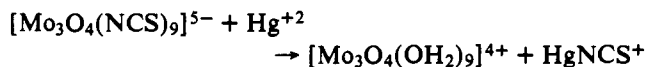


ditions and has the  $\text{Mo}_3\text{O}_4$  structure, the results suggest that the parent aqueous ion also contains the  $\text{Mo}_3\text{O}_4$  entity. To establish that no oxidation-reduction or reversible Mo-O-Mo bond breaking occurs during the formation of the  $\text{SCN}^-$  complex, we carried out the following reaction



and showed that the starting  $\text{Mo(IV)}_{\text{aq}}$  was obtained as the sole product (ion exchange) and that it had the proper ion-exchange properties, the correct spectrum, and extinction coefficients  $\epsilon$  62.8 at 505 nm. Further, conversion of the enriched  $\text{Mo(IV)}_{\text{aq}}$ , prepared in this manner, back into  $[\text{Mo}_3\text{O}_4(\text{NCS})_9]^{5-}$  was accomplished with <2%  $^{18}\text{O}$  exchange of the Mo oxygens with the solvent.

Similar behavior is shown by a (rapid forming) oxalate complex ion, prepared by eluting  $\text{Mo(IV)}_{\text{aq}}$  from Dowex 50W  $\times 2$  with 0.13 M  $\text{H}_2\text{C}_2\text{O}_4$ . When crystallized from solution by  $\text{Co(en)}_3^{3+}$ ,  $\text{Pt(en)}_2^{2+}$ , or  $\text{Pt(en)}_3^{4+}$ , it retains the Mo-O oxygens without exchange and all three complexes give a Mo-O/(Mo-O + Ox-O) ratio of  $4/(23 \pm 2)$ . Further, the  $\text{C}_2\text{O}_4^{2-}$  may be reversibly removed by  $\text{Pb}^{2+}$  precipitation and the  $\text{Mo(IV)}_{\text{aq}}$  generated may be converted into  $[\text{Mo}_3\text{O}_4(\text{NCS})_9]^{5-}$  with complete ( $\pm 2\%$ ) retention of  $^{18}\text{O}$  in the Mo-O oxygens. This oxalate complex ion is similar to but not identical with that in the structure determined by Cotton et al.<sup>6</sup>

It is not difficult to conceive of reactions which reversibly form the  $\text{SCN}^-$  trimer from  $\text{Mo(IV)}_{\text{aq}}$  in some other state of oligomerization, thus negating the structural relationship between the  $\text{SCN}^-$  complex and  $\text{Mo(IV)}_{\text{aq}}$ . However, it seems impossible to accomplish this reversibility without simultaneously causing considerable, if not complete, bridging oxygen exchange. Since oxygen exchange does not occur, the  $\text{Mo}_3\text{O}_4$  entity found in the  $\text{SCN}^-$  complex is also present in  $\text{Mo(IV)}_{\text{aq}}$ .

We conclude that the structure of  $\text{Mo(IV)}_{\text{aq}}$  in acidic media consists of a trimer with three bridging oxygens and a capping oxygen (Figure 1). These oxygens are very slow to exchange.<sup>9</sup>

Each molybdenum probably has three additional waters (more labile) in its primary solvation sphere, two of one type (on capping-O side) and one on the bridging-O side, completing the distorted octahedral configuration around each molybdenum. There is some evidence that all of these oxygens (four types) are slow enough to exchange isotopically to be kinetically studied by conventional methods. Studies with these goals are in progress. A complete description of this work with a discussion of its relationship to previous investigations will be presented with the  $^{18}\text{O}$  kinetic studies.

**Acknowledgment.** We express our appreciation to Dr. E. O. Schlemper and Dr. M. S. Hussain for the cooperative effort on the X-ray studies, to M. Johnson for some of the  $^{18}\text{O}$  analyses, and to the University of Missouri Research Council for partial support.

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- (10)  $F_n$  is the normalized ratio of  $^{18}\text{O}$  in the measured sample compared with a normal standard which are arbitrarily given the value  $4 \times 10^{-3}$  ( $4 \times 10^{-3}$  is the mole fraction of  $^{18}\text{O}$  found in nature).

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## Book Reviews

**Polymer Surfaces.** By D. T. CLARK and W. J. FEAST. xiv + 441 pp. John Wiley & Sons, Inc., Somerset, N.J. 1978. \$63.50.

The first six chapters of the book cover the fundamental aspects of the mechanical, physical, and electrical properties of the surfaces. These chapters assume a lot of fundamental knowledge. There is not enough detail for a novice to the field of polymer surfaces, and probably these chapters are of limited use to the expert. However, the rest of the book (Chapters 7-19) is well written, cohesive, and flows smoothly from chapter to chapter even though each chapter is written by a different author. Overall, the book provides an up-to-date discussion of the techniques that are used for making polymer films and/or for modifying the surfaces of synthetic polymers. The book also presents state-of-the-art methods that are being used to characterize these surfaces.

In particular, Chapter 8 contains an excellent description of the experiments that have been done for the preparation of films under controlled conditions. In addition, it includes a fairly extensive survey of the types of films that have been synthesized. Chapters 9 and 10 provide useful information on how surfaces can be modified, particularly through the application of plasma techniques. Also, the latter chapter contains a good discussion of the various theories of adhesion.

The major methods of probing polymer surfaces such as IR, ESCA, and SEM are well represented. Chapter 15 and sections in a few other

chapters give a good overview of the kinds of information that can be obtained about polymer surfaces through the use of infrared spectroscopy. For example, the multiple internal reflectance (MIR) infrared spectra of various polyethylene samples clearly show the effects of oxidation and/or etching.

The book provides a good combination of technical review and historical perspective. Many of the chapters are interesting and readable even by a novice in the field.

Adrian J. Vanderwielen, Steven J. Borchert, *The Upjohn Company*

**Conservation of Resources.** The Chemical Society, London. 1977. ix + 245 pp. \$12.00.

This is a collection of papers presented at the Annual Chemical Congress in Glasgow in April 1976, and is a broad overview of the problems of conservation of material and energy resources, both in the United Kingdom and worldwide. Topics are widely varied, ranging from the effect of human activity on climate to the role of photosynthesis and oxidative phosphorylation in biological energy consumption.

The papers are written by specialists to convey to specialists in other fields the problems, both technical and philosophical, that they are trying to solve, and some of the proposed solutions. As such, in addition to succinct prose, the well-referenced articles include numerous informative charts, graphs, and tables, with only a few simple equations.

Controversial issues such as industrial safety of plutonium and the ultimate size of the world's population are rationally analyzed. Ramifications of current thoughts and practices are investigated in an attempt to predict the future realistically and to solve a few of the problems of the present before they get out of hand.

J. I. Brand, *Oak Ridge National Laboratory*

**Surface and Colloid Science. Volume 8.** Edited by EGON MATIJEVIC (Clarkson College of Technology). John Wiley & Sons, Inc., New York. 1976. vi + 420 pp. \$32.00.

The first chapter, entitled Adhesion of Colloidal Particles, presents an overview of an area of colloid chemistry with considerable fundamental and practical interest. The author reviews a number of experimental techniques for measuring the force of adhesion, separating them into two groups, direct and indirect methods. This is followed by a somewhat detailed description of the various interactive forces generally considered to be at play in colloidal systems. The description is divided into two major areas, non-immersed systems and immersed systems. In the former, London-van der Waals forces are considered and the calculation of Hamaker constants using both Hamaker's approach and the method of Lifshitz and co-workers is discussed. In the latter, other types of interactive forces including electrostatic, entropic, enthalpic, and ion bonding are discussed, as well as London-van der Waals forces. The chapter is well referenced with an extensive bibliography and serves as a useful introduction to the field of colloidal adhesion.

The second chapter is entitled Periodic Colloid Structures and provides a good review of a number of these interesting systems, e.g., tactoids, thixotropic gels, Schiller layers, etc., as well as a general discussion of the forces that establish and maintain these periodic structures. The author also includes a section devoted to physical properties of the colloid structures. Considerable time is spent discussing long-range interactions of colloidal particles including the effects of ions, particle size and shape, and external fields. The paper is well referenced and includes a number of fascinating photomicrographs demonstrating periodic colloid structures and making clear many of the authors' points.

The third chapter in the book, Surfactants in Organic Solvents: The Physical Chemistry of Aggregation and Micellization, contains a review of the properties of surfactants in organic solvents. In the authors' words, "... this is a rather limited field ..." compared to aqueous surfactant chemistry, but it is just this limitation which makes the paper particularly useful. It serves to review, rather well, an area of colloid science which has not received a great deal of attention. The authors concern themselves with the physical chemistry of these nonaqueous surfactant solutions and include sections on physical properties, solubility behavior, and aggregation. From the outset, the authors claim the CMC concept is not appropriate for organic solvent micellization and that it is necessary to consider stepwise aggregation in terms of mass-action-law equilibria to adequately describe aggregation and micellization in organic solvents. The authors either present or reference a considerable amount of data making this paper not only a review but a reasonable introduction to the field.

The last chapter, Homogeneous Nucleation in Vapor, is a review of recent developments in the theory of homogeneous nucleation. The authors first present a general review of the thermodynamic foundations of nucleation theory. This is followed by relatively brief discussion of the statistical mechanical aspects of nucleation which serves to lay the groundwork for a review of the controversial Lothe-Pound nucleation model and several short discussions of papers challenging the L-P model. The authors review recent numerical approaches, e.g., molecular dynamics, Monte Carlo, and normal mode methods, used to calculate the cluster free energy, and comment briefly on experimental methods. By and large, the authors assert that the L-P controversy has not been laid to rest, and they list several liquids whose critical supersaturations are said to follow the L-P theory.

Richard H. Heist, *University of Rochester*

**Principles of Colloid and Surface Chemistry.** By PAUL HIEMENZ (California Polytechnic Institute, Pomona). Marcel Dekker, Inc., New York. 1977. 536 pp. \$19.50.

This book is Volume 4 in the publisher's Undergraduate Chemistry series. The treatment of the areas covered is both clear and delightful to read. Particularly commendable are the chapters on viscosity, osmotic pressure, light scattering, and micelles.

In the treatment of surface energy of solids, I believe there should have been some discussion of the work of R. J. Good and of A. W. Neumann. However, this section is presented in an excellent manner and has a very good section on the application of the Laplace equation. The problems at the end of each chapter are well chosen to reinforce the material presented before them.

This textbook should be a valued reference for undergraduate students and will provide an excellent introduction to the fields of colloid and surface chemistry.

G. A. Cave, *S. C. Johnson & Son, Inc.*

**Annual Review of Materials Science. Volume 8.** Edited by R. A. HUGGINS (Stanford University), R. H. BUBE (Stanford University), and D. A. VERMILYEA (General Electric Co.). Annual Reviews, Inc., Palo Alto, Calif. 1979. x + 499 pp. \$17.00.

This volume presents 14 critical evaluations of recent developments in materials science. An essay by H. J. Welker entitled "From Solid State Research to Semiconductor Electronics" introduces the volume.

Haydn Chen, R. J. Comstock, and J. B. Cohen examine local atomic arrangements associated with ordering in concentrated alloys and ceramic solutions by X-ray and neutron diffraction techniques. A. Atalar, V. Jipson, R. Koch, and C. F. Quate review principles and operation of the scanning acoustic microscope. A. R. Reinberg reviews reactive plasma deposition of inorganic nonconducting thin films.

Brian Ditchek and L. H. Schwartz discuss recent developments in characterization, properties, and applications of spinodal alloys. J. A. Borders reviews research of metastable phases produced in metals by ion implantation as studied by energetic ion channeling and transmission electron microscopy. D. L. Kendall discusses vertical etching of silicon at very high aspect ratios and applications. V. V. Boldyrev discusses control of the reactivity of solids in terms of the process, position and mechanism of the reaction front.

D. M. R. Taplin, G. L. Dunlop, and T. G. Langdon examine the mechanical characteristics of superplasticity and the development of plastic instabilities during tensile flow of engineering alloys. A. K. Mukherjee reviews basic mechanisms for deformation in superplasticity. H. C. Rogers reviews adiabatic plastic deformation. J. O. Stiegler and L. K. Mansur review radiation effects in structural materials.

C. M. Perrott describes the service behavior of tool materials for drilling and mining. J. W. Nielsen reviews the preparation of magnetic garnet films for bubble domain memory. R. Collongues, A. Kahn, and D. Michel review superionic conducting oxides.

John M. Powers, *School of Dentistry, University of Michigan*

**Advances in Polymer Science. Volume 29: Structure and Properties of Polymers.** Chapters by M. STOLKA and D. M. PAI, Y. IKADA, and B. R. M. GALLOT. Springer-Verlag, New York. 1979. 161 pp. \$41.80.

Volume 29 in the series "Advances in Polymer Science" contains three chapters, namely, "Polymers with Photoconductive Properties" by M. Stolka and D. M. Pai, Xerox Corporation, Rochester, N.Y., containing 45 pages with 150 references (10 of authors); "Characterization of Graft Copolymers" by I. Ikada, Kyoto University, Japan, containing 36 pages with 36 references (18 of author); and "Block Copolymers with Ordered Structures" by B. R. M. Gallot, Centre de Biophysique Moleculaire, Orleans, France, containing 64 pages with 285 references (46 of author). Stolka and Pai provide a useful review of photoconductive polymers and outline theoretical considerations and experiments in several polymer systems. Ikada presents a review of his work in the field of graft copolymerization. He properly indicates that this review article does not deal with all the subjects relating to the characterization of graft copolymers, but only with some of the fundamental ones. An elegant statistical analysis of grafting processes is presented. Gallot gives an excellent review of 38 block copolymers with varying structural order. He discusses synthesis, morphology, theories of microdomain formation, copolymers with amorphous and crystalline blocks, and biologically interesting copolymers. Property vs. percent solvent and electron micrographs are the principal experimental data used to support Gallot's discussion of the above topics.

This volume does not contain a unity of subject matter, a fact which may detract from its value. However, the reader should find at least one chapter of considerable merit.

Richard P. Wool, *University of Illinois at Urbana—Champaign*