

CONTENTS

CONTRIBUTORS	ix
PREFACE	xi

Predictive Kinetics: A New Approach for the 21st Century

WILLIAM H. GREEN, JR

I. Introduction	2
A. The Historical Applications of Kinetic Modeling	2
B. The Goal of Chemical Kinetic Modeling	5
II. Construction of Predictive Chemical Kinetic Models.	7
A. The Challenge of Documenting Large Simulations	8
B. Data Models for Chemical Kinetics	9
C. Automated Construction of Lists-of-Reactions.	11
D. A New Data Model for Chemical Reactions and Properties.	13
E. The Reaction Mechanism Generator (RMG).	26
F. Applications of RMG.	27
III. Efficiently and Accurately Solving Large Kinetic Simulations	29
A. Fast Solution of Large Systems of Chemistry Equations Using Sparsity	31
B. Using Reduced Chemistry Models in Multidimensional Simulations without Introducing Error	32
C. Constructing Reduced Chemistry Models Satisfying Error Bounds Over Ranges	34
IV. Are Model Predictions Consistent with Experimental Data?	38
A. How to Prove Inconsistency Even if Some Parameters Are Highly Uncertain	39
B. How Standard Operating Practice Must Change in 21st Century.	41
C. Estimating Error Bars on Model Predictions	42
V. Summary and Outlook.	46
Acknowledgments	47
Nomenclature	47
References	48

Kinetic Modelling of Pyrolysis Processes in Gas and Condensed Phase

MARIO DENTE, GIULIA BOZZANO, TIZIANO FARAVELLI, ALESSANDRO MARONGIU,
SAURO PIERUCCI AND ELISEO RANZI

I. Introduction	52
II. Kinetic Modelling of Pyrolysis Reactions.	55
A. Automatic Generation of Pyrolysis Mechanism	64
B. Pyrolysis of Large Hydrocarbons.	72

C. Reactions between Alkyl Radicals and Oxygen and Transformations of Alkylperoxy Radicals	243
D. Capabilities of Process Influencing, Governing and Design	246
VI. Concluding Remarks	250
Acknowledgments	251
List of Symbols	251
References	253

Kinetic Methods in Petroleum Process Engineering

PIERRE GALTIER

I. Introduction	260
II. Kinetic Modelling by Single-Events	269
A. Introduction	269
B. Bifunctional Catalysis Mechanisms	270
III. Generation of Reaction Networks	271
A. Computer Representation of Species and Chemical Reactions	273
B. Results Obtained for Computer Generation of Networks from nC_8 to nC_{15}	273
IV. Kinetics by Single-Events	273
A. Single-Events Microkinetic Concept	273
B. Separation of Chemical and Structural Contributions	275
C. Free Enthalpies of Reactants and Activated Complexes	276
D. Thermochemical Restrictions and Constraints	278
V. Late Lumping Kinetic Model	279
A. Three-Phase Model	280
B. Catalytic Act	280
C. Composition of the Reaction Intermediates	281
D. Lumping by Families	281
E. Lumped Kinetics	282
F. Summing Up	285
VI. Extrapolation to Heavy Cuts	286
A. Estimation of Kinetic Parameters	286
B. Extension to Heavy Paraffins	289
C. Extrapolation Capacities in Number of Carbon Atoms: Heavy Paraffinic Waxes	294
VII. Perspectives	299
References	302
Further Reading	304
INDEX	305
CONTENTS OF VOLUMES IN THIS SERIAL	313
PLEASE SEE COLOR PLATE SECTION IN THE BACK OF THIS BOOK	