Table I. Sulfur 2p Binding Energies in Plastocyanins

| Species | S2p (eV)[a] |
|---|---|
| Cu(II)–S– | 169.8 ± 0.3 |
| Cu(I)–S– | 167.5 ± 0.3 |
| Co(II)–S– | 168.8 ± 0.2 |
| H–S–(apo) | 164.5 ± 0.3 |
| $CH_3$–S–(apo) | 164.0 ± 0.2 |

[a] Referenced to C1s at 285.4 eV.

proteins. The ratio of the intensity of this peak to the one at 164 eV is approximately 1:2, showing that one of the three sulfurs has been affected significantly by metal incorporation.

The S2p energy difference between uncoordinated methionine and cysteine sulfur atoms can be estimated by examining the change in the average energy $\bar{E}$ of the 164 eV peak on metal incorporation. The average energy (first moment) is defined as

$$\bar{E} = \sum_i E_i I_i \Big/ \sum_i I_i$$

where $I_i$ is the electron intensity at a binding energy $E_i$. The baselines were subtracted, and the high energy tail was estimated to resolve its overlap with the shifted peak. Thus, there is more error in the copper moment due to the greater overlap with the shifted peak. The vertical lines near each peak maximum give the average energy shifts relative to that of the apoprotein (the dotted vertical line). It may be observed that the average energy of the 164 eV peak decreases upon metal incorporation, strongly suggesting that the sulfur at slightly higher binding energy in the apoprotein is the one that coordinates to the metal. It is reasonable to assign the cysteine sulfur at higher binding energy, as a $CH_3$ group is more electron donating that is hydrogen. Further, the cysteine–methionine energy difference is given by three times this change in average energy, and is found to be 0.56 ± 0.3 eV.

Several comments should be made about the nature of each sample. The broadening of the coordinated sulfur peak in the copper protein is due to partial reduction of the central metal, which shifts S2p to lower binding energy. This effect was monitored, and estimates of the sulfur binding energies of Cu(II) and Cu(I) plastocyanins were made. These binding energies are given in Table I, along with those of the other sulfur species measured. The cobalt plastocyanin samples contained 20–30% apoprotein, which accounts very well for the lower intensity ratio, $I_{169}/I_{164}$, of the cobalt as compared to the copper spectrum (0.45 vs. 0.32 eV). Finally, a small signal, about one-sixth of that found for the cobalt derivative, is observed in the higher binding energy region of the apoprotein, consistent with the presence of traces of copper and disulfide.

These X-ray photoelectron experiments establish directly that sulfur binds to copper in bean plastocyanin. Further, the sulfur most probably is contributed by the cysteine residue in the protein. The S2p energy shifts that we have found are quite large and indicate that sulfur electron density is substantially delocalized to the copper upon coordination. This evidence for a delocalized Cu(II)–S(Cys) structure accords well with the assignment[2] of the intense, low-energy absorption spectral features in "blue" proteins to one or more S → Cu(II) charge transfer transitions. The XPS studies also show that cobalt(II) occupies the same sulfur binding site as copper(II) in plastocyanin. These experiments are now being extended to other copper-containing proteins.

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# Book Reviews*

**Selective Oxidation of Hydrocarbons.** By D. J. HUCKNALL (The City University). Academic Press, Inc., London. 1974. vii + 212 pp. $14.00.

The stated objective of this book is to critically review the current knowledge of the catalytic oxidation of $C_2$-$C_5$ alkanes and alkenes. The data are purported to be "collated in such a way that the search for a new oxidation catalyst will be less empirical." Unfortunately, the author has allotted only five pages for an introduction to this complex field. There is only a brief mention of the chemical and physical aspects of catalysis and the analytical methods used in this type of research. Only a few more pages of discussion at this point would have made the book of more value to a broader range of readers. The final chapter of the book is devoted to a general discussion of the mechanism of catalysis with the primary emphasis on the application to selective oxidation. Since this chapter is self-consistent, it might well be considered as part of the introduction.

As the author warns, the book may appear to be a "compendium of catalysts and kinetic schemes, etc." Indeed, 121 of the 156 pages of written text are devoted to a systematic discussion of the product distributions, the kinetic parameters, and the reaction schemes for the catalytic oxidation of ethylene (Chapter 2), propylene (Chapter 3), $C_4$ hydrocarbons (Chapter 4), and $C_5$ hydrocarbons (Chapter 5).

Although I personally have always been somewhat uncomfortable with the British syntax, I have found their works to contain a

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* Unsigned book reviews are by the Book Review Editor.

great deal of data and to be well referenced. Professor Hucknall's work proved to be no exception. It contains 14 figures, 36 tables, and 727 references. In addition, there is both an author index and a thorough subject index. Thus, the book contains an enormous amount of useful information and can be recommended to anyone working directly in the field as well as a general library reference book. However, it is far too specialized to be of value to the average reader.

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**Handbook of Materials Science. Volume 1. General Properties.** Edited by C. T. LYNCH (Air Force Materials Laboratory). CRC Press, Cleveland, Ohio. 1974. 752 pp. $35.00.

This work is largely a collection of tabulated data, arranged in five sections: The Elements; Elemental Properties; Miscellaneous Tables of Physical Properties; Conversion Tables, Miscellaneous Materials Properties, and Binary Phase Information; Materials Standards. There is also an enormous folded chart which summarizes binary phase diagrams for the elements.

There is more information of use to chemists in this book than the title might suggest. There are, for example, extensive tables of bond strengths, ionic radii, vapor pressure, surface tension, free energies of formation, dissociation constants of acids and bases, etc., etc. The emphasis is, understandably, heavily inorganic. The last section is subdivided into Analytical Standards, General Standards, and Tables of Specific Compositional Standards.

**Microstructural Science. Volume 1.** Edited by R. J. GRAY and J. L. MCCALL. American Elsevier, New York, N.Y. 1974. xiii + 304 pp. $19.95.

This volume is The Proceedings of the Fifth Annual Technical Meeting of the International Metallographic Society, held in Chicago in 1972. It consists of 31 articles plus an appendix on the associated metallographic exhibit. The articles are accounts of original research in the area of metallography, conceived broadly.

**Spouted Beds.** By K. B. MATHUR and N. EPSTEIN (University of British Columbia). Academic Press, New York, N.Y. 1974. xv + 304 pp. $24.50.

The authors, pioneers in the subject since its introduction in 1955, begin their preface "when the idea of reviewing the field of spouted beds first occurred to us, in 1967, we both had no more than a sentimental interest in the subject, since we had separately been occupied with nonspouting activities for over a decade". They recognize that the process cannot simply be characterized as "Canadian fluidization", and then turn to a dispute with Soviet practitioners over priority, a matter that seems to have arisen out of semantic differences. Whatever the case, the subject has grown rapidly, culminating in the International Symposium on Spouted Beds in 1973.

The scope of the book is revealed by a selection of chapter titles and subheadings: The Spouted Bed; History; Requirements for Spouting; The Onset of Spouting; Spout Shape; Spouting Stability; Between Wall and Bed; Multiple Spouting; Pulsed Flow Spouting; Some Practical Suggestions. The book ends with a six-page appendix on nomenclature, abbreviations, and conversion factors, twelve pages of references (including the title of each) with heavy representation of the Soviety literature), and a modest subject index. The "nomenclature" dealt with consists entirely of symbols and does not define such mysterious terms as "slugging bed", "bubbling bed", "voidage profile", etc., which appear in the text. The chemical engineer concerned with reactors for solid-gas or solid-liquid interactions should find this book most intriguing.

**The Organic Chemistry of Nickel. Volume 1.** By P. W. JOLLY and G. WILKE. Academic Press, Inc., New York and London. 1974. xiv and 517 pp. $58.00.

The authors state in their preface, our major task was to supply a reference work . . . ." They then offer the disclaimer that "reference works, although useful, are generally boring." Having stated the problem for many reference works, Jolly and Wilke admirably manage to avoid it. This was accomplished via a lucid, impersonal style of writing and by the placing of data for known complexes at the end of each chapter, thereby freeing the text of the chapter for illuminating, uninterrupted discussion.

As a member of the notable series of monographs on organometallic chemistry published by Academic Press, this volume constitutes a well-ordered, painstaking, and thorough journey through the current and past fields of interest in organonickel chemistry. Beginning with the properties, substitution chemistry, and toxicology of the best known of organonickel species, nickel tetracarbonyl, the reader is guided through a maze of organonickel complexes of greater and greater complexity. Each of the nine chapters has been comprehensively related to the other eight. The text is replete with orderly tables of physical and chemical data and each chapter closes with a copious list of journal references; in addition, a separate listing of review articles has been gathered to complete each chapter. Most refreshing is the elimination of the clutter of numbered equations by having all equations intimate with the appropriate paragraph. Unfortunately, a measure of confusion is added by the use of Roman numerals for the chapter subheadings as well as the chapter headings. The book is well produced and contains only three errors that these reviewers noted.

Each area of current and past investigation in organonickel chemistry is described with attention to detail. The authors have coordinated in this volume such areas of current interest as $\sigma$- and $\pi$-bonded complexes of all types, organic catalysis, and dynamics induced by or involving organonickel intermediates, electrochemistry, homo- and heterometal "cluster" chemistry of nickel, organoboron chemistry of nickel, as well as electronic, ir, nmr, and mass spectral data on static and dynamic nickel systems. X-Ray and electron diffraction studies are also widely cited.

In addition to an exhaustive presentation of the physical, chemical, and spectroscopic data on organonickel species published through the middle of 1973, the authors have devoted a suitable amount of time and space to the current and evolving theoretical approaches to explanation of the data. Rather than devote specific chapters to theory, they have interspersed it among the data in order to tie things together; in this manner temporary relief from the abundance of experimental results is provided. There emerges an accurate picture of organonickel chemistry as an area of active and concentrated interest of chemists from diverse disciplines. We feel that this volume, although very expensive, is the most comprehensive monograph available in its area and as such should make an attractive and invaluable addition to the libraries of both chemistry departments and chemists. Volume II, which the authors state in their preface will deal with the organic chemistry of nickel, is to be anticipated.

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**Inorganic Reaction Mechanisms. Volume 3.** Senior Reporter: J. BURGESS (University of Leicester). The Chemical Society, London, 1974. xviii + 500 pp. £14.00.

This latest volume of the Chemical Society's Specialist Periodical Reports provides coverage of the literature from December 1971 through July 1973. The book is divided into the four areas of Electron Transfer Processes, Substitution and Related Reactions, Reactions of Biochemical Interest, and Organometallic Compounds, and each area is further subdivided into shorter chapters. Because of the appearance of the Specialist Periodical Reports on Organometallic Chemistry, coverage in this area is limited to references in which kinetics or reaction mechanisms form the principal interest. Contributors to the volume are J. Burgess, R. D. W. Kemmett, M. A. R. Smith (University of Leicester), D. N. Hague (University of Kent), and A. McAuley (University of Glasgow).

The coverage is somewhat brief in the biochemical section (22 pages) and also in the important area of homogeneous catalysis, but is quite extensive elsewhere (>1800 references). Nearly one-half the volume is devoted to mechanisms of substitution and related reactions. The publishers aim of this series is "to provide systematic and comprehensive review coverage of the progress in inorganic reaction mechanisms," and this volume does exactly that, although it does not provide a "*critical* in-depth account" of the literature. The volume is well written and easily readable, and in many of the chapters data from several references are organized and presented in tabular form. Since the coverage is quite recent and comprehensive in the areas of substitution reactions and electron transfer reactions, the volume would be an invaluable addition to the library of workers in these fields.

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