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Book review

Kinetics of Homogeneous Multistep Reactions: Comprehensive Chemical Kinetics

Volume 38, Edited by F.G. Helfferich, R.G. Compton and G. Hancock, Elsevier, Amsterdam, 2001, pp. xv + 410. ISBN 0-444-82606-8; US\$ 244, NLG 495, \in 224.62

From the first sentence of the introduction it is quite clear that here is a book that is out of the ordinary: a text on chemical reaction kinetics from the perspective of an engineer. The author tells us that this book was written as an aid and guide for the hands-on industrial chemist and development engineer. It is therefore with some trepidation that a purely laboratory-based chemist turns the page. What you discover is an interesting, thought-provoking book, which concentrates on kinetics, not engineering, and on methodology rather than abstract theory. Theory is only covered in sufficient details to allow the design of experiments and the interpretation of results.

The book is divided into 12 chapters. Chapter 1 introduces the basic concepts such as rate, reaction order, molecularities etc., but also includes some terms such as conversion and rank with which chemists are probably not so familiar. Chapter 2 outlines the fundamentals of kinetics and the construction of rate laws for multistep reactions. Chapter 3 discusses the techniques used to study reactions including batch, differential and stopped-flow reactors. After explaining how to determine reaction orders and rate coefficients, Chapter 4 examines rate-controlling steps and elucidation of the rate law. Chapters 5-7 introduce reversible, consecutive and concurrent pathways and the associated mathematics for these systems, whilst Chapters 8-10 concentrate on the areas of homogeneous catalysis, chain reactions and polymerization. Chapter 11 outlines mathematical modelling of multistep reactions and Chapter 12 discusses unusual thermal and mass-transfer effects that are of interest primarily in reactor design.

The book is in the most part easy to read and certainly this is helped by highlighting important points in boxes throughout, and the excellent use of summaries at the end of each chapter. For those less familiar with kinetics of complex systems, a series of examples illustrating the application to industrially important catalysis such as hydroformylation with $[CoH(CO)_3(PR_3)]$; hydrocyanation with $[Ni(PR_3)_4]$ and hydrogenation of alkenes by Wilkinson's catalyst is a very good feature. One point I found irksome was in Chapter 8 where the author uses Ph as the abbreviation for PR₃; a strange choice when Ph is so universally accepted to represent the phenyl group.

This is not a book for the novice in kinetics. The presentation of the kinetics and the mathematical terminology employed seem to me to be more suited to someone with a firm understanding of the subject. In places, I think the novice would get confused. For example, I admit that at first I was confused in Chapter 2 by the phrase, "Rate equations of steps are power laws with integer reaction orders that can be directly deduced from molecularities". It seemed that the author was muddling kinetic order and molecularity. But, of course, the author is specifically talking about elementary reactions. As anyone who has derived a rate law using the steady-state hypothesis will know, for elementary reactions kinetic order and molecularity are the same. However, it is easy to see how a student reader might go away with the idea that there is a more general relationship between molecularity and order.

There is much in this book for all kineticists. If nothing else, the presentation from an engineer's point of view challenges chemists to re-think even their most basic understanding of kinetics. In addition, the book introduces some concepts with which not all kineticists will be familiar. This is particularly evident in Chapters 1 and 2 where the concept of rank (at what stage in a multisep mechanism a reactant gets involved in a multistep reaction) is introduced. Whilst the idea of rank is useful in a more general sense, the designation of network is in my opinion less so. Network refers to the series of elementary reactions that makes up the whole reaction. The terminology seems more in tune with someone thinking about a reaction mechanism in purely mathematical terms rather than in the chemistry involved.

All those interested in the use of kinetics to investigate multistep reactions including catalytic systems should put this on their 'ought to read' book list. This is a book that I know I will use regularly to help me in analysing the kinetics of complex reactions.

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