PREFACE

The cross fertilization of physico-chemical and mathematical ideas has a long historical tradition. A conference ''Mathematics in Chemical Kinetics and Engineering'' (MaCKiE-2007) was held in Houston, Texas in 2007 bringing together about 40 mathematicians, chemists and chemical engineers from 10 countries (Australia, Belgium, France, Germany, Sweden, Russia, Switzerland, Ukraine, the United Kingdom, and the United States) to discuss the application and development of mathematical tools in their respective fields. More attention was paid to biological applications at this conference than at the first conference at Ghent University (Belgium) in 2002. In order to make sure that the main messages of this conference would not be lost, it was decided to publish some of the important contributions in an archival journal. The series *Advances in Chemical Engineering* was considered to serve best this purpose, among other things because there would be no page limitations on the different contributions. Volume 34 of Advances in Chemical Engineering is therefore mainly dedicated to MaCKiE-2007.

The problem of dispersion of a solute in a flow through a small diameter channel, with or without adsorption or reaction at the wall, has stimulated a great deal of research since the classical work of G.I. Taylor in 1953. The popularity of this topic arises from at least two properties of the problem: it is a canonical version of technologically important flows (e.g. transport in a pipeline or porous medium), and it is amenable to analysis. Consequently, the Taylor dispersion problem is a good setting for the development and testing of *effective* (low dimensional) descriptions of multiscale phenomena. The contribution by C.J. van Duijn, A. Mikelic, I.S. Pop and C. Rosier, entitled ''Effective dispersion equations for reactive flows with dominant Peclet and Damkohler numbers'' discusses the use of anisotropic singular perturbation methods to obtain an effective equation for the solute concentration similar to what has been obtained before by other methods, but which also obtain a rigorous estimate of the error.

Non-linearity is one of the main problems of theoretical chemical kinetics.

The paper by M. Lazman and G. Yablonsky ''Overall Reaction Rate Equation of Single-Route Complex Catalytic Reaction in Terms of Hypergeometric Series'' presents a further development of the approach formulated by the authors in the early 1980s using contemporary algebraic methods. For a single-route catalytic reaction with a non-linear mechanism, the authors previously showed that under assumptions of the steady state or quasi-steady state the non-linear kinetic model corresponding to the complex mechanism can be transformed into just one algebraic equation, so called ''kinetic polynomial''(K.P.), that is an overall (steady state or quasi-steady state) rate equation. However, in contrast to traditional overall equations, in a general case the K.P. is not an explicit function of reaction conditions, $r = f(c, T)$, but an implicit function $F(r, c, T) = 0$. Many properties of the K.P. which are interesting from the physico-chemical point of view have been described before:

(a) K.P. may have several physically meaningful solutions (roots), and this fact can be used for understanding of the multiplicity of steady-states.
(b) A free term of the K.P. relates to the overall reaction, so despite the non-linearity under equilibrium conditions K.P. is transformed into a simple equilibrium relationship which does not depend on the details of the complex mechanism.

In this contribution the authors posed and solved a new problem: how to find an explicit reaction rate expression r at least for the thermodynamic branch of the K.P. Such rate equation was obtained in terms of hypergeometric series, "the four-term rate equation". The mentioned terms are following: (1) *the kinetic apparent coefficient*; (2) *the potential term* or *driving force* related to the thermodynamics of the overall reaction; (3) *the resistance term*, i.e. the denominator, which reflects the complexity of reaction, both its multistep character and its non-linearity; finally, (4) *the non-linear term* which is caused exclusively by non-linear steps. Known rate equations, such as Langmuir–Hinshelwood, Hougen–Watson and Horiuti–Boreskov ones, are particular cases of the presented "four-term equation". Distinguishing the fourth, "non-linear", term is the original result of this chapter. In classical theoretical kinetics of heterogeneous catalysis (Langmuir–Hinshelwood and Hougen–Watson equations, and equations for linear mechanisms), such term is absent.

Chemists have always tried to overcome the mathematical difficulties of analyzing detailed kinetic models introducing simplifying hypotheses such as a hypothesis on the existence of a single rate-limiting step. Reaction rate equations grounded on these assumptions found a wide area of practical application including situations far beyond the assumptions of the original theory. However the validity of the popular assumption on the limiting step is not trivial. In their contribution, "Dynamic and static limitation in multiscale reaction networks, revisited" A. N. Gorban and O. Radulescu analyzed the mathematical status of this classical hypothesis and found many non-trivial cases and misinterpretations as well. They rigorously studied differences between transient and steady-state (quasi-steady-state) regimes and classified different scenarios in chemical kinetics. Studying networks of linear reactions, the authors introduce the concept of the "dominant system", i.e. the system that produces the main asymptotic terms of the steady-state and relaxation in the limit when rate constants are well separated, i.e. of clear separation of time scales. In the simplest case, the dominant system is determined by the ordering of the rate constants. For distinguishing dominant systems of complex networks, a special mathematical technique was developed. It is defined as a "surgery of cycles", because its main operations are gluing and cutting cycles in graphs of auxiliary discrete dynamic systems. The interesting fact is that the limiting step for relaxation of complex chemical reaction is not the slowest reaction, nor the second slowest reaction in the hierarchy of the full spectrum of kinetic constants, but the slowest reaction of the dominant system. Moreover, the limiting step constant is not obligatory a reaction rate constant of the initial system. It can be represented by a function (monomial) of kinetic constants as well. The obtained results are illustrated by concrete examples of complex mechanisms. Computationally, the proposed methods are quite cheap. It is worth mentioning that the concept of ''dominant systems'' goes back to classical ideas proposed by Newton.

The last contribution to this volume ''Multiscale theorems'' by L. Wang, M. Xu and X. Wei is exceptional in two ways. It does not correspond to a contribution to MaCKiE-2007 and it is longer. It comes from the Department of Mechanical Engineering of the University of Hong Kong and provides a comprehensive overview of the mathematical foundations of multiscale modeling. This overview extends way beyond the ''classics'' of multiscale theorems such as the Gauss divergence theorem, the Reynolds transport theorem and the Leibnitz rule. The authors not only present but prove a selected set of 71 (!) mathematical theorems. They emphasise the role of so-called indicator functions. These are an extension of Heaviside step functions and can be used to identify a region of interest by taking the value of one in the interior and zero exterior to the region. In this way they allow to transform line, surface and volume integrals into integrals over all space while they and/or their derivatives are appearing in the integrand. In doing so, ''the indicator functions are mathematical catalysts: they facilitate the derivations but do not appear in the end product.'' It is their strong belief that ''without detailed proofs, users have little structured access to the physics, application conditions and the ways of improving the theorems'' and little chances to address successfully what they consider to be the key questions to develop a good scaling approach: ''(1) When is simple aggregation (i.e. linear addition of elements) sufficiently accurate for upscaling? (2) Are processes which are observed or models which are formulated, at points or small spatial scales transferable to larger scales? (3) Where such scaling is possible, how should it be done? (4) How do these means change with scale? (5) How does the variability change with scale? (6) How does the sensitivity change with scale? (7) Under what circumstances would non-linear responses be either amplified or dampened as scales change? (8) How does heterogeneity change with scale? (9) How does predictability change with space and time scales? (10) What types of conceptual errors are involved, wittingly or unwittingly, by scientists in their up- or downscaling assumptions? and (11) How can observations made at two scales be reconciled?'' Applications in the fields of modeling of single-phase turbulent flow, heat conduction in two-phase systems and transport in porous and multiphase systems are discussed.

Of course the axiom of separability of length scales, more precisely of the molecular scale, the microscale, the macroscale and the megascale, is taken as the starting point. The molecular scale is characterized by the mean free path between molecular collisions, the microscale by the smallest scale at which the laws of continuum mechanics apply, the macroscale by the smallest scale at which a set of averaged properties of concern can be defined and the megascale by the length scale corresponding to the domain of interest.

Certainly, the rigorous mathematical nature of this contribution may deter part of the readership. It is our conviction, however, that it will become a reference text for those active in the field of multiscale modeling. It provides the foundations for techniques such as mathematical homogenization, mixture and hybrid mixture theory, spatial averaging, filtering techniques, moment methods, central limit or Martingale methods, stochastic-convective approaches, projection operators, renormalization group techniques, variational approaches, space transformation methods, continuous time random walks, Eulerian and Lagrangian perturbation schemes, heterogeneous multiscale methods, serial methods, onion-type hybrid methods, coarse-graining methods, multigrid-type hybrid methods, parallel approaches, dynamic methods and concurrent methods.

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