MATHEMATICAL MODELLING OF CHEMICAL PROCESSES

RABINOVICH

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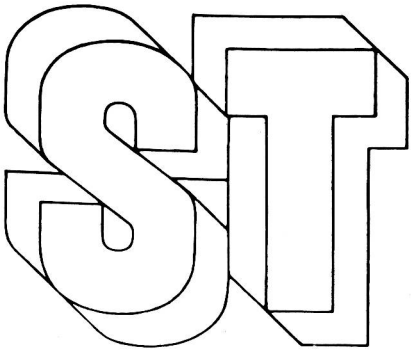

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PREFACE

This collected volume is concerned with problems arising in mathematical modelling of chemical processes, in particular, catalytic and electrochemical processes as well as polymerization, separation, heat and mass transfer.

Contributors to this book are competent Soviet specialists professionally engaged in this field which, during the last decades, has taken a firm stand in the foreground of scientific and technological research. The issues considered reflect the conceptual ideas of mathematical modelling at different hierarchical levels, starting from studies of chemical kinetic and macrokinetic relationships, including elementary steps of hydrodynamics and transport processes, via model construction of separate reactors or apparatuses, and ultimately ending in modelling and optimization of complex chemical engineering schemes.

Despite seemingly different nature of the objects of study, a common feature of the adopted approaches has been the use of experimental physicochemical data as the basis for constructing a model, as well as the application of advanced analytical and numerical methods to process modelling.

An exceptionally important aspect of modelling, along with the study of major features of a chemical process, is the upgrading of operative commercial technologies, including the development of process intensification methods and the design of innovative high-efficient technologies, especially those aimed at energy- and material saving.

The opening paper by G.M. Ostrovsky, A.G. Zyskin, and Yu.S. Snagovsky considers a number of problems concerned with the software and mathematical support of comprehensive studies on kinetics of complex heterogeneous catalytic reactions. Dedicated program complexes are described that have been developed to make computer-aided kinetic computations more effective. To this effect, the System for Automatization of Kinetic Computations (SAKC), including a kinetic rate computation program for multi-step mechanisms, has been developed. A rigorous analysis of the dynamics of complex chemical reactions with nonideal kinetics for closed systems has been carried out; also, conditions for uniqueness and stability of a chemical equilibrium in systems of different type have been examined.

The paper by E.B. Brun and V.A. Kaminsky is concerned with problems specific of polymerization modelling. Major issues dealt with in this paper

are the physical fundamentals of the theory of free-radical homo- and copolymerization and the current aspects of the theory of diffusion-controlled reactions in polymer solutions as applied to free-radical polymerization. A number of new problems related to mathematical modelling of polymerization in heterogeneous systems, in particular, emulsion and suspension systems, have been considered. Specific features of free-radical polymerization regimes have been analyzed from the standpoint of the theory of combustion and thermal explosion. Within the framework of an ultimate model for multicomponent copolymerization, a quantitative theory has been developed enabling prognostication of the properties of copolymers produced at high monomer conversions.

The paper of A.B. Goldberg and L.I. Kheifets deals with major steps in mathematical modelling of electrolytic cells within the framework of an hierarchical approach. A special emphasis has been put on the charge transfer kinetics and on the problems arising in situations that have no analogues in nonelectrolytic systems. Referring to such situations, one should mention the electric potential distribution in solutions of varied composition; the relation between hydrodynamic factors and current density distribution, magneto- and hydrodynamic effects. The data thus obtained have been used for calculation of the volt-ampere reactor characteristics, for optimal design of electrolyzer bus arrangement, also for estimating the current efficiency for formation of target products, and for handling other problems arising in electrolysis technology. A special merit of this paper is an unconventional approach to constructing the mathematical model of a chlorine solid-cathode electrolyzer.

The paper by L.M. Rabinovich focuses on the theory of self-organization phenomena as applied to the surface tension instability at the liquid-liquid or gas-liquid interface in heterophase systems with mass transfer and chemical reactions. This paper summarizes original results on hydrodynamics of interfaces and mathematical modelling of mass transfer attended by Marangoni convection. Potential utility of the developed methods for intensification of solvent extraction and gas absorption using novel technologies based on interfacial instability is also discussed.

The main issue of the paper by V. M. Platonov and coauthors is the problem of synthesis of energy-saving systems for multicomponent distillation and its solution within a hierarchical-system approach. A structural-analysis method, based on the concept of conjugate singular points of the initial vapour-liquid simplex has been developed. Of special interest is the minimum-reflux theory that has been worked out for a separate column section in a manner enabling

its extension to a distillation scheme of arbitrary configuration. This approach allows synthesizing energy-saving schemes for distillation of pseudoideal mixtures in levelling such an essential parameter as the number of theoretical plates at separation stages.

Finally, the concluding paper by G.M. Ostrovsky, Yu.M. Volin, and T.A. Berezhinsky considers various formulations and approaches to the problem of optimization of chemical engineering systems, including issues concerned with synthesis, global optimization and multiobjective optimization under the conditions of partial uncertainty of the input data and model parameters. The authors have also considered a continuous optimization approach and situations where certain variables can take only discrete values.

The limited space of the book has precluded the presentation of other papers on the mathematical modelling of chemical processes that might with certainty find their interested readers. We entertain a hope that the materials collected in this volume will be useful for both scientific researchers and practical engineers and can give a clearer idea of the current achievements of Soviet specialists in certain areas of chemical engineering science.

This book is primarily intended for chemical engineering scientists; still, we feel that the presented material may prove to be useful also for practical chemical engineers, mathematicians, physicists and post-graduate students interested in applied problems of chemistry.

L. M. Rabinovich

1 Design and Analysis of Kinetic Models for Heterogeneous Catalytic Reactions

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1.1 Introduction

The construction of kinetic models for heterogeneous catalytic reactions (HCR) is an essential stage in computer-aided design and optimization of reactors and processes of chemical engineering.

The kinetic model [1, 2] is defined as a family of equations that describe the rates of sequential chemical and physical steps through which the initial reactants and intermediates are converted to end products. The kinetic model is also presumed to take into account effects arising from the eventual change in the catalyst state at different reaction steps.

The kinetic model, derived from an analysis of process mechanism, experimental reaction rates, and the fundamental laws of chemistry, constitutes the basis for designing reactors and specifying critical conditions, stability regions, and other performance characteristics of the process.

Two kinds of problems emerge in the mathematical and computer-assisted treatment of kinetic models: (i) development of software facilities for kinetic computations; (ii) theoretical analysis of mathematical models chosen for a given kinetic model. These problems may arise in the analysis of HCR carried out under both steady-state and dynamic conditions. The authors wish to present in this paper certain results relevant to the aforementioned problems.

Sections 1.2-1.4 are concerned with computational algorithms and automation of programming in a computerized study of steady-state regimes of complex HCR. Commonly, the final target is to obtain rate equations, that is, expressions for reaction rates as a function of partial pressure, temperature, and kinetic parameters. Rate equations can be derived in an explicit form only for linear reaction mechanisms, that is, those in which each elementary reaction involves a single intermediate particle. For nonlinear mechanisms, in the general case, only a computational algorithm for reaction rates can be developed. Next, a program for computing the reaction rates and their derivatives with respect to kinetic parameters is to be designed and debugged. The derivatives are used in the search for kinetic parameters, in statistical analysis and

kinetic experiment planning. The design and debugging of such programs performed "manually" is a laborious and time-consuming procedure. An essential point is that, if a computer is made use of, the computations should be carried out rationally, that is, the computational algorithm and designed programs must provide for a minimal expenditure of computer time.

The problem of deriving the rate equations for linear mechanisms was dealt with in [3, 4]. In [5] a program was described for deriving the rate equations for HCR linear mechanisms on the basis of a structured form of rate equations expressed in terms of reaction mechanism graph.

We have succeeded in solving completely a problem of computer-assisted programming for reaction rates and their exact derivatives with no restrictions imposed on the reaction mechanism. To accomplish this objective, a number of theoretical postulates for complex steady-state reactions have been formalized enabling one to develop the appropriate mathematical apparatus and program complexes realizable within the System for Automation of Kinetic Computations (SAKC). A version of SAKC, designed on the basis of the operating system (OS) for IBM- or EC-type computers, has been described in detail elsewhere [6-9] et al. Therefore, in Section 2, we have confined ourselves to a brief description of the function and structure of SAKC. In Sections 1.3 and 1.4, a description is given of newly-designed SAKC software facilities: a syntactic analysis (SYA) program package and programs for deriving the rate equations for linear mechanisms and steady-state equation system for nonlinear mechanisms in character form on the basis of REDUCE-2 computer language. We are unaware of reports concerned with automated programming methods for kinetic computations at a sufficiently high level of sophistication.

Section 1.5 is concerned with the development of a nonlocal method for solution of nonlinear equation systems. The program designed on the basis of this method permits exploration of the multiplicity of steady-state HCRs, which is essential for the analysis of their regimes—both stationary and dynamic.

The dynamic properties of complex reactions carried out in closed nongradient systems are discussed in Sections 1.6-1.9. The dynamics of complex chemical reactions in closed and open nongradient systems has been under intense study for over two last decades. Major results, achieved in this field, have been outlined in monographs [10-13]. The most spectacular achievements bearing upon the uniqueness and types of steady state, stability and existence of Lyapunov functions in HCR mechanisms have been signalled for closed systems. The authors of this paper were the first to explore the dynamics of

complex HCR within the framework of generalized, correctly defined kinetic laws, with allowance made for nonideality of the adsorption layer [14-17]. The relevant results are given in Sec. 1.6.

Presented in Secs. 7 and 8 are the results of studies on the mode of approach of a system to equilibrium [18] and on the conditions providing for the stability of equilibrium in a closed system [19]. A specific feature of the adopted approach is that the reported results have been obtained for arbitrary chemical systems without specifying the kinetic law, but through applying strict mathematical methods to general thermodynamic relations. Finally, in Sec. 1.9, a nonideal HCR exhibiting a complex dynamic behaviour in a closed system has been exemplified.

As has already been mentioned, the dynamics of closed chemical systems is at present well understood, and major properties of such systems have been characterized and formulated. However, there remain a number of problems that await further consideration. These will be dealt with below, each in the context of appropriate sections of the book.

1.2 Function and Structure of SAKC

In what follows, we understand by the study of steady-state HCR regimes the choice of a reaction mechanism that would provide for the best agreement with the available experimental data and would enable determination of respective kinetic parameters. The adopted approach may be divided into the following stages.

Stage 1. A hypothetical mechanism is advanced for the process in question. This is understood as the devising of a set of reaction steps constitutive of the mechanism, and the specification of both types for catalyst surface and for adsorption of intermediate species (single-site adsorption or multiple-site adsorption) on the catalyst surface. The mechanism, thus accepted, enables deriving expressions for the rates of elementary reactions.

Stage 2. Expressions for reaction rates of key species (rate equations) are derived, preferably within the framework of a steady-state reaction theory [20-24]. The reaction rates and the steady-state system for reaction steps may be written as

$$\mathbf{r}(\mathbf{x}, \theta, \mathbf{z}) = B_1^{\mathrm{T}}\mathbf{u}(\mathbf{x}, \theta, \mathbf{z}) \tag{1}$$

$$B_2^{\mathrm{T}}\mathbf{u}(\mathbf{x}, \theta, \mathbf{z}) = 0 \tag{2}$$

where $\mathbf{r}$ is the reactant rate vector; $\mathbf{u}$ is the reaction step rate vector; $\mathbf{x}$ is the experimental condition vector; $\mathbf{z}$ is the concentration vector for a reaction in-

termediate expressed in fractions of occupied surface area (surface coverage); θ is the kinetic parameter vector; B_1 is the stoichiometric submatrix for the reactants (initial and end products); and B_2 is the stoichiometric submatrix for the reaction intermediates. The rates $\mathbf{r}$ are obtained—either in an explicit form, or as computed values—from Eq. (1) by substituting the expression for $\mathbf{z}$ defined by Eq. (2).

Stage 3. At this stage, the kinetic parameters are derived and the agreement between computational and experimental rates is estimated. This procedure is carried out by minimizing a function S chosen as optimization criterion with respect to its parameter θ, for example:

$$S = \sum_{n=1}^{N} \sum_{p=1}^{N_1} W_{np}[\omega_i r_{np} - r_p(\mathbf{x}_n, \theta)]^2 \tag{3}$$

where r_{np} is the experimental pth reaction rate in the nth experiment; r_p is the computed reaction rate; W_{np} is the weight factor; ω_i is the catalyst activity correction factor (to be determined); N is the number of experiments performed; N_1 is the number of elementary reactions (respectively, reaction rates); and $\mathbf{x}_n$ is the experimental condition vector for the nth experiment.

The S function having been minimized, the subsequent procedure comprises a comparison of experimental and computational results (reaction orders, selectivity, inhibition by end products, etc.) and a statistical analysis of the derived kinetic parameters.

Also, compared among themselves are the data computed within the framework of feasible hypotheses. The results thus obtained enable one either to suggest the most probable reaction mechanism, or to outline further research program, especially if more than one of the hypotheses tested have been found to compare well with the experimental evidence.

The origination of data for computer-aided solution of a problem includes: (i) the construction of a system of steady-state equations (2); (ii) the development, if possible, of rate equations; (iii) the development, in an explicit form, of the derivatives of $\mathbf{r}$ and S with respect to θ and their programming, or the programming of computational algorithms for the derivatives.

This procedure is to be done for each of the reaction mechanisms. The development and programming of rate equations and their derivatives, if performed manually, are laborious and consume much time to obtain an acceptably representative set of mechanisms; in addition, human errors cannot be excluded. Our experience has shown that the preliminary work prior to minimization, if carried out manually for a 7-10 reaction step mechanism, requires weeks or even months of strenuous efforts.