PREFACE

Understanding and modeling the kinetics of chemical reactions certainly is crucial to any research and development effort aimed at process optimization and innovation. This issue provides four complementary points of view. It reflects the state-of-the-art as well as views on the way to proceed by reporting on the efforts of a, I hope representative, sample of research and development groups. I was in particular happy to find a group having close commercial ties with the process industry willing to communicate some of their results and methods. In order to stress as much as possible the generic nature of the messages that are conveyed, the focus is not on catalytic processes.

The blessing of the latter, i.e. the possibility to suppress specific undesired side reactions, renders any kinetic model strongly catalyst dependent which is a curse to the modeler. Accounting in a clever way for so-called catalyst descriptors deserves a separate issue.

A first contribution by W. H. Green Jr. from Massachusetts Institute of Technology sets the scene. The author advocates a paradigm shift in chemical kinetics from ‘‘postdictive’’ to predictive models. The latter would provide a sound basis for process and product design and, hence, not only accelerate the pace of innovation but also allow an *a priori* assessment of the societal, e.g. environmental, impact of new technologies. Predictive modeling requires further progress at three different levels. The construction of the models, the numerical solution of the conservation equations accounting also for the appropriate transport phenomena and finally the validation of the models are discussed.

A ‘‘data model’’, i.e. a standard way of expressing information different from the classical lists-of-reactions is proposed. The core of it is constituted by the concept of functional groups well known from organic synthesis. The latter is implemented in ‘‘hierarchical functional group tree structure(s) which can easily incorporate new chemistry information’’ because ‘‘it will be many decades before the functional group trees will be at all complete’’. Focusing on functional groups rather than elementary reactions allows to calculate rate coefficients based on ‘‘an extension of the thermochemical group-additivity to transition states’’. The elementary reactions are generated automatically by computer codes in which ‘‘reaction recipes’’ based on the reactivity of the functional groups are formalized. Criteria and computational techniques which allow to have the size of a reaction network large enough to account for the important features of a process but not larger than that are discussed. The importance of accounting for uncertainty is stressed throughout the paper. The propagation of uncertainties in both the reaction network and the rate coefficients via the solution of the model equations is presented in a very systematic way. This allows to give a statistically justified answer to the question of validation: ‘‘Are model predictions consistent with experimental data?’’

At each of the levels addressed the author refers to available software and databases, which makes this chapter visionary as well as practical.

The contribution from the Politecnico di Milano reports on the tremendous experience accumulated over the years by the team of Mario Dente and Eliseo Ranzi in the field of steam cracking, one of the largest scale production processes of the petrochemical industry. The authors have been pioneering the substitution of global power law rates by what today is often called microkinetics, i.e. by kinetics accounting fully for the elementary reactions and the radicalar reaction intermediates. An overview is given of the challenges that have to be overcome in order to describe the kinetics of complex mixtures. The contribution is not limited to clearly explaining the developed methodology. It also explicitly indicates the introduction of simplifications. The latter are required not only to maintain the computational efforts within reasonable limits but also, and more fundamentally, because of the uncertainties concerning feed composition. It is fascinating to see how the introduced simplifications are based on insight in the reaction mechanism. Nevertheless, the authors illustrate the generic nature of their methodology by applying it to other free radicalar processes such as polyaromatic, i.e. coke or soot, formation and thermal degradation of polymers.

The Russian school of chemical kinetics is represented by a chapter on oxidation of alkanes by Mikhail Sinev and coworkers from Moscow. Their contribution addresses more ‘‘philosophical’’ issues. What should modeling be aimed at? According to the authors, obtaining insights in the important reaction paths rather than a ‘‘perfect’’ description of experimental data should be pursued. The latter are considered to be too often affected by phenomena such as transport limitations, certainly during the oxidation of alkanes. Most of the examples relate to the oxidation of methane to methanol/formaldehyde, to synthesis gas or, by oxidative coupling, to ethene. The importance of the interaction between homogeneous gas phase reactions and heterogeneously catalyzed steps is stressed. For the homogeneous reactions the use of kinetic parameters obtained from quantum chemical calculations is advocated. Although some examples are given, it is realized that this is much less within reach for the elementary reactions involving the catalytic active sites. The possible optimization of either the process conditions or the catalyst formulation for oxidative coupling of methane based on the insights provided by kinetic modeling is illustrated.

The last chapter gives an indication about the state-of-the-art in an industrial environment. The author Pierre Galtier reports on the activities at the Industrial Studies and Development Center of the French Petroleum Institute (IFP) by a ‘‘Kinetics and modeling’’ group of several researchers performed over a period of more than 10 years. The aim of the research work is to develop basic knowledge on the kinetics of the main reactions involved in refining and petrochemical processes. This methodological research is designed to reduce development costs by constructing detailed and predictive kinetic models. The results of kinetic studies conducted at laboratory and pilot scale allow to improve the economics of industrial processes and to minimize the risks inherent to industrialization of new processes. Galtier focuses on the so-called "single-event" methodology as applied to a bifunctionally, i.e. involving both a (de)hydrogenating and a carbon skeleton conversion function, catalyzed process: the hydrocracking of heavy crude oil cuts. The second function is provided by acid sites, which lead to reactive carbenium ion intermediates. As carbenium chemistry is well known, its formalization in reaction recipes is straightforward. It turns out that the number of elementary reaction *families* to be considered and, hence, the number of kinetic parameters is relatively small. Still, the number of elementary reactions becomes huge for heavy crude oil cuts.

The author shows how the single-event methodology can be extrapolated to heavy cuts without generating the corresponding reaction network.

Finally, let me point your attention to volume 28 of Advances in Chemical Engineering on "Molecular Modeling and Theory in Chemical Engineering" published five years ago. Several chapters elaborate on the use of quantum chemical calculations to obtain thermochemical and kinetic data. This is the only reason why I opted not to include similar material in this volume. Clearly, *ab initio* computational techniques, or at least the results of the latter, should be part of the toolkit to obtain chemical engineering kinetics.

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