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Book Reviews

Advances in Catalysis, Vol. 15. Edited by D. D. Eley *et al.* Academic Press, New York, 1964. x + 355 pp. Price $14.00.

Each quadrennial "Advances in Catalysis" must reckon with the presence of the International Congress as a competitive forum. These latter catalytic maelstroms have been deep and hungry sinks for reports on current progress in the art. As sources of stimulating discussions, Professor Eley questions their merit. He and his co-editors have resolved the 1964 quadrennial problem by offering a comprehensive review by Bond and Wells of the hydrogenation of unsaturated hydrocarbons over transition metals. This core, which makes nearly half the text, is surrounded by five shorter topics, including adsorption, dissociation kinetics, low-energy electron diffraction, electronic spectroscopy, and isotopic oxygen exchange.

The impact of the new organometallic chemistry on catalysis has furnished stimulating concepts: the σ- and π-bonded complex, the π-allyl structure, ligand-field theory, and continuity between heterogeneous and homogeneous catalysis. The review by Bond and Wells leaves no doubt as to the importance of this impact. It is, in fact, a competent taxonomy of what Professor Burwell has called the "organometallic zoo." The important monoolefin reactions compared are hydrogenation, H/D exchange, and isomerization (*cis–trans,* and double-bond shift). The important reaction of diolefins and acetylenes is selective partial hydrogenation, with stereoselectivity often of critical interest. The authors have chosen to retain the classic metal-by-metal format in presenting a wealth of information on the organic moiety of the intermediate complex. This choice of format reminds us how comparatively meager in detail our picture of the metal-carbon bond remains.

The stability of this bond determines whether olefins are strongly held or are easily displaced. In the latter case, typified by iron, nickel, and palladium complexes, isomerization and H/D exchange are detected. In contrast palladium and iridium are almost inactive for these reactions. Modest and qualitative generalizations of this sort have replaced the confident predictions of the older electronic theories. The need for quantification is acknowledged. Direct measurement of the stability constants of a metal-olefin complex is one approach suggested. This information is surprisingly lacking in the case of transition metals; but it is indeed a formidable task to reproduce, in an isolable metal-olefin complex, the ligand structure that exists in the catalyst-olefin complex. The latter may comprise not only neighboring metal atoms, as postulated by the reviewers, but also oxide ions of the support, deliberately added promoters such as halide, and deliberately added poisons such as sulfur.

By condensing a massive amount of experimental evidence into a very well organized and readable review, Bond and Wells have performed a notable service. They have also realistically deferred immediate prospects for the unitary theory of catalysis, which seemed so imminent 15 years ago.

Boreskov has attempted a similar task for oxidation catalysts. Regrettably, the English translation is heavy-handed and awkward. The type of reaction reviewed is isotopic oxygen exchange, and the approach is via kinetics rather than structural chemistry. Even with this relatively simple reaction the kinetics are inevitably complicated, since the exchange may or may not involve lattice oxygen. Few firm generalizations can be drawn. For the study of specific catalytic oxidations, however, the technique appears to be very promising. One obvious example is the oxidation of olefins over nonstoichiometric bismuth molybdate, a reaction which seems to implicate lattice oxygen more than many of the systems cited in the review.

A current dictum for those using surface reaction kinetics as an approach to catalysis is that their analysis must correlate energies of activation with heats of adsorption. This is illustrated in Tamaru's discussion of surface decomposition reactions, such as decomposition of germane over germanium, and of formic acid and ammonia over various metals. An interesting exception to the rule appears in Brennan's treatment of the kinetics of atomization of diatomic molecules. The activation energy for this reaction correlates with the heat of dissociation, rather than the heat of adsorption. Brennan proposes a mechanism which will lead to this relationship, as well as to the observed half-order kinetics, and he defends it with convincing skill.

Chemical physicists contributing to the volume are Terenin, reviewing the electronic spectroscopy of adsorbed species, and Farnsworth, who discusses his own approach to low-energy electron diffraction (LEED).

Surface reactions relevant to catalysis which can be studied by LEED include epitaxy, adsorption, place exchange, and oxidation. Farnsworth's techniques differ in important details from those reported by Bell Laboratories. In particular the fluorescent display of diffraction patterns is augmented by semiautomatic scanning with a Faraday collector. This is somewhat slower than the visual readout, but is claimed to give more quantitative measurements of intensity.

Infrared spectroscopists lately have had to face criticism that the species they observe are too stable to be really involved as activated intermediates. The ultraviolet spectroscopists are less vulnerable in this respect. The carbonium ions and carbanions which Terenin describes have had a respectable history as catalytic intermediates. The added possibility of single electron transfer to or from the surface to give the corresponding radicals, broadens the field of mechanisms that can be supported by spectroscopic evidence. Those concerned with applications of electron spin resonance in catalytic research will find this review particularly helpful.

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Recent Progress in Surface Science, Vol. 1. Edited by J. F. Danielli, K.G.A. Pankhurst, and A. C. Riddiford. Academic Press, New York and London, 1964. xii + 414 pp. Price $16.00.

This is the first volume of a series which attempts to bring together critical reviews on all areas of surface science. Although it is undoubtedly important to emphasize the common basis of subjects as widely apart as metal corrosion and adhesive properties of cell membranes, several of the chapters in this volume have clearly been written by experts and for experts, and it is difficult to see what purpose is served by collecting these contributions in a single volume. Thus, the extensive literature review on electrode reactions (by S. Schuldiner) and the detailed description of a method for making artificial lipid membranes (by P. Mueller and co-workers) can hardly be expected to be of interest to the same class of research workers.

It was evidently intended to have the articles written in such a way that the subject matter can be understood by experts in quite different fields, who have no desire to study the specialized terminology used for communication among the workers on that subject. An example of how this can be achieved is the brief chapter on "Chemistry of Semiconductor Surfaces" by E. Tannenbaum Handelman. The chapters on "Foams and Free Liquid Films" (by J. A. Kitchener) and on the "Electrical Double Layer and Electrokinetic Phenomena" (by D. A. Haydon) are very complete and authoritative reviews of recent developments in these fields. Of the four final chapters on biological surfaces, those by W. D. Stein ("Facilitated Diffusion") and by E. J. Ambrose ("Cell Contacts") summarize our lack of understanding of these phenomena.

The contribution of Ambrose is especially interesting for the discussion on movements and mechanical properties of cell membranes. The chapter on "Cell Adhesion" by E. H. Mercer is not so much a review article as a collection of the evidence supporting the hypothesis according to which this adhesion is due to the presence of specialized adhesive molecules.

There seems to have been a regrettable delay in publication. Most of the contributions contain references up to 1961, in few cases part of the literature of 1962 was also covered, and only the chapter by P. Mueller and co-workers (which is not a review article!) mentions literature of 1963. This is especially unfortunate in those cases where recent developments have rendered many of the older concepts obsolete. Thus, M. Joly's article on "Surface Viscosity" considers only the shear viscosity, to the exclusion of dilational properties, but recent evidence shows that surface dilational properties are far more important for understanding other surface phenomena such as foaming and emulsification.

Not many printing errors were discovered, the most disturbing being in Chapter 9 where the name of Professor van Deenen is misspelled in the tables and in the author index, but not in the text.

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