

to conjugated enones,<sup>6</sup> but hetisine, which has been oxidized to mono- and dicarbonyl compounds, gives no such enone. Further, the infrared spectrum of Jacobs' desmethylhetisine,<sup>2</sup> III, shows no  $>C=O$  absorption but does have peaks at 8.75 and 8.99  $\mu$  consistent with a hemiketal formulation.<sup>7</sup> Similar peaks 8.72 and 8.98  $\mu$ , no  $C=C$  absorption, are found in the spectrum of an aqueous sulfuric acid-catalyzed isomerization product of hetisine, m.p. 278–279.5°. (*Anal.* Found: C, 72.94; H, 8.04.)

$CrO_3$ -pyridine oxidation of hetisine produces the keto-"lactam," IV,  $C_{26}H_{23}NO_3$ , m.p. 236–238° (*Anal.* Found: C, 74.01; H, 7.02). The low  $pK_a'$  of IV (6.72) compared to that of hetisine (9.85) (both in 1:1 methanol-water) is explicable in IV on the basis of inductive effect,<sup>8</sup> but is too great to be so explained by a carbonyl further removed from nitrogen than the  $\alpha$ -position.<sup>9,10</sup> A

(6) S. W. Pelletier and W. A. Jacobs, *THIS JOURNAL*, **76**, 4496 (1954).

(7) Models indicate that the ketone derived from the secondary alcohol in I would not be suitably disposed for internal hemiketal formation.

(8) 2,2-Dimethylquinuclidone-6 has a  $pK_a'$  5.33 (water)<sup>11</sup>; quinuclidine has a  $pK_a'$  10.65 (water).

(9) The low  $pK_a$ 's reported for some alkaloids having carbonyl groups  $\gamma$  or  $\delta$  to the nitrogen atom undoubtedly are caused by transannular effects the type  $O=C \cdots C$ .<sup>10</sup> The stereochemistry of



hetisine prohibits such an interaction.

comparison of the infrared spectrum of VI (5.82  $\mu$  with shoulder at 5.81  $\mu$ ) with that of 2,2-dimethylquinuclidone-6 (5.77  $\mu$ )<sup>11</sup> is the basis of the assignment of an  $N-C_9$  bond (bicyclo-2,2,2 system) rather than a  $N-C_3$  or  $N-C_{10}$  bond (bicyclo-2,2,1 system) to hetisine.<sup>12</sup> Base hydrolysis of IV produces a keto-carboxylate, 5.85  $\mu$  ( $C=O$ ), 6.33 and 7.27  $\mu$  ( $CO_2^-$ ).

Jacobs' oxidation product of dihydrodesmethylhetisine must be a carbinol-amine ether<sup>3</sup> because borohydride reduction reconverts it to dihydrodesmethylhetisine (infrared evidence) and because its spectrum shows reduced hydroxyl absorption, no carbonyl absorption, but has peaks at 8.67, 8.75, 8.90 and 9.07  $\mu$  ( $O-C-O$  and  $O-C-N$ ). If the nitrogen is bonded to  $C_9$  or  $C_{10}$ , the third hydroxyl must be *cis* to nitrogen and on  $C_3$  or  $C_4$ . The stability of the hydrolysis product of IV leads us to tentatively assign the hydroxyl to  $C_3$ .<sup>13</sup>

THE ROCKEFELLER INSTITUTE<sup>14</sup>  
NEW YORK 21, NEW YORK

A. J. SOLO  
S. W. PELLETIER

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(10) N. J. Leonard, R. C. Fox and M. Oki, *ibid.*, **76**, 5708 (1954).

(11) H. Pracejus, *Chem. Ber.*, **988** (1959).

(12) As no evidence has appeared to the contrary, hypogoninave also may have a  $N-C_9$  rather than an  $N-C_{10}$  bond.

(13) If the hydroxyl is at  $C_4$ , then IV would give a  $\beta$ -ketocarboxylate on hydrolysis.

(14) This investigation was supported in part by grant RG5807 from the National Institutes of Health, United States Public Health Service.

## BOOK REVIEWS

**Gmelins Handbuch der Anorganischen Chemie.** Achte Völlig Neu Bearbeitete Auflage Zirkonium. System-Nummer 42. E. H. ERICH PIETSCH, Editor. Verlag Chemie-G.m.b.H., (17a) Weinheim/Bergstr., Pappelallee 3, Germany. 1958. xxxvii + 448 pp. 17 × 25 cm. Price, Kart. DM 261.-; Geb. DM 266.-.

**Gmelins Handbuch der Anorganischen Chemie.** Achte Völlig Neu Bearbeitete Auflage. Hafnium. Ergänzungsband. System-Nummer 43. E. H. ERICH PIETSCH, Editor. Verlag Chemie, G.m.b.H., (17a) Weinheim/Bergstr., Pappelallee 3, Germany. 1958. ii + 23 pp. 17 × 25 cm. Price, Kart. DM 17.-; Geb. DM 22.-.

The high standards of the earlier volumes of the eighth edition of Gmelin have been continued in the digest of zirconium publications. Both the breadth of the coverage and the absence of errors in the details were noted with approval; the extensive use of diagrams and graphs is commendable. The discovery, geochemistry, and mineralogy of zirconium are covered in the first 50 pages. The treatment of ores and the applications of the metal and its compounds require 34 pages. Then a very complete discussion of the preparation of the element in various forms and of the physical properties is contained in the next 70 pages. The rest of the book describes the preparations and the properties of alloys and compounds of zirconium.

The short supplementary volume on hafnium devotes a proportionate amount of space to each of the above topics to review articles published mostly between 1940 and 1949. The Table of Contents shows in parallel columns the page numbers of the items in the supplement and in the main volume on hafnium, system number 43, published in 1941.

Although there are a few references to articles published after 1949 and some books published as late as 1957 are listed, the complete coverage as stated in the publication pages extends only through 1949 for both books. As examples of what can be done, the volume on selenium published in 1953 reviews the literature through 1952 and the

volume on platinum published in 1957 reviews through 1953, and it seems unfortunate that the coverage for zirconium and hafnium, particularly the latter as a supplementary volume, was not extended beyond 1949.

Despite this limitation these books will be valuable additions to the shelves of every major chemistry library. One only wishes that a lower price could be established for individual purchasers, as is done by *Chemical Abstracts*, so that the specialist could afford pertinent volumes for his private library.

DEPARTMENT OF CHEMISTRY  
THE UNIVERSITY OF CONNECTICUT  
STORRS, CONNECTICUT

CARL W. MOELLER

**Vapor-Liquid Equilibrium.** By EDUARD HÁLA, Jiří Píck, VOJTĚCH FRIED and OTAKAR VILIM. Translated by G. STANDART. Pergamon Press, Inc., 122 East 57th Street, New York 22, N. Y. 1958. xviii + 402 pp. 16 × 23.5 cm. Price, \$14.00.

This book is intended primarily for the chemical engineer or technologist who is concerned with vapor-liquid composition data in the design and operation of fractional distillation equipment.

For convenience the book is divided into three parts. The first deals with the basic thermodynamic equations expressing the relation between the vapor-liquid composition and the temperature and pressure. An excellent review is given of the various methods that have been proposed for calculating these data. The practical value to the technologist is greatly enhanced by the inclusion of illustrative examples showing how to apply the theoretical equations.

In the second part the direct determination of vapor-liquid equilibrium data including the measurement of temperature and pressure and the correlation of the results, is described in considerable detail. Much helpful information is given about the design and operation, and the weak points

and strong points of many equilibrium stills described in the technical literature.

The last part presents a comprehensive bibliography of binary and multicomponent systems whose vapor-liquid equilibrium composition data have been reported up to 1957. This list amounts to a total of 1232 references.

The book is well written and quite free from misprints and other defects of manufacture. The only criticism that can be offered is that the experimental treatment is confined principally to stills operating at pressures in the vicinity of atmospheric pressure. It is hoped that in a future edition the authors will include all kinds of high pressure vapor-liquid equilibrium cells.

This book is highly recommended as a reference text to all persons in any way concerned with the vapor-liquid equilibrium relations of liquid mixtures.

CHEMICAL ENGINEERING DEPARTMENT  
OHIO STATE UNIVERSITY  
COLUMBUS 10, OHIO

WEBSTER B. KAY

**Advances in Chemical Physics. Volume I.** Edited by I. PRIGOGINE, University of Brussels, Brussels, Belgium. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y., 1958. xi + 414 pp. 16 X 23.5 cm. Price, \$11.50.

According to the statement of the publisher on its dust cover, and that of the editor in his introductory foreword, the present volume is the first in a new series that has the purpose of supplying interpretative reviews of advances in the field of Chemical Physics in a form digestible by non-specialist physical scientists. Rather than simply supplying critical surveys of the literature in a specific field, it is the stated intent of this new series to supply collections of comprehensive articles, written by experts, in which the authors may explain their views on a subject freely and without limitation of space. Professor Prigogine in the foreword points up the need by the following, only too apt, description of original papers as published in the journals, "have of necessity been made as short as is compatible with a minimum of scientific clarity."

Prior to setting down the reviewer's opinion of the manner in which the various experts followed the charter provided by the editor, it seems desirable to set down the chapter titles. These, with their authors, are: I, Heat Transfer in Binary Liquid Solutions, Bearman, Kirkwood and Fixman; II, Theoretical and Experimental Aspects of Isotope Effects in Chemical Kinetics, Bigeleisen and Wolfsberg; III, Dielectric Properties of Dilute Polymer Solutions, de Brouckere and Mandel; IV, Some Physical Aspects of Gaseous Chemical Kinetics, Careri; V, Transport Processes in Liquids, Collins and Raffel; VI, Structure, Reactivity and Carcinogenicity of Hydrocarbons, Daudel; VII, Molecular Theory of Surface Tension, Harasima; VIII, Recent Developments in Molecular Orbital Theory, Longuet-Higgins; IX, Intermolecular Forces and Equation of State of Gases, Kihara; X, On Statistical Mechanics and Electromagnetic Properties of Matter, Mazur; and XI, The Application of the Theory of Stochastic Processes to Chemical Kinetics, Montroll and Shuler. About half of the volume, chapters I, III, V, VII, IX and X, is concerned with the statistical-mechanical treatment of the physical properties of matter, about one fourth, chapters II, IV and XI, with reaction kinetics, and the other fourth, chapters VI and VIII, with quantum chemistry.

The character of the individual chapters is as varied as the characteristics of their authors. Chapter I, for example, is a short paper, the tenth in a series on the Statistical-Mechanical Theory of Transport Processes, that the reviewer found neither more nor less comprehensible than other papers by the same senior author. In Chapter II, Bigeleisen and Wolfsberg do an excellent job of putting together a critical account of the state of knowledge of isotope effects in reaction kinetics. The chapter by Longuet-Higgins, entitled Recent Developments in Molecular Orbital Theory, is in fact an exceptionally readable critique of the status of the discussion of the electronic absorption spectra of unsaturated hydrocarbons in terms of the M-O theories.

The reviewer should probably be seriously embarrassed by the necessity for the admission that his interest in problems concerned with intermolecular forces, which has lain dormant for many years, was not titillated to even semi-somnolence by his browsing in the six chapters dealing with various

aspects of these problems. This statement is not meant to reflect on the scientific quality of the six chapters involved, but simply to indicate that these chapters did not appear to be readily assimilable by the reviewer. In my browsing in these chapters I could not find clear explanations of why I should expend the effort that would be required to plow through the complex mathematics the authors employ to obtain their results and to describe what they are doing. I am afraid that these chapters will have their appeal primarily to those practicing statistical mechanics.

In summary it may be said that the objectives that the publisher and editor hope to attain in this new series are indeed admirable ones. However, it apparently will take some time for authors to change the writing habits that have been inculcated by the editors with whom they most frequently deal. It is to be hoped that the editor of this series will be more successful in communicating his objectives to authors of chapters of future volumes, than he was on the whole in the case of this first volume. It may be an encouraging sign that he was successful in the cases of the authors of chapters II, VIII and XI of this present volume.

SHELL DEVELOPMENT COMPANY  
EMERYVILLE, CALIFORNIA

D. P. STEVENSON

**Big Molecules.** By SIR HARRY MELVILLE. The Macmillan Company, 60 Fifth Avenue, New York 11, N. Y. 1958. 180 pp. 13 X 19 cm. Price, \$3.95.

A book whose purpose is to bridge the ever-widening gap between scientists and laymen is most welcome. This little book demonstrates how the rather complex field of polymers can be made palatable and simple for the non-technical reader. It contains a minimum of technical language and terms and is written in a pleasant, narrative style. The book is designed to provide the reader with a broad general view of the entire polymer field in terms of end-use applications of big molecules and a little of the elementary chemistry involved in their preparation. The subject matter has been necessarily oversimplified both for the sake of brevity and in order not to confuse the non-technical reader.

The book consists of six chapters, the first of which serves as an introduction to what polymers are and how they are made. The second chapter describes methods of determining the "size of big molecules," complete with simple diagrams of equipment used. No attempt is made here to define number average and weight average molecular weight and the reader would certainly not gain the impression that the various methods discussed are measuring different things.

The next three chapters are Fibers, Rubbers and Plastics. Under fibers, brief descriptions are given of melt spinning and of dry and wet spinning, with diagrams and photographic illustrations. Crystallization phenomena, cold drawing and heat setting are discussed in simple terms, as are also the waterproofing, fireproofing and improvement of crease resistance of fibers.

The chapter on rubbers touches briefly on the theory of elasticity and describes some simple experiments to illustrate various points. Vulcanization, reinforcement with fillers, conductive rubber and special purpose rubbers are described.

Compression and injection molding, and extrusion of common thermo-plastics are outlined in the Plastics chapter. Also discussed are the manufacture and use of reinforced thermosetting resins, laminated resins for printed circuits, and adhesives.

The final chapter deals with miscellaneous applications of polymers to show how versatile big molecules have become. These applications include viscosity index improvers for lubricating oils, synthetic lubricants, water-soluble thickening agents, blood plasma extenders, soil conditioners and ion exchange resins. A short description of the behavior of polyelectrolytes (without using the term as such) is included.

This book can be recommended as most interesting and informative reading particularly to our non-chemist friends and to young people who have had an elementary chemistry course and who wonder whether to enter chemistry. The book also would serve as appropriate collateral reading for college chemistry courses. In spite of over-simplification and minor errors, even the technical reader may gain something from an over-all general description of the polymer field.

SUMMIT RESEARCH LABORATORIES  
CELANESE CORPORATION OF AMERICA  
SUMMIT, N. J.

CARL N. ZELLNER