The reaction of $Pt(PPh_3)_4$ with $K_4[Sn_9]$ in en, in an equimolar ratio, causes the solution to change from deep orange-red to dark brown. The solution was investigated by ^{119}Sn NMR, and only two sets of resonances at 1218 and 736 ppm upfield from tetramethyltin (TMT) were observed (see Figure 1). The quintet at −1218 ppm is assigned to Sn_9^{4-} by comparison with an authentic sample of this anion in en. The triplet in the triplet of quintuplets at −736 ppm and with intensities 1:4:1 we assign, as in $Pb_xPtL_y^{q-}$, to one platinum per cluster. Each of the components is further split by the ^{117}Sn and ^{115}Sn present in the sample. ($J_{^{119}Sn-^{117}Sn}$ = 79 Hz). Unlike lead, spin–spin coupling is observable for tin even when all chemical environments are averaged by a rapid intramolecular process due to the fortuitous occurrence of three magnetically active isotopes each of spin $^1/_2$. The relative ratio of the areas is 0.06:0.33:1:0.33:0.06 while the expected values for a cluster of nine tin atoms are 0.04:0.31:0.31:0.04.[13a]

Due to the similarity of Pb_9^{4-} and Sn_9^{4-} and comparable reaction conditions, it is logical to expect that both compounds have the same stoichiometry, i.e., $L_zPtPb_9^{4-}$ and $L_zPtSn_9^{4-}$. The 4− charge is the only plausible value since there has not been any variation in the content of tin (and presumably lead). On the other hand, formal negative oxidation states of platinum, which could lead to a closo cluster, occur very rarely in other platinum compounds and, to our knowledge, only when carbonyl ligands are present.[13b]

Unlike the composition of the core, which seems to be a well-defined $PtPb_9$ or $PtSn_9$ moiety, the nature of the ligand L is uncertain. The ^{31}P NMR of the $L_xPtSn_9^{4-}$ cluster solution 2 days after mixing the reagents shows a triplet with areas 1:4:1 ($J_{^{195}Pt-^{31}P}$ = 5220 Hz) at 147 ppm and a singlet due to a free triphenyl phosphine at −6 ppm.[17] The ratio of the intensities is very close to 1:1, which indicates the reaction

$$Pt(PPh_3)_4 + Sn_9^{4-} \rightarrow (PPh_3)_2PtSn_9^{4-} + 2PPh_3 \qquad (1)$$

After the solution stood for a few weeks, only the free triphenylphosphine absorption was observed. This is attributed to the total, or partial, substitution of PPh_3 by the less bulky en.[15a] This partial substitution by en is supported by the ^{31}P NMR of $L_zPtPb_9^{4-}$, which as well as the free PPh_3, has a triplet of triplets with relative intensities of 1:4:1 at +308 ppm. ($^1J_{^{195}Pt-^{31}P}$ = 6218 Hz and $^3J_{^{195}Pt-^{31}P}$ = 419 Hz).[15b] An extensive search to find the ^{195}Pt NMR resonances was not successful.

Attempts to obtain crystals of X-ray structure determination are underway. The $Pt(PPh_3)_2$ moiety being considered has a framework electron contribution of two electrons, as does tin.[16] The total number of electrons is then 24 or $2n + 4$. Consequently, a nido structure similar to $B_{10}H_{14}$[17] is predicted, the metal occupying one of the positions of the open mouth.

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(13) (a) This slight discrepancy is attributed to partial overlap of the signals, which clearly favors the smaller peaks with respect to the central peak. (b) A referee has questioned our assignment of a nido count, $L_zPtM_9^{4-}$, rather than a closo count, $L_zPtM_9^{2-}$. We have found that addition of 2,2,2-crypt to a solution of the compound in question results in the disappearance of the ^{207}Pb and ^{119}Sn NMR signals and the evolution of H_2 gas. Analysis of the crystals results show them to be closo in nature. These results strongly suggest the original solution species to be nido.

(14) Free PPh_3 was assigned after comparison with an authentic sample of PPh_3 in en. All chemical shifts were obtained compared to PPh_3, which was assumed to have δ −6 referenced to PO_4H_3 (80%).

(15) (a) Either a precipitation process, which would exaggerate the proportions of free PPh_3 with respect to PPh_3 attached to Pt, or the partial decomposition of $(PPh_3)_2PtSn_9^{4-}$ to an insoluble phase would also explain the ^{31}P NMR. (b) The solution remained free of solid phases, and the $^{207}Pb/^{119}Sn$ NMR spectra remained unchanged over the time period investigated.

(16) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446–452.

(17) Tippe, A.; Hamilton, W. C. *Inorg. Chem.* **1969**, *8*, 464–470.

Book Reviews

Solubility in Inorganic Two-Component Systems. By M. Broul (Chemopetrol-Research Institute of Inorganic Chemistry, Usti nad Labem), J. Nyvlt (Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague), and O. Sohnel (Chemopetrol-Research Institute of Inorganic Chemistry, Usti nad Labem, Czechoslovakia). Elsevier Scientific Publishing Company, Amsterdam, The Netherlands. 1981. 7 + 569 pp. $90.25.

This book begins with a theoretical introduction consisting of a brief discussion of temperature dependence of solubility, concentration units, smoothing of experimental data, evaluation of data on solution supersaturation, material and heat balance of crystallization, temperature dependence of solubility in a three-component system, and crystallographic and structural characterization of substances. This is followed by a list of symbols and a brief discussion of how the data were tabulated.

The major part of this book consists of tables in which temperature–concentration data of some 500 inorganic substances are evaluated (listed alphabetically in a formula index). A page is devoted to each substance and consists of such information as temperature–concentration data tables, along with a solubility equation describing the tabulated data. Temperature coefficient of solubility data, crystal lattice parameters, and crystal modification parameters are included when available. The temperature range for each substance varies with the substances in the 0–100 °C range with tabulations given at 0.1 °C intervals. Older solubility data (up through the 1950's or 1960's) were obtained from Linke and Seidell ("Solubilities of Inorganic and Metalorganic Compounds", Van Nostrand, New York; 1958, American Chemical Society: Washington, 1965). More recent data were obtained from the original papers.

The available data appear to be carefully evaluated by the authors and this book should be a valuable guide to various workers involved in liquid-phase water systems at moderate temperature. The book is important in its convenience of having under one cover data that are otherwise widely distributed and varied in nature in the original literature. It is thus much more useful than the usual brief solubility information found in chemical handbooks. The reviewer would like to have seen included data on hydrolysis such as pH values.

Karl Gayer, *Wayne State University*

Chronicles of Drug Discovery. Volume I. Edited by Jasjit S. Bindra and Daniel Lednicer. John Wiley and Sons, New York. 1982. XIII + 283 pp. $32.50.

The scientific approaches, the consideration of chemical factors, and the utilization of experimental results which lead to the discovery of a new drug are seldom available in the scientific literature. This volume provides an account of scientific investigations which led to the discovery of 12 useful drugs in the past 15 years. These accounts of drug development should provide interesting material for teachers of courses in medicinal chemistry and should be read by chemists considering a career in the pharmaceutical industry.

While individual chapters deal with the discovery of a single drug, most provide an insight into research on compounds of that therapeutic class. Individual chapters describe research which culminated in the discovery of a histamine (H_2) antagonist, two unique antipsychotics, two antihypertensives, a diuretic, two peripherally acting analgetics–antiinflammatories, two antibiotics, an anthelmintic, and an agent for the treatment of schistosomiasis.

The book is well written and, while providing interesting reading, gives an accurate view of research in medicinal chemistry. Most chapters include some information on the synthetic approaches employed in the study.

James E. Gearien, *University of Illinois*

Copper Deficiency and Toxicity. Acquired and Inherited in Plants, Animals, and Man. By Charles A. Owen, Jr. (Mayo Clinic). Noyes Publications, Park Ridge, New Jersey. 1981. xv + 189 pp. $28.00.

Inorganic biochemistry, a subject too long overlooked by its major discipline, is enjoying a resurgence of interest. The "trace elements" as they are called represent a growing and active field of research contributing information to chemists, biochemists, nutritionalists, plant and animal physiologists, toxicologists, and just about anybody in the biomedical sciences. This audience is clearly in mind when we consider the present undertaking by Owen. The book is the first of a five-part series on the biological roles of copper. One could argue that such a seemingly minor trace element surely does not require five volumes to tell its story. But then one must first see the compendium of information available on this one metal alone before making that statement. Owen has done that for us.

Volume one in the series describes the nutritional and toxicological properties of copper. Both are given balanced and comprehensive treatment. Workers in the field have long known that copper is a "double-edge sword", harmful both in excess and in insufficient supply in the diet. The present book in six chapters explores biochemical implications and causes of copper deficiency in plants, animals, and microorganisms as well as the sources and consequences of copper toxicity. The writing is crisp and pointed, never burdensome. The discussions are both general and concise. We see, for example, in Chapter 2 (Copper Deficiency from Use of Chelators) a chapter that is only two pages in length but yet cites 50 references. Chapter 4 discusses the effects of copper toxicity on more than 40 different enzyme activities. In this chapter as in the others, the references cited are bountiful and many are for work published within the past 5 years.

Regrettably, the style chosen by the author forces him to omit important theoretical considerations or even a detailed elaboration of his own contributions to the field. We are thus deprived of Owen's keen insight into the subject and must instead rely on the efforts of others to tell the story. Hopefully this may be amended in future volumes of the series. The overtones of the presentation are strongly biological. The chemist may feel left out in many of the discussions, but then this book is intended to focus on the library of information on the biology of copper. This is done exceptionally well. The organization of the subject matter by species allows the reader to gain a fuller perspective of the importance of copper to all species of plants and animals thus allowing the reader to draw comparisons to his own interests.

In summary, the present book dealing with copper deficiency and toxicity by Owen in but one in a series of monographs devoted to the properties of copper in biology and medicine. Yet to come will be "Wilson's Disease", "The Biochemistry of Copper", "The Physiological Aspects of Copper", and "The Biological Aspects of Copper". I am sure the reader will find, as I have, a very strong updated reference series dealing with this one metal. The reader may unwittingly discover an unwritten message from Owen that although a great deal is known about copper, a great deal more remains to be discovered.

Edward D. Harris, *Texas A&M University*

Otto Warburg, Cell Physiologist, Biochemist, and Eccentric. By Hans Krebs in collaboration with Roswitha Schmid. (Translated by Hans Krebs and Anne Martin.) The Clarendon Press; Oxford University Press, New York. 1981. xii + 141 pp. $24.95.

Sir Hans Krebs, who died in November 1981, was one of the winners of the 1953 Nobel Prize in Medicine and Physiology. From 1926 to 1930 Krebs was an assistant to Otto Warburg, a scientist of eminence and great ability. Krebs and Warburg kept in contact until Warburg's death in 1970. Krebs expanded the obituary memoir he wrote for the Royal Society of London into this short biography.

Warburg, a member of a distinguished German Jewish family, was able to remain in Germany during the rise and fall of the Third Reich unharmed by the Nazis because Reichsmarschall Herman Goering ruled that Warburg was a quarter-Jew. Warburg's acceptance of this compromise disturbed many of his colleagues outside Germany, to say the least.

Warburg's father was Professor of Physics at the University of Berlin. He saw that his son received as good an education as he could possibly get in Germany. After Warburg finished a doctoral thesis with Emil Fischer in Berlin he went on to receive an M.D. from Heidelberg. Warburg was a lieutenant in a crack cavalry regiment during World War I, was wounded in action, and was decorated with the Iron Cross, First Class.

There are just three chapters in this book. They are, Early Years, Main Scientific Achievements, and Personality. Krebs explains Warburg's great scientific achievements assuming his reader has a knowledge of biochemistry. Krebs tells a good deal about what he calls "Warburg's irritating personal qualities" in the chapter on personality. In the foreward, however, Krebs mentions that the time was not yet ripe for the revelation of all the materials he collected. The "warts and all" biography that someone will probably write someday will be interesting to read.

The book is excellently illustrated with 23 photographs, some from Kreb's personal collection. The frontispiece is an unusually fine photographic portrait of Warburg.

This book is a valuable addition to the list of scientific biographies. It will be read with enjoyment by all those who want to learn something about the background of modern biochemistry.

David H. Kenny, *Michigan Technological University*

Characterization of Solutes in Nonaqueous Solvents. Edited by Gleb Mamantov (University of Tennessee). Plenum Press, New York. 1978. viii + 325 pp. $35.00.

This book consists of contributions by participants in the symposium Spectroscopic and Electrochemical Characterization of Solute Species in Non-aqueous Solvents which took place at the 1976 ACS Meeting in San Francisco. The original symposium title indicates the limits of the coverage and the sector of the larger topic suggested by this book's title, which the papers actually cover. The book has the strengths and weaknesses of a symposium volume. Among those strengths are important presentations of a variety of interesting studies by the original workers in which their insight and invention shows. I mention (without meaning to suggest that someone with research interests different from mine might not highlight others) the paper by Coetzee et al. on the interaction of first and second coordination sphere solvent molecules in ligand substitution, Detillier and Laszlo's paper on NMR study of Na^+ coordination in organic solvents, Evans and Nelson's paper on measurement of conformational rates by cyclic voltammetry, and Mamantov and Osteryoung's review of chemistry in molton chloroaluminates. This list may give some idea of the scope of the volume.

The weakness is the inevitable discontinuity of symposium volumes. A reader should expect neither comprehensiveness nor connectedness. One misses classification of solvents, analysis of types of general problems, and a systematic intercomparison of method. The volume does include the perspectives of analytical, inorganic, physical, and organic chemists on the common problem area of solutes in nonaqueous media. A modern and similarly interdisciplinary monograph to complement this symposium volume would be most welcome.

Cooper H. Langford, *Concordia University*

Undergraduate Chemistry Series. Volume 5. Principles of Solution and Solubility. By Kōzō Shinoda (Yokohama National University). (Translated in collaboration with Paul Becher (ICI Americas Inc.).) Marcel Dekker, Inc., New York; Basel. 1978. x + 222 pp. $17.50.

This book appears to be directed toward two classes of reader: undergraduate or beginning graduate students who have had at least an introductory course in thermodynamics, and practicing chemists and chemical engineers who require or desire a general knowledge of the factors that determine the solubility of (for the most part) nonelectrolytes. The first four chapters are devoted to Introductory Solution Thermodynamics, Ideal Solutions and Athermal Solutions, Dilute Solutions, and Regular Solutions. The elementary thermodynamics and molecular arguments in these chapters emphasize both qualitative and semiquantitative aspects of solubility phenomena. The next three chapters (Estimation of the Solubility of Gases, Liquids and Solids in Liquids; Enthalpy and Entropy of Solution; Aqueous Solutions) are essentially applications and extensions of regular solution theory as developed in earlier chapters. The traditional Flory–Huggins theory of polymer solutions is discussed in a separate chapter, following which are two chapters (Surfactant Solutions; Solubilized Solutions) that reflect the research interests of the author and cover important subjects that are usually to be found only in more specialized books. The final chapter summarizes Factors which Control Solubility. Eight of the eleven chapters contain exercises and problems with answers. There are some instances of less-than-fluent translations from the Japanese and some annoying typographical errors, especially in the first chapter. (The answer to problem 1.1 is given as Table 3.2, which finally was found in Hildebrand and Scott's "Solubility of Nonelectrolytes"!) Despite this, the book is quite readable and resembles, in its general method of approach, Hildebrand, Prausnitz, and Scott's 1970 book "Regular and Related Solutions". The title is somewhat misleading: apart from a page on polyelectrolytes and a few pages on ionic surfactants, the subject matter is concerned only with nonelectrolytes in organic solvents and water.

The reviewer would have preferred a little more rigor in the thermodynamic discussions, with emphasis on chemical potential and activity rather than on fugacity, and the use of SI units. However, the treatment and nomenclature are in the tradition of Lewis and Randall, and thus will be familiar to most North American readers. Most chapters contain references to comprehensive monographs, but few of these are of recent date. A separate, brief bibliography that would direct the reader to more comprehensive and recent books would have been a valuable addition.

This volume could serve as useful supplementary reading for a senior-level undergraduate or beginning graduate course in solution thermodynamics and should be especially useful to the specialist or generalist whose knowledge of solubility phenomena is slight.

J. W. Lorimer, *University of Western Ontario*

Introduction to Molecular Energy Transfer. By J. T. Yardley (Allied Chemical Corporation). Academic Press, Inc., Publishers, New York, NY. 1980. xi + 308 pp. $34.00.

The preparation of an introduction to any active area of research is a challenge. The author must select material and references from a vast supply that is increasing at a rapid pace. "Introduction to Molecular Energy Transfer" is a concise, well-organized, and well-written book that meets this challenge well. It is intended for graduate students and researchers in related fields, but it has very convenient summaries of experimental data that will probably make it valuable to researchers in molecular energy transfer as well.

A strong point of the book is that it is reasonably self-contained so that a student (or researcher) can sit with it and read it profitably without reference to other material. This is accomplished by the inclusion of appropriate basic theory both in separate sections and along with discussions of experimental results. There are adequate references to the original literature for those who want to explore some aspect of energy transfer more extensively.

If one looks for a theme, it is the treatment of energy transfer involving small molecules. Transfers of vibrational, translational, rotational, and electronic energy are considered under various conditions with emphasis on gas-phase collisions. The ten chapters are brief and to the point.

Chapter 1 (28 pages) presents a summary of the theoretical background for molecular energy transfer. It starts with the postulates of quantum mechanics and manages to derive most of the formulas used later in the text. The student does not learn quantum mechanics from this chapter, but it is a convenient reference for users of the book. The next five chapters (half the book) are involved with vibrational energy transfer. They start with a theoretical treatment of vibrational energy levels of molecules, continue with experimental methods for study of vibrational energy transfer, and then present summaries of experimental results on various kinds of energy transfer involving vibrations. The next three chapters are concerned with electronic energy transfer. The first of these (Chapter 7) contains a brief treatment of fundamentals and the next two present experimental results and their interpretation. The last chapter (10) takes up rotational energy transfer. There is a subject index.

The book is small but it manages to summarize and analyze critically a large amount of experimental data. It should be valuable to a wide variety of students and researchers who are interested in molecular energy transfer.

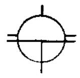
John L. Magee, *University of California*

Electrophilic Additions to Unsaturated Systems. Second Edition. By P. B. D. De La Mare (University of Aukland, N.Z.) and R. Bolton (Bedford College, U.K.). Elsevier Scientific Publishing Co., Amsterdam and New York. 1982. xiv + 378 p. $91.50.

After establishing a broad framework of mechanistic possibilities, the authors take the reader through the many varieties of electrophilic additions to multiple bonds. The main topics of their eleven chapters are: mechanisms (Chapters 1 and 2); Brønsted acids, HX (Chapter 3) group VII halogens and interhalogens (Chapters 4 and 5); group VI oxygen to tellurium (Chaper 6); groups I–IV, VIII (Chapter 8); alkynes, alkenes (Chapter 9); conjugated, aromatic systems (Chapter 10) other multiple bonds, CO, CN, etc. (Chapter 11). Obviously, the authors have had to make hard decisions: their treatment ranges from extensive on the additions of acids and halogens to modest or cursory on those of carbocations, carbenes, boron hydrides, etc. Relative to alkenes and alkynes, allenes and heteroatom π bonds are lightly covered. As for data on rates, product distributions, and structure–reactivity effects, the authors have chosen to be illustrative rather than exhaustive.

This book will be useful to a specialized group that should recommend it for library acquisition. Others with particular interests in the field of electrophilic additions should do as well or better with alternate sources and reviews, e.g., the series edited by S. Patai. A general reader or student who wishes to acquire background in the field will find the first edition as well as recent textbooks of physical organic or mechanistic chemistry (Lowry and Richardson; Carey and Sundberg; etc.) as useful.

Some comments on the production of this book may be in order. The cost per page ($0.24) of this book is substantially higher than that of other books recently listed in this section. Although there are occasional citations from early 1979, most are of earlier data. The typescript, which was copied, emerges clean and legible. On the other hand, some equations and formulas that are too casually or informally executed could lead to misinterpretation: the bicyclohexane looks like a bicycloheptane (p 169); substituted ethanes are inexplicably drawn in a mixed eclipsed and staggered conformation (p 28), i.e., the Newman projection is



transition states, complexes, and bonds are all indicated by dots or dashes in different places; etc. In place of an index, this edition lists the names of compounds and refers one to the Table of Contents; thus, it may often be difficult for readers of varying interests and perspectives to retrieve specific material of interest to them.

Sidney I. Miller, *Illinois Institute of Technology*

Aspects of Homogeneous Catalysis. Volume 4. Edited by R. Ugo (University of Milan). D. Reidel Publishing Company, Dordrecht, Holland. 1981. viii + 204 pp. $58.00.

Volume 4 of "Aspects of Homogeneous Catalysis" is a useful addition to the series, one volume of which has appeared approximately every 3 years since 1971.

The first of the four articles in Volume 4 concerns metal-catalyzed epoxidations of olefins with hydroperoxides. Except for a relatively small number of key early papers, most of the papers that are discussed and summarized have appeared between 1970 and 1979. The author (R. A. Sheldon) not only packs a remarkable amount of information into the article but also manages to present it in a balanced and readable fashion. Most of the article concerns homogeneous transition-metal-catalyzed oxidation of olefins by alkylhydroperoxides, but the author also touches on oxidations with hydrogen peroxide, heterogeneous oxidation catalysts, and oxidation of other functional groups such as amines. The reader is made aware of the importance of oxidations in the chemical industry in addition to important details of certain oxidation reactions. This is an excellent article for the beginner as well as the specialist.

The second short article concerns the reduction of carbonyl, azomethine, and nitro functionalities. Most of the literature that is covered appeared during the 1970's. The authors restrict themselves to a discussion of the relatively rare phenomenon of reduction by a well-characterized homogeneous catalyst under fairly mild conditions. Therefore the older, less well-understood reductions of aldehydes (for example) by cobalt or iron carbonyl catalysts are not mentioned. The authors emphasize hydrogenation via H_2 transfer from one substrate to another.

The third article by Julemont and Teyssie is entitled Catalysis of Diolefin Reactions by η^3-Allyl Metal Complexes. Most of the material in this article does little to enlighten those who are relatively knowledgeable in this mature area. For example, the article begins by discussing bonding and dynamic behavior of allyl complexes. It is a useful article for those who are relatively unfamiliar with allyl complexes and the role they play in olefin isomerization, oligomerization, or polymerization.

The last contributions by Markó and Bakos is unusual to the extent that it consists almost entirely of two tables. One table lists the chiral phosphines that have been used as ligands in rhodium-catalyzed asymmetric hydrogenation reactions and the other the substrates that have been hydrogenated asymmetrically. This contribution is intended for those thoroughly familiar with the field or perhaps for someone who would like to know quickly what is the best way to asymmetrically hydrogenate a certain type of substrate. The tables appear to be comprehensive through 1978.

Richard R. Schrock, *Massachusetts Institute of Technology*