11 pp), special forms including colloidal gold (48 pp.), and surface treatments of the metal and its alloys (6 pp.).

the interal (11 pp), special forms including conordar gold (46 pp.), and surface treatments of the metal and its alloys (6 pp.). 4. *Gold*, Part 3. System-Nummer 62. xxi + 558 pp. Price \$74.88. No. 3 of the volume on Gold. Completes the volume. Covers the literature through 1949 on physical properties (156 pp.), electrochemical behavior (58 pp.), chemical behavior (23 pp.), analytical methods (25 pp.), compounds (113 pp.) and alloys (193 pp.).

NATIONAL BUREAU OF STANDARDS WASHINGTON, D. C.

Edward Wichers

Cancérisation par les Substances Chimiques et Structure Moléculaire. By ALBERTE PULLMAN, Maître de Recherches au Centre National de la Recherche Scientifique, and BERNARD PULLMAN, Maître de Conférences à la Faculté des Sciences de Paris. Masson et Cie, Editeurs, 120 Boulevard Saint-Germain, Paris VI, France. 1955. 306 pp. 16.5 × 25 cm. Price, 2.800 Fr.

One of the important developments in recent years in the study of carcinogenesis by polycyclic aromatic compounds has been the attempt to relate carcinogenic activity to electron distribution as calculated by quantum mechanics. This work, which has been carried out mainly by the Pullmans, the Daudels and Coulson, and their collaborators, has been summarized in several places, notably in the various volumes of the "Advances in Cancer Research" series, and it now receives a detailed presentation in the present volume.