

switching from E_c to anodic potentials, but shows a double or multipeaked pulse on switching back to E_c . Addition of up to 5% water to the DMF had no effect on the chemiluminescence. When tetra-*n*-butylammonium bromide (TBAB) is used as supporting electrolyte, luminescence is observed with the platinum electrode at potentials more positive than 0.9 v., but not with the mercury electrode, which oxidizes at considerably more negative potentials (*ca.* -1.0 v.). No luminescence is observed with tetra-*n*-butylammonium iodide as supporting electrolyte with either platinum or mercury (anodic limits of 0.1 and -0.4 v., respectively).

The results suggest that the chemiluminescence occurs only during the chemical reaction of the anion radical and an oxidant generated anodically and not during the direct electrooxidation of DPA^- . In TBAP solutions the oxidants are probably perchlorate radical or an oxidant derived from it at platinum, and mercury(II) at mercury. In TBAB solutions bromine is probably the oxidant. Since the potentials at which these oxi-

dants are generated are sufficiently positive to allow DPA^- to be oxidized directly at the electrode, the reaction must occur some distance from the electrode surface and involve DPA^- diffusing toward the electrode and oxidant diffusing away from it. The results indicate that neither mercury salts of bromide or iodide nor iodine produce chemiluminescence in any reaction with DPA^- . One might question why the direct oxidation of DPA^- at the electrode, at potentials sufficiently positive to cause formation of DPA^* when produced by an electrogenerated oxidant, does not produce luminescence. Perhaps DPA species formed at the electrode surface rapidly dissipate any excess energy to the electrode. These chemiluminescent reactions, as well as those of other compounds, during electrolysis, is currently being investigated.

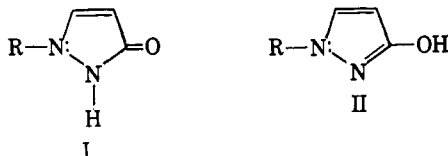
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Book Reviews

The Chemistry of Heterocyclic Compounds. Pyrazolones, Pyrazolidones, and Derivatives. By RICHARD H. WILEY, University of Louisville, Louisville, Ky., and PAUL WILEY, Upjohn Laboratories, Kalamazoo, Mich. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1964. xv + 539 pp. 16 × 23.5 cm. Price, \$26.00.

This volume is the twentieth in the series "The Chemistry of Heterocyclic Compounds" edited by Arnold Weissberger. It is divided into three main parts. Part I (142 pp.) deals with the chemistry of pyrazolinones and pyrazolidinones and their nitrogen and sulfur analogs. Part II (19 pp.) deals with uses of these compounds as medicinal agents, in color photography, as dyes, and as analytical reagents. The third part (322 pp.) is an appendix made up of tables listing the various pyrazolinones and pyrazolidinones which have been reported in the chemical literature.

This book might be of value to some as a rather complete compilation of the pyrazolinones and pyrazolidinones which have been reported in the literature up to 1956. With the exception of this prominent virtue, however, there seems to be little else about which one can comment very favorably. It is admitted that the great volume of literature must have posed a challenge to the authors. Yet it appears that they have largely avoided the greater challenges of critical comment and evaluation of data from the vantage point of current theory, which could have given rise to a really valuable treatise. Typical examples (many could be cited) illustrating this deficiency are: (1) classification of two canonical forms of 3-pyrazolin-5-one as "ionic tautomers" of 5-pyrazolinone (p. 63); (2) absence of discussion of factors known to affect orientation of alkylation (p. 22); and (3) rationalization of acidity of 3-pyrazolin-5-ones unsubstituted at N-1 (I) in terms of tautomerism to II (p. 49), when in actuality the same anion is obtained on removal of a proton from



either, and it is really the relative stability of this anion which is responsible for the observed acidity.

There is a substantial amount of repetition (*e.g.*, the discussion of ultraviolet spectra of 5-pyrazolinones on pp. 6, 10, and 19), yet

the regrettable practice of using numbers in place of structural formulas in depicting reactions, presumably in the interest of saving space, is commonplace. This practice is particularly annoying when one must scan back over several pages to locate the structure to which reference is being made.

Allusion is made to numerous reactions in the text of discussion (some of which, in the reviewer's opinion, were among the most interesting in the book), but depiction in terms of structures is lacking. Space considerations may have been the justification for this, but it seems to the reviewer that in a book of 500 pages, the inclusion of an additional 20 pages of text (added to the present total of 161 pages) would be justified in view of the great increase in readability to be gained.

One also wonders why an archaic style of printing and structural formulas were used in this volume when several of the preceding volumes in this series have print and formulas which are substantially easier to read.

Typographical errors and errors in formulas are relatively rare, but not absent. A check of 30 references randomly taken from the tables in the appendix revealed no discrepancies.

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X-Ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies. By A. GUINIER, University of Paris. W. H. Freeman and Co., 660 Market St., San Francisco 4, Calif. 1963. x + 378 pp. 16 × 24.5 cm. Price, \$11.00.

Since the discovery and development of X-ray diffraction 50 years ago, the crystal structure problem has dominated research in this field. The basic physics of the interaction of X-rays with solids was fairly well understood by 1920, and a new breed of scientist, the X-ray crystallographer, recruited from the ranks of physics, chemistry, mineralogy, and somewhat later, metallurgy, began the accumulation of the great volume of structure determinations which remains today perhaps our most important deposit of knowledge of the nature of solids.

About 30 years ago a few crystallographers began to turn their attention to materials not perfectly periodic. Glasses and liquids were studied first, and the famous Guinier-Preston zones associated with age-hardened alloys were discovered. By 1950 the study

of deviations from perfect periodicity by X-ray scattering experiments had become a well-developed secondary area of diffraction research.

It is with this area of interest that Professor Guinier's book is concerned. The crystal structure problem is specifically omitted. Perhaps a third of the book is devoted to a very elegant and complete development of kinematic diffraction theory, and the remainder to the interpretation of X-ray scattering by materials not perfectly periodic. A careful distinction is made between imperfections of the first and second kinds—those which leave the diffraction maxima sharp but weaker with diffuse scattering, and those which cause line broadening. There are then detailed treatments of the various specific imperfections and their diffraction effects: particle size and strain line broadening, order-disorder phenomena in alloys, thermal motion, stacking faults, and low angle scattering. Scattering from liquids and gases is also discussed. Ample literature references are given, and an excellent English translation has been provided by Professor and Mrs. Lorrain.

It seems clear that this book will fill a need both of the researcher for a reference source and the advanced materials science student for a text. The reviewer knows of no other treatment of X-ray diffraction from imperfect materials as detailed and satisfying.

It is perhaps unfortunate that the book is limited to cases of X-ray scattering which may be interpreted in terms of the kinematic theory. The subject of the anomalous transmission of X-rays and its ability to reveal the shapes and relative orientations of imperfections in nearly perfect crystals has in recent years attracted much attention. This phenomenon may be understood only in terms of the Ewald-von Laue dynamical theory, which Professor Guinier chooses to mention only in passing. The discussion of thermal motion, its diffraction effects, and their interpretation could have been made more modern by mention of inelastic neutron scattering experiments.

The scientist interested in the general study of imperfections in solids by the scattering of radiation in general—X-rays, electrons, and neutrons—has a need for a text treating all of these closely related questions, and for that he must still wait. In the meantime, Professor Guinier's book constitutes a very useful partial fulfillment of that need.

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An Introduction to Crystal Chemistry. By R. C. EVANS, Fellow of St. Catharine's College and Lecturer in the Department of Mineralogy and Petrology, University of Cambridge. Second Edition. Cambridge University Press, 32 East 57th St., New York 22, N. Y. 1964. 410 pp. 16 × 24 cm. Price, \$9.50.

The first edition of this popular book appeared in 1939 and was reprinted in 1946, 1948, and 1952; it has been translated into French. Now reset in a larger format, the text has been rewritten and expanded; the nomenclature has been improved ("layer lattices" are properly called *layer structures*); the style has been polished (*co-ordination* remains hyphenated: bravo!); the figures have been skillfully redrawn, even though most of them still lack any indication of scale. The new edition, even more than the first, sets out to teach crystal chemistry "at an elementary level": it appears to be aimed at a hypothetical student largely ignorant of crystallography, for he must be taught that equivalent sites are related by symmetry (p. 196) and what the cell looks like in the various crystal systems (p. 401); yet he must be thoroughly familiar with such phrases as Bragg's law, Joule-Thompson effect, Boltzmann distribution, and Planck's and Madelung's constants.

After a review of the electronic structure of the elements, the four bond types are introduced together with some qualitative discussions: "lattice theory" of ionic crystals, valence bond and molecular orbital theories of the covalent bond, several theories of metals (Drude-Lorentz, Sommerfeld, Bloch, Brillouin), the theory of the van der Waals bond. The various atomic radii are compared. Then follows a systematic description of the significant features of a number of carefully selected crystal structures. Facts are confronted with theoretical predictions. Principles are well brought out, particularly Pauling's Five Rules for ionic structures. Physical and chemical properties are correlated with structure. The classification of crystal structures into "hetero- and homodesmic," and the further subdivision of the latter into "iso-, meso-, and anisodesmic" according as bonds differ in kind or in degree, which was the leitmotiv of the first edition, has proved unrealistic and is

wisely abandoned. This second part, which covers nearly three-quarters of the book, is by far the more satisfying.

Most of the adverse criticism I have to offer is peripheral. Here are some objectionable statements quoted from the appendix, followed by my comments between brackets: (1) "the edges of the cell . . . are taken parallel to the crystallographic axes" [it is the other way around; axes are chosen parallel to edges]; (2) "it is sometimes more convenient to describe trigonal and hexagonal structures in terms of a rhombohedral cell" [only *some* trigonal and *no* hexagonal structures have rhombohedral lattices; only for these would a rhombohedral cell be more convenient]; (3) "triclinic system relationship $a \neq b \neq c, \alpha \neq \beta \neq \gamma$ " [the definition of crystal systems stems from symmetry—it cannot rest on metric considerations; one should explain that the unequal sign \neq does not have its usual meaning, but stands for *not required to be equal*]; (4) "the clinographic projection, in which the structure is shown as viewed in a convenient direction from a point at infinity . . ." [if so, this is an *orthographic projection*, in no way different from what the author calls a "plan"].

A section, misleadingly entitled "Crystal Structure and Morphology," deals with polymorphism and isomorphism. It is to be deplored that the word "isomorphous" is here redefined to mean *isostructural*, a well-established term presumably unknown to the author. The assertion (p. 193) that "in the cubic system . . . all crystals of a given class are morphologically identical" ceased to be correct in 1849 with the advent of the law of Bravais (to say nothing of its subsequent generalizations). Some readers will regret the omission of the new silicate chains; many will wonder why no mention is made of vitamin B₁₂ and proteins, these resounding successes of structure analysis. It is hard to condone the author's decision to delete all references to original papers, especially since the work reported is still so recent. (The good student will say, "What a beautiful story! *Who* ever found out, and *how*?") A three-page bibliography gives a partly annotated list of reference works, monographs, and textbooks.

I shall continue to recommend this book to chemistry students, but only after they have had a course in crystallography.

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The Gas-Phase Oxidation of Hydrocarbons. By V. YA. SHTERN. Edited by B. P. MULLINS, Deputy Chief Scientific Officer, Ministry of Aviation, Farnborough, Hampshire. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. x + 710 pp. 16 × 24 cm. Price, \$28.50.

Professor Shtern's monumental work deals with the thermal reaction between hydrocarbons and molecular oxygen in the gas phase under slow oxidation conditions, *i.e.*, in the temperature range 200–600°. The approach is historical, and by so limiting his subject matter, the author is able to discuss essentially every study on the problem from the pioneering work of Bone in 1902, to 1960, the publication date for the Russian text. In addition, for the present translation, the author has made revisions which extend his literature coverage into 1962.

According to the author, there are three periods in the history of research on slow oxidation. In the first, which ended in the late twenties, emphasis was on end-product identification and non-chain mechanisms. There followed a short period in the early thirties, dominated by the Semenov school, from which emerged the concept of slow oxidation as a chain reaction with degenerate branching. The third period, which is still in progress, is characterized by studies of individual steps in the oxidation sequence, together with the development of detailed free-radical mechanisms for the over-all process.

Since the slow oxidation of hydrocarbons is not only of considerable fundamental interest, but also has broad industrial significance, a vast amount of pure and applied research effort has been expended on the system, especially on paraffin oxidation. Yet the reaction is so complex that even today only the initial stages can be considered firmly established. The author justifies his historical treatment of the subject by stating that the most meaningful conclusions concerning the mechanism can only be drawn when all of the available data are objectively evaluated. Certainly the method has the advantage of properly assigning prime credits for contributions to the field. To the English-speaking reader there is the added advantage of having thereby a detailed treatment of the important work of the Russian school of combustionists.