Book Reviews

Some Problems in Chemical Kinetics and Reactivity. vol. 1 (revised and expanded edition). N. N. Semenov. Translated by Michel Boudart. Princeton University Press, Princeton, N.J., 1958. 239 pp. Paper, $4.50.

The aroma of the laboratory is very strong in this book. The author is steeped in a wide range of experimental results, and there is a complete lack of interest in theories which solve problems "in principle." The field covered is very broad: a wide range of atoms and radicals is considered, and the reactions of these with a wide range of molecules are given. In addition to the usual subjects of decomposition, recombination, and atom-transfer reactions, difficult topics such as oxidation, polymerization, free radical reactions in solution, and surface reactions are included. Extensive tables of data are given; documentation is thorough, especially for Soviet articles; and there is a substantial amount of correlation and interpretation.

The unifying theme of the book is the almost universal importance of free radical chain reactions. A free radical is defined (not abstractly, as a molecule with an odd electron) in accordance with the logically tenuous but practical and chemical criteria of great reactivity, tendency to dimerize, and so forth; a diradical is taken to have two highly reactive unsatisfied valences. In the author's pioneering book *Chain Reactions* (written 20 years earlier) there were many instances of the use of elaborate algebra to express the build-up and decay of abstract chain entities; here there is introduced a simple and powerful arithmetic of free radical reactions. The numbers represent the radicals—0 for a molecule, 1 for a radical, 2 for a diradical, and so forth. Chain initiation becomes $0 \longrightarrow 1 + 1$; chain propagation steps are of the form $1 \longrightarrow 1$; chain branching is typically $1 \longrightarrow 1 + 2$. It is highly instructive to apply this simple, chemical arithmetic to each step of any chain reaction.

To give the broad picture of the entire field, Semenov has not hesitated to use principles which are known to be incorrect or imperfect upon close inspection—for example, the constancy of Arrhenius A-factors or the Polanyi relation between activation energy and heat of reaction. In the last chapter, on the mechanism of the production of free radicals on surfaces, we find stimulating suggestions rather than established ideas.

In all, the book gives a mature, critical, personal survey of the field. A large amount of material is intelligently and originally presented in a small volume.

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Some Problems of Chemical Kinetics and Reactivity. vol. 1 (revised and enlarged edition). N. N. Semenov. Translated by J. E. S. Bradley. Pergamon, New York and London, 1958. x + 305 pp. $12.50.

The author tells us that an all-union conference on chemical kinetics and reactivity was arranged by the chemistry department of the Academy of Sciences of the U.S.S.R. and held in 1955. This book is an expansion of the opening paper for this conference, published in 1954. The conference, at which 69 papers in addition to that of Semenov were presented, was held in June 1955.

The first edition of this work was soon sold out; this is a revised and expanded edition which has been translated into English and German. This book is a sequel to *Chain Reactions,* written 20 years earlier. It is a thoughtful, systematic account of the various types of chain reactions, written from the experimentalist's point of view. Semenov has neglected quantum mechanical and statistical mechanical considerations, except for a ten-page appendix on the activated complex, contributed by M. I. Temkin, and a second ten-page appendix written by N. O. Sokolov, on the quantum-mechanical calculation of activation energies.

It is particularly useful to have this well-written account of chemical reaction rates since it calls attention to many interesting Russian papers which, because of language difficulties, are not sufficiently well known to English-speaking chemists. Reaction-rate theory poses many as yet unanswered questions. This complexity arises from the fact that reactions proceed by every imaginable mechanism and the important one is that one which, under the particular set of circumstances, contributes most to the rate. Thus qualitative reasoning is insufficient. To be successful one requires a quantitative theory. Further, even though from experiment we know the concentration dependence of a chain reaction, this may involve many alternative elementary reactions, each with its particular activated complex.

In this book Semenov steers us surprisingly well through the chemical maze. He offers mechanisms, supported by evidence, for very many chain reactions and emphasizes that these chains often compete on nearly equal terms with radical-free reactions.

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Digging into History. Popular series, Anthropology, No. 38. Paul S. Martin. Chicago Natural History Museum Press, Chicago, Ill., 1959. 157 pp. Illus. $1.50.

All too frequently, at the conclusion of a protracted and concentrated study of the archeology of a region, archeologists are content to let their labors come to rest with the publication of the technical reports, designed for the specialist. *Digging into History* is an exception to this trend because Martin, after having concluded 15 years of excavation in the ruins of west-central New Mexico, sets out to share his experiences by distilling the development of a 5000-year record of human progress in language designed for the lay reader.

Martin first sketches the background of Southwestern culture history, wrestling with such problems as shifts in the continuity of economic dependency, from the big-game hunters of late glacial times to the emergence of sedentary village life based on agriculture. The four tribal, or cultural, units, as now recognized by Southwesternists, are reviewed in understandable terms; this leads to discussion of the Mogollon people, whose history Martin and his colleagues have done so much to elucidate.

How the archeologist works and what he seeks to accomplish by digging is clearly stated. Explanations of such principles as stratigraphy, culture change, and the meaning of periods and phases add further to the clarity of the booklet.

The 5000-year story of man's tenure of this part of New Mexico is described under "way of life" rubrics such as "The time of limited wandering," "Emergence