Bubbles, Drops, and Particles in Non-Newtonian Fluids

By R. P. Chhabra, CRC Press, 1993, $169.95

The author is a professor of Chemical Engineering at the Indian Institute of Technology, Kanpur. He has not only published widely in the field of non-Newtonian fluid mechanics and multiphase flow, but written a book that reviews his own work, as well as that of the others who have played a major role in clarifying the issues regarding the dynamics of multiphase flow in non-Newtonian (and Newtonian) liquids.

The book is easy to read, and its 400 pages are organized logically. After a brief introductory chapter, the author presents a fairly compact review of non-Newtonian rheology. Those readers already conversant with the topic will not find a need to read this chapter. Those whose main interest is in the dynamics of multiphase systems will find this a sufficient introduction to support their reading of the rest of the book.

Chapters 3 and 4 deal with the dynamics of rigid spheres in time-independent and viscoelastic liquids. These chapters, as well as those that follow, are clearly written. Review papers are cited, and specific studies are illustrated with a presentation of relevant equations and correlations, and displays of experimental data. The reader gets a good idea of what correlations are useful, and the extent to which simple theoretical models mimic the observations.

Chapter 5 covers the important topic of drops and bubbles in non-Newtonian fluids. Some sections of this chapter are very brief (coalescence of bubbles and drops covers only two pages). Wisely, the author has avoided the presentation of sophisticated theory here and instead describes clearly the variety of studies that others have carried out, so that the reader may go to the source literature where theory and experiment are presented.

Chapter 6 covers the topic of flow through fixed beds and porous media, followed by a brief chapter (Chapter 7) on fluidization and sedimentation. Chapter 8 reviews the topic of heat and mass transfer very briefly, but quite well referenced.

The final chapter is a review of the technique of falling ball viscometry.

In summary, this is a valuable and well written book. Those interested in this field will find brief reviews of specific topics accompanied by citations of the relevant literature. As such, the book is especially well recommended to those who are beginning a study of the issues that surround the complex flow of non-Newtonian fluids in particulate systems.

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The Microkinetics of Heterogeneous Catalysis

By J. A. Dumesic, D. F. Rudd, L. M. Aparicio, J. E. Rekoske, and A. A. Treviño, ACS Professional Reference Book, American Chemical Society, Washington, DC, 1993, 315 pp.

Impressive advances in both surface spectroscopy and catalyst characterization techniques now allow for the near molecular resolution of surface reactants, products, and in some instances controlling surface intermediates on various catalytic surfaces. These techniques also serve as probes in elucidating the nature of active catalytic sites. Despite these advances, a quantitative identification of many of the governing intermediates is at best a difficult task due to their fleeting surface lifetimes. As a result, the rather extensive set of fundamental information available in the literature is extremely fragmented, thereby making it difficult to utilize in any quantitative manner. In addition, complex and competing physicochemical effects obscure the way in which this information relates to industrial conditions. For example, many processes operate at substantially high reactor pressures where the relevance of single crystal experimental results which were carried out under ultrahigh vacuum has to be carefully examined. Together the fragmented fundamental database and its application at industrial conditions have limited the development of mechanism-based reaction models for catalytic processes. A majority of the industrially relevant reaction models, such as those based on Langmuir-Hinshelwood-Hougen-Watson and empirical power-law kinetics, have been derived from limiting approximations.

The authors of this book, however, have identified a general methodology which enables detailed surface science experiments, theory, and kinetic information to be directly incorporated into robust simulations of the surface chemistry. This allows for reliable predictions of the industrial catalytic reaction process over an extensive range of operating conditions. The aim, therefore, is to develop a mechanism-based model which incorporates and describes a continuum of experiments which start from well-characterized molecular processes on single crystal surfaces and end with the complex catalytic system at operating conditions. The two basic tools in the authors' approach are *microkinetic analysis* and *catalytic reaction synthesis*. Microkinetic analysis is defined as "an examination of catalytic reactions in terms of elementary chemical reactions that occur on the catalytic surface and their relation with each other and with the surface during a catalytic cycle." Catalytic reaction synthesis is "the combining of surface chemical information from diverse experimental and theoretical sources to create a coherent description of how the catalyst, catalytic reaction cycles, and reaction conditions may be formulated to achieve high yields of particular desired products."

The major focus of the book is, understandably, the microkinetic analysis, that is, the development of comprehensive reaction models. As microkinetic

modeling matures, there will undoubtedly be significant contributions to catalytic reaction synthesis and catalyst design. The first four chapters of this book are devoted to defining the elements of microkinetic analysis and catalytic reaction synthesis and provide a nice overview of the experimental and theoretical techniques available to analyze catalytic systems.

Chapter 1 not only outlines the methodology and the layout of the book, but defines microkinetic analysis and catalytic reaction synthesis. Chapter 2 provides a broad, yet concise, overview of chemical kinetics in heterogeneous catalysis and establishes its role in microkinetic analysis. The basic target of this is elementary step reaction kinetics. Short subchapters review some very basic features from both collision theory and transition state theory and their application in estimating kinetic parameters for various adsorption, desorption, surface reaction steps. In addition, there is a short summary of other useful kinetic analysis tools, such as thermodynamic consistency checks, parameter estimation, and surface nonuniformity. Lastly, Monte Carlo simulation of surface reactions, basic reactor design, and analysis of transport limitations are discussed. The example problems scattered throughout this chapter are quite helpful. In general, this chapter serves as a basic guide and touches only on most relevant kinetic techniques for the mechanism-based analysis. A more in-depth and extensive discussion on each of the topics in this chapter would have strengthened this chapter considerably and made the book somewhat more valuable as a reference source. For example, while parameter estimation plays an important role in each of the ensuing examples, there is only a very elementary description of its definition, with no discussion on the available methods, robust searching techniques, or sensitivity analysis. A short subchapter on reaction path analysis would have also been beneficial.

Chapter 3 describes structure-reactivity relationships and their important role in estimating kinetic data for systems which have yet to be studied experimentally. While rather short, the message of this chapter is quite powerful; a simple and limited set of fundamental experimental information can be used to formulate structure-reactivity relationships which then supply the necessary kinetic parameters for an extensive set of reactants undergoing various competing reaction paths, required for the microkinetic analysis.

Essential experimental techniques which are available to characterize the structural and electronic configuration of both the bulk catalyst, as well as the active surface, are described in Chapter 4. Kinetics and thermodynamics of adsorbate-surface interactions, as described, can be probed via temperature-programmed desorption, isotropic tracing, microcalorimetry, and chemisorption. The laundry list of items is a valuable reference guide for all. In particular, catalytic reaction modelers who might not be aware of the breadth of techniques available, their levels of resolution, and what each method targets will enjoy this chapter.

The remaining seven chapters are devoted to specific detailed examples which are taken from some of the authors' most recent publications:

Chapter 5: Ethylene Hydrogenation Catalyzed by Platinum
Chapter 6: Ammonia Synthesis Catalyzed by Iron
Chapter 7: Ethane Hydrogenolysis Catalyzed by Group VIII Metals
Chapter 8: Methane Oxidation Catalyzed by Molybdenum and Vanadium Oxides
Chapter 9: Methane Dimerization Catalyzed by Li-MgO
Chapter 10: Redox Catalysis by Transition Metals Exchanged in Zeolites
Chapter 11: Isobutane Cracking Catalyzed by Acid Zeolites

Collectively, these examples cover an extensive range of different catalytic chemistries and effectively demonstrate the powerful utility of the microkinetic approach. They start from the simple and fairly well-understood chemistry of ethylene hydrogenation and move to more and more complex systems, thus ending with the zeolite cracking of isobutane which requires accounting of both the complex distribution of acid sites and the competing array of different reaction pathways. The diversity between each of these systems allows the authors to highlight unique features of the microkinetic approach and explore different issues for each example.

In Chapter 5, detailed spectroscopic and isotopic labeling data on ethylene hydrogenation are used to test the validity of various proposed mechanisms. Chapter 6 demonstrates how adsorption-desorption experiments performed at ultrahigh vacuum on iron single crystals can be used to simulate the industrial ammonia synthesis process which operates at pressures over 11 orders of magnitude higher than UHV-derived input data. The role of various group VIII metals in the hydrogenolysis of ethane is established in Chapter 7 through the application of Evans-Polanyi relationships and Bond Order Conservation principles. These techniques were used to relate elementary activation barriers for various hydrogenation/dehydrogenation and carbon-carbon bond scission steps to the carbon-metal and hydrogen-metal bond strengths. The application of Evans-Polanyi correlations is further extended in Chapter 8 where they are used to estimate activation energies for methane oxidation over molybdenum and vanadium oxides. Molecular orbital calculations are used here to probe the effects of sodium on the electronic structure of the oxide. This use of quantum techniques, however, is somewhat introductory.

Chapter 9 covers methane dimerization over Li-MgO, whereby a number of conjectures from known experimental evidence are used to formulate a microkinetic model and establish general operating conditions which will yield higher conversions. Redox catalysis by transition metals exchanged in zeolites is outlined in Chapter 10. Microkinetic analysis is used to develop and calibrate a detailed reaction model for CO oxidation and N_2O decomposition over iron exchanged in zeolite-Y and Mordinite. The basic framework of this model is then extended to a series of additional transition metals exchanged inside the Y-zeolite, thus providing the basis for catalytic reaction synthesis. The final chapter covers isobutane cracking by acid zeolites and nicely illustrates how a complex sequence of elementary steps (β-scission, hydrogen transfer, isomerization, and proton transfer) can be summarized in terms of a manageable number of Evans-Polanyi correlations for carbenium ion chemistry and developed into an overall model for the catalytic cracking of model hydrocarbon components.

Despite the minor criticisms mentioned above, the book is well written and easy to follow. It is the first text aimed at mechanism-based modeling of

heterogeneous catalysis and does an excellent job of capturing the essential elements and tools required. This book is a valuable reference guide and is highly recommended for anyone working in the field of heterogeneous catalysis and in particular those interested in catalytic modeling. This book could also serve as a useful supplemental text for both basic and advanced courses in catalysis.

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Applied Statistical Thermodynamics

By Klaus Lucas, Springer-Verlag, Berlin Heidelberg, 514 pp., 1991

This text takes the reader from the foundations of statistical and quantum mechanics, through the theory of intermolecular forces, and to the prediction of fluid-phase behavior of real systems. It is intermediate in level between Prausnitz et al.'s *Molecular Thermodynamics of Fluid Phase Equilibria* and Gray and Gubbin's *Molecular Theory of Fluids*. Like these texts, *Applied Statistical Thermodynamics* does not address complex fluids or other applications of statistical thermodynamics, such as adsorption. However, it more than adequately fulfills its stated objectives.

While many of the existing texts on statistical thermodynamics and computer simulation emphasize theory and technique above application, Lucas is clearly motivated by the description of real fluids. According to the author, the book could form the basis for a two-semester senior or first-year graduate course. The text covers a broad range of topics from elementary molecular theory to advanced aspects of liquid-state perturbation theory. Although the author claims that the text is suitable for newcomers to the field, it would certainly help if the reader had some previous knowledge of quantum and statistical mechanics.

A most appealing feature of the book is the remarkably clear and convincing argument for the use of molecular approaches in the evaluation of thermodynamic properties of fluids. The interpolation and extrapolation of experimental thermodynamic data and the prediction of mixture properties from properties of the pure components are, of course, topics of considerable importance for chemical engineers. Lucas notes that even the most complex empirical equation is likely to give poor estimates outside the fitting range. This is well illustrated in the text by the Bender equation of state with 20 adjustable parameters. For mixtures, the problem is still more acute. The remedy for this situation is to use equations which have a sound physical basis. If the interaction parameters cannot be obtained accurately from first principles (which is often the case), it is still possible to fit the theoretically derived equations over a relatively narrow range of experimental data and extrapolate with confidence. Numerous examples in the text demonstrate the success of this approach over the empirical route.

Chapter 1 presents a succinct review of classical and molecular thermodynamics. Chapter 2 deals with the tools for the calculation of the intermolecular forces—quantum mechanics—and the evaluation of macroscopic thermodynamic functions from these interactions—statistical mechanics. Chapter 3 is devoted to the ideal gas. Various thermodynamic functions are evaluated as well as the reaction equilibrium constants. Most of this is standard material which is also well treated in other texts, such as McQuarrie's *Statistical Mechanics*.

Chapter 4 presents a thorough discussion of intermolecular forces, beginning with a useful overview. The later sections emphasize the derivation of working formula for pair and three body potentials at long and short range. Some of the multipole expansions are extremely complex. For example, that for interaction between carbon monoxide and methane occupies nearly one page. If induction and dispersion forces are included, the expressions are even more forbidding. One has to wonder, in these days of symbolic computation programs, if it is really necessary to present all the gory details. For practical applications, the author suggests using the Maitland-Smith-Kihara potential for isotropic interactions and the site-site repulsion—multipole approximation (SSR-MPA) for anisotropic interactions. Chapter 5 concentrates on the application of the material developed in the previous chapters to real gases. The properties of real gas mixtures are accurately described with pure component data. Transport properties are also briefly discussed.

Chapter 6 begins with a short discussion of the ideas behind Monte Carlo and molecular dynamics simulation. The reader would need to consult other texts, such as Allen and Tildesley's *Computer Simulation of Liquids*, for detailed information on how to write simulation programs. It is unfortunate that *Applied Statistical Thermodynamics* does not mention a number of powerful new techniques, including the Gibbs Ensemble and Gibbs-Duhem integration, which have revolutionized molecular-based phase equilibria calculations. Other topics considered in Chapter 6 include the corresponding states principle for liquids, distribution functions and their use in evaluating thermodynamic properties, and fluids of spherical and nonspherical hard bodies. Building on this material, the chapter continues with an extended discussion of perturbation theories. Finally, semiempirical models, such as the BACK and COR equations of state, are considered within the framework of generalized van der Waals theory. In Chapter 7, the concepts developed for pure liquids are extended to mixtures.

In general, the book is very well written. The author maintains a sharp focus on the more important issues. A helpful feature is the inclusion of a summary at the end of each chapter. The example problems are also welcome. However, *Applied Statistical Thermodynamics* would be even more attractive as a course text, if it included additional (exercise) problems after each chapter.

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Handbook of Industrial Crystallization

Edited by A. S. Myerson, Butterworth-Heinemann, Boston, 242 pp., 1993

The editor of the handbook points out in the Preface that the literature on crystallization is scattered, and that this book will correct the situation "by providing a means for scientists or engineers to de-