

History of the Development of Mathematical Modeling of Catalytic Processes and Reactors

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Problems of industrial catalysis and chemical engineering often require one to solve systems of nonlinear ordinary and partial differential equations. In most cases, their analytical solutions are either difficult or impossible to obtain. Therefore, initially in Germany from 1925 and then in the United States, the similarity theory began to be developed. However, practical application of this theory led to errors in scale-up and, in Western countries, a system of pilot plants of gradually increasing scale was created for scale-up from laboratory studies to industrial conditions.

In our country, the first shoots of the modeling-based theory of chemical reactors emerged in design organizations of the chemical industry in the early 1930s. A number of chemical reactors and other apparatuses for the industries of production of sulfuric acid, nitrogen-containing substances, and synthetic rubber were designed and put into operation, in essence, on the basis of mathematical modeling in 1935–1940. For example for the Voskresensk Chemical Integrated Works, in 1937, the GIPROKhim Institute for Design of Plants for the Basic Chemical Industry designed an apparatus for the oxidation of SO_2 into SO_3 in the production of sulfuric acid by the contact process with adiabatic catalyst layers and intermediate cooling between the layers. The apparatus was designed by solving nonlinear differential equations by graphic and other approximate methods. The apparatus was put into operation without any difficulties. Its basic flowsheet has been the basis for all apparatuses for the production of sulfuric acid by the contact process to date in our country and all over the world.

The deep understanding of the essence of chemical engineering, high patriotism, and acute sense of duty of chemical engineers ensured that they rapidly solved the problems of designing new processes and equipment in the prewar and first postwar years. From experimental data through abstract thinking to models and, thereafter, to practice—this path favored acceleration of design and implementation of new catalytic processes and reactors.

In 1945–1946, a large number of chemical researchers and chemical engineers were sent to Germany to examine the chemical industry and control war repara-

tions. At chemical integrated works, engineers saw a great number of pilot plants of various scales. This had an adverse effect since design organizations began to follow the idea of multistep transition from laboratory-scale to industrial-scale equipment and higher educational institutions (especially the Lensovet Leningrad Technological Institute) cultivated the use of similarity theory. Highly qualified skilled specialists in the postwar period were redirected from solving current problems of the chemical industry to designing new technologies (heavy water production, safety of nuclear plants, isotope separation, etc.) by detailed calculations and direct scale-up without pilot plants. Otherwise, the tasks assigned in catalysis and in missile and nuclear technologies would not have been fulfilled within a short time.

The novelty of mathematical modeling of chemical engineering processes and chemical reactors in 1957–1960 consisted in the expansion of the possibilities of solving mathematical problems owing to the development of computers.

The first scientific basis for modeling was the computer MN-7, a vacuum-tube analog simulator, which could solve systems of nonlinear ordinary differential equations up to the sixth order. In 1958, V.B. Skomorokhov at the Institute of Catalysis, Siberian Division, USSR Academy of Sciences, using this computer modeled the exothermic heterogeneous catalytic reaction of ethylene oxidation to ethylene oxide. This was the world's first case of mathematical modeling of a catalytic process on a computer.

In 1961, a second, also vacuum-tube, analog computer, MN-14, modeled more complex processes, albeit using qualitatively the same methods for solving equations.

The first digital computer, M-20, was used in 1959 to model apparatuses for producing sulfuric acid by the contact process. M-20 was installed at the Institute of Mathematics, Siberian Division, USSR Academy of Sciences. This computer played a revolutionary role in modeling of catalytic processes.

However, the real breakthrough in methods of modeling and scientific analysis was caused by the creation of the ES EVM Unified Computer System, a complex

of third-generation integrated-circuit computers. In 1979, an attempt was also made to perform modeling on the GVS-100 hybrid computer system, designed in 1970 by the Institute of Control Problems, USSR Academy of Sciences, and the Mihajlo Pupin Institute, Belgrade, Yugoslavia. GVS-100 was used to solve several complex problems, e.g., modeling of the transfer processes in a polymer grain; GVS-100 was also online connected to an experimental setup for studying the local mass transfer from a particle to a liquid.

The development of mathematical modeling was very closely related to significant achievements in computational mathematics. The finite-difference method as an efficient technique for solving differential equations had been considerably developed. Previously, this method was fundamentally impossible for wide use to solve industrial catalysis problems because of the necessity of performing a large number of arithmetic operations. Differential equations were solved by converting to nonstationary problems, which were approximated by systems of finite-difference equations. In a one-dimensional case, implicit finite-difference schemes were solved by the sweep method and the running count method. For multidimensional problems, the split method (the fractional step method) was most efficient.

The first paper in the first number of the journal (*Teoreticheskie osnovy khimicheskoi tekhnologii*) [1] was written by me and G.K. Boreskov about the initial experience and basic principles of mathematical modeling of catalytic reactions, processes, and reactors on a computer. This paper briefly presents some results of the development of mathematical modeling of catalytic systems in the past years at the Institute of Catalysis and the Karpov Institute of Physical Chemistry. Since then, this journal has systematically informed readers of the development of mathematical modeling of catalytic reactions, processes, and reactors [2–14].

In 1958 in Western Europe, the European Symposium on Chemical Reaction Engineering (ISCRE) began to be held, which actually became a symposium on mathematical modeling of chemical engineering processes. I and G.K. Boreskov presented lectures at the second (Netherlands, 1960) and third (United Kingdom, 1964) symposia [15, 16]. Later, these symposia became international and were held every two years in various countries.

STRUCTURE OF MATHEMATICAL MODELS

In 1946, a plant for heavy water production by multistage electrolysis in combination with catalytic isotope exchange of deuterium between hydrogen and water vapor was very rapidly designed by mathematical modeling. Heavy water production was difficult to design because of the low (~0.015 at %) deuterium content of natural water, because of which, in the early stages of the process, it was necessary to process 10–100 m³ of feed water per liter of heavy water pro-

duced and construct a multistage cascade from separating elements of complex structure. The mathematical model of the isotope separation process was based on the idea of structural levels [17]. At the first, molecular, level, thermodynamic and kinetic problems were solved; at the second, catalyst-grain, level, kinetic equations taking into account diffusion processes were determined; at the third level, the structure of a separating element was determined; and at the fourth, the optimal cascade was calculated. The interdependence and interrelationship of these levels characterized the integrity and specificity of the catalytic separation process. This approach was later developed and used in modeling chemical reactors [18]. Chemical reactors are quite diverse and used in many industries. However, they have many common features. Their models have a spatiotemporal hierarchical structure. One can distinguish six main hierarchical levels: the quantum-chemical level, nanolevel (<100 nm), microlevel (<1 mm), mesolevel (<10 cm (particles, drops, bubbles, grains)), macrolevel (10 cm–10 m (apparatus)), and megalevel (environment, plant, integrated works). The scale of chemical systems ranges from 10⁻⁸ to 10⁶ m, and its associated time scale ranges from 10⁻¹⁵ to 10⁸ s.

At the present time, it is impossible to begin mathematical modeling with the quantum level; therefore, modeling of catalytic systems is started with the atomic-molecular level. Necessary information obtained by quantum-chemical calculations can be taken into account. The atomic-molecular level is of great importance in solving catalysis problems. This level determines the catalyst selectivity, the catalyst activity, and features of the catalytic process at the next scale levels. Modeling at the atomic-molecular level is necessary to understand the process and ensures its modeling at the meso- and macrolevels with correct (usually nonlinear) expressions for the dependences of the chemical reaction rate on the composition of the reaction mixture, the properties of the reaction surface, temperature, and the heat- and mass-transfer coefficients. Kinetic equations describe the macroscopic properties of the catalytic system in terms of molecular-kinetic concepts and underlie mathematical modeling.

Representing a catalytic system (reactor) as a spatiotemporal structure, one can

study a complex catalytic process separately by applying special investigation methods to individual parts;

reveal and understand the relationship and mutual effect of partial processes and determine their role in the entire catalytic process;

explore the effect of the mass, heat, momentum, and charge transfer on the catalytic transformation rate;

find the optimal solutions for catalytic reactions, processes, and reactors sequentially at all the structural scale levels;

solve the problem of scale-up from the results of laboratory studies to industrial conditions; and

more completely use the knowledge and experience of modeling of various reactors and establish analogies and common features of industrial catalytic reactors.

Multilevel investigation of catalytic processes required the creation of a group of like-minded specialists in many areas. To reduce the research time, the group simultaneously, if possible, involved physical chemists, physicists, mathematicians, computer specialists, and specialists in application of physical methods for studying catalysts. The interdisciplinary approach and collective intellect favored achieving high-quality results and improving the understanding of a catalytic process.

The basic principles of the functioning of the Siberian Division of the USSR Academy of Sciences of the—the development of the natural sciences and humanities on the basis of physical and mathematical knowledge in unity with practice, solution of large scientific and technical problems and the accord of scientists of different generations, and integration of science and education—all this created particularly favorable conditions for the development of mathematical chemistry.

The chemical industry of our country from the first steps of the development of the national economy grew at an advanced pace. This growth became particularly intense in 1960. The advanced development of the chemical industry increased the fraction of the product of this industry from 3.7% in 1960 to 6.8% in 1990. The creation of process lines, reactors, and high-capacity apparatuses was the main direction of the development of the chemical industry. An increase in reactor capacity involves certain difficulties, e.g., higher nonuniformity of mixing and distribution of flows, more complex design of apparatuses, longer dynamic (start up, transient) modes, more rigorous requirements for equipment safety, and more complex treatment of industrial waste. Design and departmental institutes of the USSR Ministry of Chemical Industry using mathematical and aerodynamic modeling surmounted many of these difficulties and designed and implemented new high-output equipment of increased unit capacity for ammonia production of 400000 t/year, sulfuric acid production from sulfur of 450000 t/year, ammonium nitrate production of 450000 t/year, and others. Such equipment of increased unit capacity enabled the country to significantly increase labor productivity and decrease the capital intensity and the cost of the product.

MATHEMATICAL FOUNDATIONS

In heterogeneous catalysis, the catalytic activity of the surface is caused by a large number of interacting atoms of adsorbed substances and the catalyst. A thin layer of these atoms is an open nonequilibrium nonideal nonlinear multiparametric multidimensional system exchanging matter and energy with both the gas

and solid phases. Mathematical models generally consist of systems of nonlinear algebraic equations and/or ordinary and partial differential equations.

The main feature of kinetic, physicochemical, and chemical engineering systems is nonlinearity, when the superposition principle is invalid and a direct analytical solution is unknown. In nonlinear systems, changes may often have a threshold character: with a gradual change in external conditions, the characteristics of a catalytic system may change in a stepwise manner. These phenomena, which are consequences of deviation from linearity, present significant difficulties in predicting the behavior of catalytic systems.

By the early 1960s, there was no satisfactory qualitative theory of nonlinear systems of differential equations with distributed parameters. Therefore, the problems of the qualitative theory of evolutionary partial differential equations began to be systematically studied. Researcher T.I. Zelenyak and his disciples at the Institute of Mathematics studied general stationary and dynamic problems for nonlinear parabolic and hyperbolic systems [7, 12, 19–21]. The stabilization conditions for unsteady solutions were determined, the stability of steady solutions was studied, the conditions for the emergence of self-oscillations of reaction rate were found, and the regions of attraction of steady solutions were characterized.

Methods of qualitative theory allowed researches to study the properties of solutions without finding the solutions themselves. Using these methods, the asymptotic behavior of solutions of evolutionary problems, the structure of limit sets, and the character of approach of trajectories to these sets were investigated. Methods of the theory of bifurcations and branching of solutions of nonlinear equations were used to explore the dependence of solutions on parameters. The results of investigations were represented as the phase and parametric portraits of a catalytic system.

The power of qualitative methods for analyzing mathematical models consists in the depth and generality of mathematical ideas. Bifurcation analysis of mathematical models of catalytic systems is of both theoretical and practical interest. It provides a much wider understanding of processes than classical approaches do. A distinguishing feature of bifurcation analysis is the consideration of all possible solutions at all possible parameters. Therefore, the results of the analysis enable one to not only explain but also predict the behavior of catalytic systems.

Kinetics and catalysis belong to exact natural sciences; however, qualitative reasoning, phase portraits, and approximate relations play a significant role; sometimes, qualitative reasoning is even more necessary because it favors the understanding of catalytic phenomena as a whole and is further followed by quantitative description. In quantitative studies, a special part is played by the simplest limiting cases allowing analytical solution.

The results of natural experiment, equations of a mathematical model, and their qualitative analysis still do not ensure success of catalytic studies. It is necessary to develop constructive algorithms for solving specific mathematical problems since software allows one to proceed from one-dimensional models to more complex two- and three-dimensional ones.

Numerical algorithms for solving nonlinear mathematical problems that are implemented as problem-oriented program complexes can give quantitative results. Therefore, of great importance for catalysis and chemical engineering is computational mathematics, which studies methods for obtaining solutions of various mathematical problems in the form of a numerical result. The numerical result is obtained on a computer using arithmetic and logical actions in the form of a sequence of operations, i.e., a solution algorithm. For practical application of an algorithm, its efficiency is important. On the basis of an algorithm of a problem, a program is written in a computer language. The methodology of mathematical modeling on the basis of the model–algorithm–program triad was successfully developed in our country by Academician A.A. Samar-skii [22].

Of prime importance for process engineers is software for mathematical modeling of chemical engineering and catalytic processes since its use allows one, on the one hand, to significantly reduce expenses and time for design and, on the other, to correctly generalize and apply the experience of operation of existing plants in the search for optimal and reliable solutions. Simultaneously, the quality of design solutions is increased because software allows one to pass to more complex two- and three-dimensional models.

An important step of mathematical modeling is the determination of the optimal conditions of a catalytic process. Process optimization studies were begun by design organizations in the prewar years. It was found that, for reversible reactions (oxidation of SO_2 into SO_3 , ammonia synthesis, etc.), to each degree of conversion, an optimal temperature corresponds. For exothermic reversible reactions, the optimal temperature decreases with an increase in the degree of conversion. In 1935, a graphical method for calculating the contact time was developed, which enables one to easily find the optimal temperature. If the inverse of the reaction rate is plotted on the abscissa and the degree of conversion is plotted on the ordinate, then the optimal conditions for exothermic reactions are given by the envelope of the family of exothermic curves.

The optimal mode of a process is expediently determined in two steps. At the first step, which is called theoretical optimization, the best conditions are found, ignoring their feasibility. This theoretical optimal mode is often sought under the condition of the maximal process intensity at a given yield of a desired product. The problems of determining the minimal contact time at a given degree of conversion and seeking a maximum of

the degree of conversion at a given contact time are solved using a kinetic model. At the second step, a reactor is chosen so that its operating conditions best approach the previously determined mode. An objective criterion for choosing the reactor design appears.

The development and implementation of mathematical modeling required the development of mathematical methods of optimization. The use of classical methods of differential and integral calculus and calculus of variations encountered significant difficulties caused by restrictions imposed on control variables. American scientist R. Aris widely applied a dynamic programming method, especially to multistep processes. The main idea of the dynamic programming method is the fact that, whatever the first solution, the other solutions should be optimal with respect to the result of the first solution. The experience of using the dynamic programming method showed that it can be successfully used to solve problems of determining the optimal conditions of multistep processes consisting of one or two reactions. However, if the process in a reactor is described by a system of equations of order $n \geq 3$, the use of the dynamic programming method meets considerable difficulties. This may require a very large capacity of computer memory.

From the first days of mathematical modeling of catalytic processes at the Institute of Catalysis, the maximum principle has been used. In 1964, at the Third European Symposium on Chemical Reaction Engineering, in the United Kingdom, I and G.K. Boreskov presented a lecture on the application of the maximum principle method to optimizing catalytic processes [16]. The maximum principle method consists in solving a boundary-value problem for a set of ordinary differential equations and determining the optimal control at each integration step, provided that a certain function is maximal [23]. On the basis of this method, it is possible to formulate a general approach to solving problems of stationary and nonstationary catalytic processes. The maximum principle allows one to take into account restrictions on the range of parameters and to find an optimum if it is reached at the boundaries of the range.

NONLINEAR DYNAMICS

Nonlinear dynamics is the branch of physics and mathematics that studies dynamic systems in which processes do not satisfy the superposition principle. Mathematical models of such systems comprise nonlinear equations of mathematical physics. The special place of nonlinear dynamics is determined by the generality of laws regardless of the specific nature of a system. A unified approach to investigating nonlinear dynamic systems enables one to separate base models, general concepts, and definitions and to develop mathematical ideas, approaches, and mathematical tools for analysis and modeling. The principles of an interdisciplinary approach to nonlinear dynamics were formu-

lated by Academicians L.I. Mandel'shtam and A.A. Andronov and their disciples at the Faculty of Physics, Moscow State University, in the late 1920s and the 1930s on the basis of works by H. Poincaré, A.M. Lyapunov, and Sir J.W. Strutt (Lord Rayleigh) in the creation of the theory of oscillations and waves.

Among nonlinear phenomena in catalysis are the multiplicity of steady states, their stability and instability, isolated states, self-oscillations and reaction rate waves (which may have a great variety of shapes, from near-sinusoidal to chaotic), their synchronization in interaction, and self-organized criticality of a process.

Among nonlinear phenomena are also processes of self-organization—the formation of spatial inhomogeneities (structures) in systems consisting of a large number of elements (atoms, molecules) and their evolution in time.

Nonlinear phenomena in chemical kinetics, catalytic processes, and reactors were discussed at all conferences on chemical reactors beginning from 1963. However, nonlinear dynamics in catalysis did not begin to be developed until P. Hugo and N. Jakubith discovered self-oscillations of the rate of CO oxidation on a platinum catalyst in 1972–1973 and, simultaneously, V.D. Belyaev and M.M. Slin'ko detected self-oscillations of the rate of hydrogen interaction with oxygen on a nickel catalyst at the Institute of Catalysis [24–36].

The theory of oscillations, particularly, the theory of nonlinear oscillations, and its ideology and methodology constitute one of the main components of the interdisciplinary approach of nonlinear dynamics.

The detection and recognition of the existence of regular, quasi-periodic, and chaotic oscillations from random sources became a scientific discovery in heterogeneous catalysis. Deterministic chaos of the reaction rate is characterized by an unrepeated irregular random sequence of state. This chaos is called deterministic because the characteristic behavior arises from the completely deterministic law of evolution of a catalytic system. Such states are also called chemical turbulence. Regular self-oscillations—a chemical clock—are a surprising coordinated change in the concentrations of adsorbed particles. Coupling, coherence, synchronization emerge, but only under highly nonequilibrium conditions. A still stronger intellectual effect was produced by chaotic self-oscillations. This led toward a probabilistic description of deterministic chaos and toward strange attractors. It turned out that all states become locally unstable in the sense of Lyapunov. Probability theory is closely related to the theory of unstable dynamic systems.

Instability is the cause of chemical turbulence. The formation of various structures on the catalyst surface is primarily a consequence of the emergence of instabilities and their further development. Therefore, it is necessary to promptly develop the mathematical theory of the dynamics of nonlinear and unstable catalytic systems (reactions, processes, reactors). In unstable sys-

tems, along with the dynamics of the physicochemical process occurring, of importance is also to specify initial values, which are information on the system. To proceed from one stable state to another and from one attraction region to another, detailed information on the phase portrait is important; i.e., it is necessary to have information on the physicochemical system.

Thus, any system consists of a dynamic part and an information part and the dynamic behavior of the system depends on the information properties [37, 38].

As already noted, in the nonlinear dynamics of catalytic systems, a significant place is occupied by self-organization theory, in which order parameters are separated and regarded as main parameters and the other parameters are considered subordinate parameters [35, 36]. A catalytic system becomes self-organizing if it acquires a certain spatial, temporal, and/or functional structure without specific external action. Spatially inhomogeneous steady states (structures) are determined by nontrivial solutions of a system of partial differential equations describing the catalytic system. Spatial structures at the micro- and nanolevels were detected by V. Gorodetskii at the Institute of Catalysis in the systems $\text{NO} + \text{H}_2/\text{Pt}(100)$, $\text{CO} + \text{O}_2/\text{Pd}(110)$, $\text{CO} + \text{O}_2/\text{Pt}(110)$, etc. [39, 40].

In nonlinear dynamics, complete understanding means the ability to construct a mathematical model of a catalytic process. However, predictability is not always reached. There are regions of parameters of a catalytic process and reactor (e.g., with a fluidized catalyst bed) in which the reality is too complex. In such a parameter region, the dynamic description should be replaced by probabilistic or game-theoretic models. A promising method is neural networks [41]. In this case, a model is neither an equation, nor an algorithm for numerically solving an equation, but a neural network trained to solve this problem. In cases where partial differential equations are impossible to write, it is expedient to use the theory of cellular automata in a discrete language. Cellular automata for solving problems of chemical kinetics have been constructed. The drawback of such an approach is that a qualitative theory is currently absent.

Self-organized criticality is a nonlinear phenomenon in which small deviations from a steady state of a catalytic system may lead to failure. Self-organized criticality arises and develops in the course of the evolution of the nonlinear system. During this, a large number of self-developing causes of deviation from the stable mode emerge and lead to an avalanche-like disturbance of the mode as a result of a small perturbation. This disturbance develops according to its own intrinsic laws, regardless of external control. A branching process of the type of chain reaction occurs, and the catalytic system by itself evolves to critical conditions leading to failure. An example can be a tubular reactor for producing ethylene oxide from ethylene–oxygen mixtures on silver catalysts [42]. In a normal mode, the

concentration of the promoter dichloroethane in the gas mixture is approximately 3 ppm. With a decrease in the promoter concentration, the ethylene oxidation selectivity decreases and the heat release increases and leads to a further increase in temperature. The process becomes controlled by internal diffusion, which further decreases the selectivity and enhances the heat release. This may lead to reactor failures [42].

Self-organized criticality may arise in multiphase catalytic systems near bifurcation points under the action of flicker noise if the distribution of the temporal characteristics of the process is a power-law function.

EXPERIMENTAL PROCEDURE

The basis for the methodology of constructing mathematical models is the optimal combination of natural and computational experiments, which gives sufficiently deep insight into the catalytic process mechanism [43, 44]. The structure of the methodology of the combination of natural and computational experiments is a sequence of cycles in which, after each next cycle, the solution of the problem to be solved is approached. A cycle is begun with preliminarily constructing a model on the basis of all known information on the problem. Then, algorithms and programs are developed and the mathematical model is analyzed. Based on the results obtained, experimental studies are planned and only then is the experiment started. During the natural and computational experiments on an automated scientific research system, a system of kinetic and mathematical models is developed to take into account physical and physicochemical factors in more or less detail and determine the applicability ranges of models at each level of description.

The computational experiment involves an interdisciplinary approach to studying a catalytic process. The combination and balanced use of all known investigation methods, including methods for processing and interpreting the data of a natural experiment, and the theoretical concepts and methods of modern calculus and programming significantly increase the investigation efficiency.

Note that, because of nonlinear phenomena far from thermodynamic equilibrium, the reaction kinetics near and far from equilibrium may differ. Therefore, the reaction kinetics should be studied throughout the range of concentrations, temperature, and other parameters under both steady-state and unsteady-state conditions.

ATOMIC–MOLECULAR LEVEL

Mathematical modeling at the atomic–molecular and nanolevels is necessary to describe the nonlinear dependence of the chemical transformation rate on the

composition of the reaction mixture at the meso- and macrolevels.

Mathematical modeling at the micro- and mesolevels was performed at the Karpov Institute of Physical Chemistry together with the Faculty of Computational Mathematics and Cybernetics, Moscow State University, under the supervision of Academician . Samarskii [45]. A group of mathematicians was created and has worked successfully to date [46–53]. The work of this group formed the basis for mathematical modeling of the dynamics of heterogeneous catalytic reactions in a nonideal adsorbate layer on the surface of noble-metal single crystals. The modeling was based on the concept of a nonideal lattice gas. Lattice models use a regular lattice consisting of nodes on a plane. Each lattice node can be in one and only one of the possible states. One of the characteristics of the nonideal layer of adsorbed particles is the energy of pairwise lateral interaction between particles at neighboring nodes. This parameter is found experimentally from the thermal reaction and thermal desorption spectra and by other methods. The evolution of the reaction system is considered a Markov process for a stream of elementary events. One of the methods for representing the evolution of a lattice system is mathematical simulation. Using distributed models, nonlinear phenomena at the micro- and mesolevels were simulated. In particular, regular and chaotic oscillations in CO oxidation on a palladium zeolite catalyst were described and their fine structure was detected. A complex of programs was developed to perform the nonlinear analysis of heterogeneous catalytic reactions at the micro- and mesolevels, including time series, whose analysis reveals chaotic states.

Further studies should be aimed at creating a system of internally consistent mathematical models describing the transitions from the atomic–molecular and nanolevels to the mesolevel and at understanding the phenomena observed in experiments. One of the main difficulties in creating the theory is the necessity of describing the complex dynamics on a solid catalyst surface far from thermodynamic equilibrium. It is necessary to create a hierarchical system of deterministic and stochastic models and efficient methods for qualitative and quantitative analysis of these models.

CONTINUOUS STIRRED TANK REACTOR

Early in the investigations for mathematical modeling of catalytic processes and reactors, much effort was made to study nonlinear phenomena in a continuous stirred tank reactor. The main features of such a reactor are the absence of gradients, a quasi-homogeneous model, a first-order exothermic reaction, and heat release only through the cooler surface [35, 54–56].

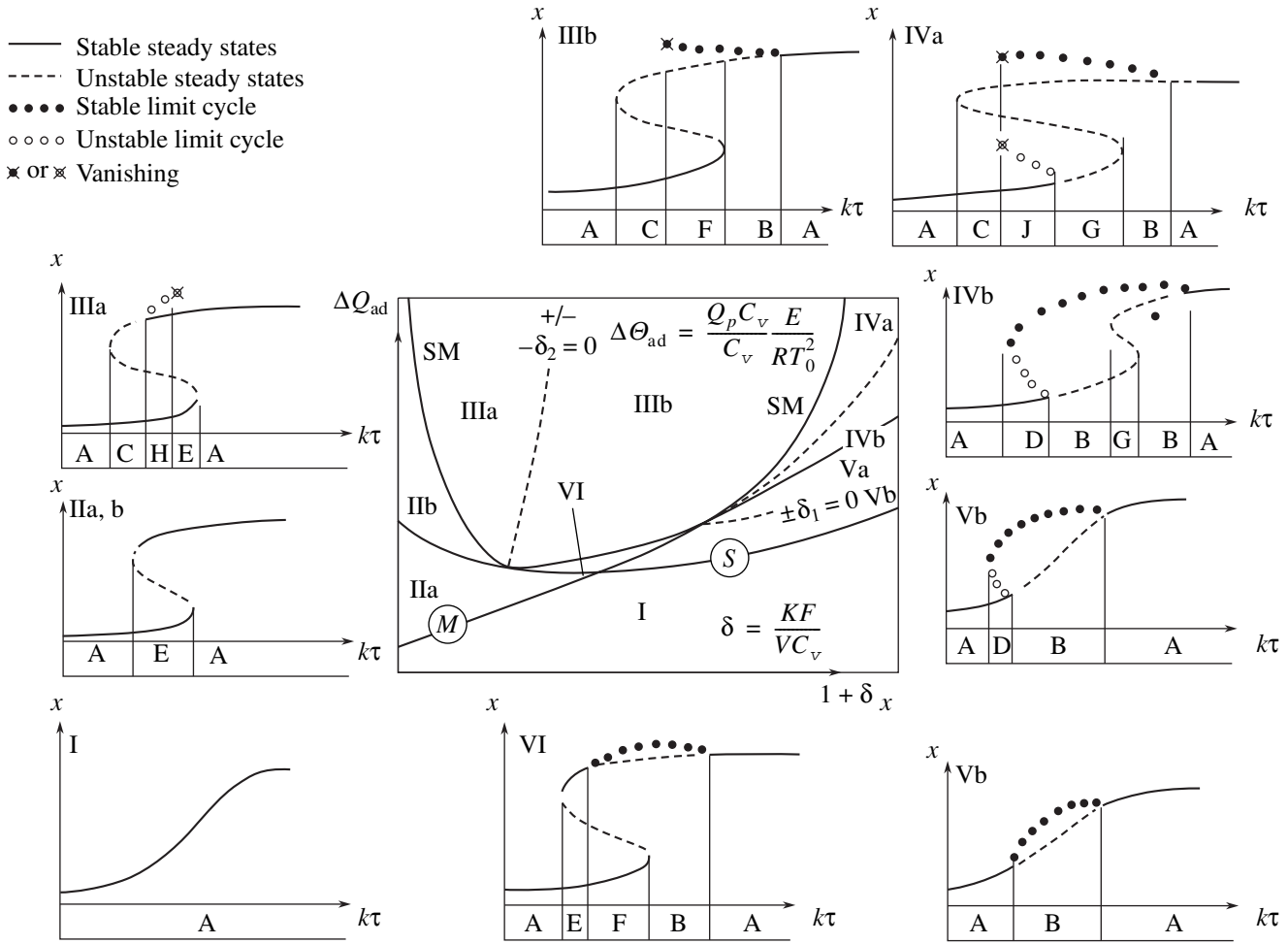


Fig. 1. Phase portraits.

A model of the reactor in dimensionless form is written as

$$\frac{dx}{d\tau} = -x + k\tau_k(1-x)e^\theta = P(x, \theta), \quad (1)$$

$$L \frac{d\theta}{d\tau} = -\theta + \Delta\theta_{ad}k\tau_k(1-x)e^\theta - A\tau_k(\theta - \theta_x) = Q(x, \theta), \quad (2)$$

where k is the reaction rate constant at the temperature

$T = T_0$ or $\theta = 0$, $\tau_k = \frac{V_K}{V}$ is the conditional time of contact of the reaction mixture, θ_{ad} is the dimensionless adiabatic heating, $L = \frac{(1-\varepsilon)c_x + \varepsilon c_p}{\varepsilon c_p}$ is a quantity similar

to the Lewis number, $A = \frac{KF}{V_K c_p}$ is a cooling parameter,

$\varepsilon = \frac{V_p - V}{V_p}$ is the porosity, $x = 1 - \frac{c}{c_0}$ is the degree of

conversion, $\theta = \frac{(T - T_0)E}{RT_0^2}$ is the dimensionless tem-

perature, $k(\theta) = k(T_0)e^{\frac{\theta}{1+b\theta}}$, and $b = \frac{RT_0}{E}$.

Further, let $b = 0$ and $L = 1$. The parameters are varied within the following ranges: $0 < \theta_{ad} < 50$, $0 < k\tau_k < 20$, $0 < A\tau_k < 10$, $0 < \theta_x < 10$, $0 < x < 1$, and $0 < \theta < 50$.

Steady states are determined from the conditions $P(x, \theta) = 0$ and $Q(x, \theta) = 0$.

Mathematical model (1), (2) is presented to show that an analysis of the simplest reactor with the simplest first-order exothermic reaction revealed unexpected features of catalytic processes. A bifurcation analysis showed a wide diversity of phase portraits. W.H. Ray with colleagues [55] found nine phase portraits (Fig. 1). Later, 35 [57] and 53 [58] phase portraits were found. However, many fewer steady and periodic states are feasible. Many parametric phase portraits have very high parametric sensitivity and exist within very narrow temperature ranges. Note that mathematical analysis

can give a more detailed structure of possible steady states than that feasible in practice. The question arises as to whether or not all this can be observed in catalysis under various initial conditions.

FIXED CATALYST BED REACTORS

Mathematical modeling of a fixed catalyst bed reactor is preceded by modeling of a catalytic process on a single catalyst grain to determine the optimal size, shape, and porous structure of the grain. Modeling methods and results are available in the literature [35, 59–61]. In various areas of the chemical, petrochemical, and petroleum refining industries, heterogeneous catalytic processes are often performed in fixed catalyst bed reactors. Because of the wide diversity of processes performed in these reactors, their design is also highly diverse. The choice of the type of reactor for exo- and endothermic processes depends on the ratio of the adiabatic heating (or cooling) ΔT_{ad} of the reaction mixture at complete conversion to the permissible temperature

range ΔT_{per} for the catalyst in the reactor. If $\frac{\Delta T_{ad}}{\Delta T_{per}} < 5$,

then it is expedient to use reactors with adiabatic catalyst layers and intermediate cooling between the layers.

If $\frac{\Delta T_{ad}}{\Delta T_{per}} > 5$, then tubular reactors should be used.

Quasi-homogeneous models are most widely used and simplest. A system of mathematical models of fixed catalyst bed reactors was described in detail in the literature [62].

FLUIDIZED CATALYST BED REACTORS

Fluidized catalyst bed reactors allow one to work with small (0.05–2 mm) catalyst particles, which enables one to completely use the internal surface of catalyst particles, create reactors of high unit capacity, increase the heat-transfer coefficient from the heat-transfer medium to the catalyst by a factor of 5–10, feed the reaction mixture into the catalyst bed without gas preheating, perform continuous contact processes requiring frequent catalyst regeneration, and work with a reaction mixture in which the initial ratio between the components is in the explosion range. Therefore, fluidized catalyst bed reactors are widely used in industry [63].

Mathematical modeling of fluidized catalyst bed reactors remains one of the most complex procedures. A fluidized bed is an open nonlinear dissipative system through which matter, energy, and momentum flows pass. In such systems far from equilibrium, there is self-organization of structures in the form of gravitational oscillations of an ensemble of particles with a subsequent transition to turbulence [64].

A turbulent fluidized bed is a system containing randomly distributed oscillating structures of different

scales. The turbulence of a fluidized bed is an embodiment of chaos and order. Chaos and order are two opposite and interacting characteristics of a fluidized bed.

For objective reasons, complete information on a fluidized bed cannot be obtained. The evolution of the bed in time is described by random deterministic processes and their superpositions. Only a few parameters (density, density oscillation frequencies) of the bed can be measured. Therefore, an approach based on obtaining one-dimensional time series was developed.

A time series is a set of a chosen dynamic variables $x(t)$ that can be measured at constant time step Δt , i.e., at the moments of time $t_i = t_0 + (i - 1) \Delta t$: $x_i = x(t_i)$, $i = 1, \dots, N$. Nonlinear dynamics shows new approaches to studying time series and determining the dimensions of the attractor, Lyapunov exponents, and entropies, i.e., to restoring the properties of the fluidized bed from the time series.

Fluidized bed reactors are most often modeled in practice using a rather simple two-phase model, which represents the main features of the bed and allows one to analyze catalytic processes in reactors of a given scale [63, 64]. It is assumed that the bed consists of two phases, bubbles and a dense phase, between which there is gas exchange characterized by a mass-transfer coefficient. The interphase transfer of the reactants and the mixing of catalyst particles are determined by the size and positions of bubbles in the bed. Hence, they are very important for predicting the reactor operation. Small bubbles form in lower layers of the fluidized bed and randomly coalesce with neighboring bubbles as they rise, which leads to random fluctuations of the bubble size distribution along the apparatus height. Therefore, no deterministic model can describe a fluidized bed even approximately. Such beds should be described by stochastic models.

Organization of a fluidized bed using various internal devices leads to a decrease in the bubble size and an increase in the degree of uniformity and in the interphase mass-transfer coefficient. A necessary degree of bed uniformity is determined by the reaction kinetics of a specific catalytic process and may vary significantly for various processes. The two-phase model of the bed cannot serve as a basis for scale-up because of the unpredictability of the change in the mass-transfer coefficient with a change in the scale. The idea of scale-up should not be based only on mathematical modeling. First of all, an active action on the bed structure is necessary to reach a suitable degree of bed uniformity and intensity of gas contact with the catalyst. Design solutions are needed to ensure the bed uniformity and intense exchange between the phases.

Catalyst particles in a fluidized bed move along random trajectories in nonuniform concentration and temperature fields. The composition and state of the active surface of catalyst particles vary with the composition of the reaction mixture and temperature. The rate of this variation may turn out to be unsufficiently high for the

particle surface state to be quasi-steady with respect to the composition of the reaction mixture at each moment of time. In this case, the composition of the catalyst surface may be unsteady-state even if the reactor is in a steady state. To model the catalytic process in this case, it is necessary to know the kinetics of reactions under unsteady-state conditions. The steady-state reaction kinetics can be used only if the reaction relaxation time is 200 times shorter than the relaxation time of transfer of particles in the bed [65, 66].

UPWARD CATALYST FLOW REACTORS

Upward catalyst flow reactors are used in the petroleum refining industry for catalytic cracking of vacuum gas oil. Replacement of a microspherical aluminosilicate catalyst by much more active zeolite-containing catalysts leads to feed overcracking in the fluidized bed because of the limited rate of interphase transfer between the dense and nondense phases. In an upward flow at high linear velocities of the reaction mixture, the mass transfer between the gas and a catalyst particle abruptly increases. In an upward flow, particles move up at a linear velocity that is much lower than the linear velocity of the gas flow past them. The composition and temperature around particles vary continuously, and so do the conditions of interaction of particles with the reaction mixture. Therefore, modeling requires one to know the unsteady-state reaction kinetics, which is currently unknown. An upward catalyst flow reactor allows one to perform catalytic processes on an active catalyst that rapidly (in less than 3 s) loses its activity and to create reactors of high unit capacity (about 3 000 000 t/year). Upward catalyst flow reactors are quite difficult to model [67]. Much information is required; along with the unsteady-state reaction kinetics, a detailed knowledge of the hydrodynamics of the flows of particles and the reaction mixture is also necessary. Catalytic processes performed under unsteady-state conditions open up possibilities of reaching higher process efficiency in comparison with stationary modes by pretreatment of catalyst particles before introduction into the reactor.

THREE-PHASE CATALYTIC SYSTEMS

Catalytic reactors with a trickle bed, through which there is a downward cocurrent flow of a gas and a liquid, are used in most of the processes of petrochemical synthesis and petroleum refining. Catalytic hydrogenation of olefins, aromatic compounds, and aldehydes; Fischer–Tropsch synthesis; ethylene and propylene polymerization on Ziegler–Natta catalysts; and other processes—all of them are carried out in reactors containing a gas, a liquid, and a fixed solid catalyst bed. A feature of their operation is large volumes of the gas fed, which leads to the fact that the catalyst bed may simultaneously contain completely flooded, partially wetted, and dry catalyst grains [68, 69]. Usually, these

reactors function in a stable steady-state mode. However, the experience of use and the experimental data obtained for the last 20 years indicate that, under certain conditions, critical phenomena may arise, namely, local overheating of the catalyst bed, hysteresis, temperature oscillations [69–72], and side reactions decreasing the reactor output [73]. There were cases where these phenomena led to a thermal explosion of reactors [74]. Critical phenomena arise because of the interaction of chemical and phase transformations and the transition of chemical reactions from the liquid to the vapor phase. Partial wetting of a catalyst grain and reaction exothermicity, which causes catalyst heating and evaporation of reactants, create conditions for vapor-phase transformations on nonwetted grains simultaneously with the liquid-phase reaction. The possibility of a reaction in the vapor–gas phase in a trickle-bed catalytic reactor was experimentally demonstrated, e.g., in benzene hydrogenation [75]. A significant effect of the reaction in the vapor–gas phase on stationary modes and on the dynamics of ignition of a flooded grain has recently been shown [76]. Other causes of critical phenomena are side reactions between the evaporating components or anisotropy or nonuniformity of the granular bed.

Because of the nonlinear dependence of the rate of chemical, including catalytic, reactions on temperature and the concentrations of the reactants, the process at the microlevel under certain conditions causes a qualitative change in the behavior of the entire macrosystem. It was shown [76, 77] that the formation of a positive feedback between the particle temperature, the liquid distribution in the bed, and the hydrodynamic modes of the flows of the phases leads to unstable stationary modes, nonlinear phenomena of the type of ignition and extinguishing of the bed, hystereses, and concentration and thermal nonequilibrium between the vapor and liquid phases.

In this respect, the hierarchical approach developed previously for constructing mathematical models is extremely useful for determining the conditions for the emergence of critical phenomena in a macrosystem. For example, it is important to understand the role of scale in the mechanism of interaction of the microlevel (e.g., a single catalyst grain or several grains) with the macrolevel (the entire catalyst bed).

Investigation of critical phenomena in catalytically active media requires the development of new experimental methods and purposeful experimental and theoretical studies. NMR tomography together with thermocouple probing is a promising experimental technique [78–80]. For example, in investigation of the modes of hydrogenation accompanied by chemical and phase transformations when a reactor with a catalyst grain was placed within the detector of an NMR tomograph, researches for the first time determined the liquid-phase distribution within the catalyst grain directly in the course of the catalytic reaction. This gave more

detailed information on the processes within a catalyst grain and suggested the mechanism of saturation of the catalytically active porous structure with the reacting liquid undergoing chemical and phase transformations. Such experiments were carried out at the Institute of Catalysis for the first time in the world, and they opened up new possibilities for applying NMR tomography to studying exothermic chemical reactions of gaseous and liquid reactants within porous catalysts. To describe the above phenomena, a number of partial mathematical models were developed, whose analysis enables one to describe experimental data and determine the regions of multiplicity of steady states [80]. However, it has not yet been possible to develop sufficiently general approaches to describing the processes on a grain and to study the mechanism of the effect of critical phenomena at the microlevel on the emergence and development of critical states on the macrolevel.

BIOTECHNOLOGY

In our country, the microbiological industry began to be rapidly developed in the 1960s. Among its products were nutrient yeast, protein–vitamin concentrates, amino acids, antibiotics for nonmedical use, etc. A characteristic feature of the modern development of biology is a further increase in its role in creating high-technology processes for medicine, industry, and agriculture. Biochemical processes belong to biocatalysis, whose role in the theory and practice of industrial catalysis is increasing year after year.

The time has come when biotechnology is becoming an important branch of the chemical industry. In their nature, microbiological processes are biochemical reactions in a complex multiphase multicomponent heterogeneous system. The catalysts are enzymes (both homogenous and involved in subcellular elements, cells, or microbial cultures) with high selectivity, whose activity depends on the situation (environment) and can be controlled.

In developing a technology of microbiological synthesis, the main and specific step of production is the cultivation of a necessary microorganism with accumulation of either the biomass of the population or its metabolic products. This involves biological, chemical, physicochemical, mass-transfer, thermal, and hydrodynamic processes. The technology of biocatalytic processes is very close to the technology of microbiological synthesis. At the KhimreaktorIV conference in 1971, a structure of a mathematical model of a fermenter was proposed that comprised six hierarchical levels: the molecular level, microbial cell, microbial population, fermenter element (macroscopic region), fermenter, and fermentation plant with stages of isolation and purification of the product [82]. The first three levels of the model are similar to the levels of a kinetic model of conventional catalytic reactors. The processes at the next levels, namely, mass-transfer, diffusion, thermal, chemical (biochemical), biological (microbio-

logical), and hydrodynamic processes, are similar to those in catalytic reactors. Therefore, in mathematical modeling of biochemical reactors, the experience of mathematical modeling of chemical catalytic reactions, processes, and reactors can be completely used.

One of the problems is to determine the ways to control an enzyme catalytic process. This problem cannot be solved without knowing the laws controlling the processes at the microlevel.

The future of biotechnology depends on investigation of elementary processes, i.e., a biocatalytic acts. In many cases, because of the high activity of biocatalysts, the rate of the entire process is limited by mass-transfer processes. The mass-transfer processes in biotechnological media have been studied poorly. Many of the media are non-Newtonian fluids. Of great importance are heat-transfer processes, the purpose of which is to prevent the formation of increased-temperature zones leading to a decrease in the activity of biocatalysts. For a great industrial future of biocatalysis, it is necessary to expand experimental and theoretical studies. Biochemical systems are very complex. Even the finest experiments do not always answer the question of what is the mechanism of enzymatic processes and what is a kinetic model. Therefore, in investigations and construction of mathematical models, it is necessary to apply a modern methodology—an optimal combination of natural and computational experiments.

Biochemical problems should also be solved using thermodynamic methods. Thermodynamics forms the basis for quantitative description of temperature, pressure, and concentration in the state of chemical equilibrium. Living organisms are dynamic in nature; are not in equilibrium; and, in most cases, are in open systems in a steady state. Therefore, along with methods of classical thermodynamics, methods of nonequilibrium nonlinear thermodynamics and nonlinear dynamics can be useful.

Successful and timely solution these problems largely determines the creation of competitive industrial processes.

Investigation of the quantitative characteristics of the development of industrial microbiological processes in time is a problem of biological kinetics, which characterizes features of the action of enzymes and cells and answers the questions as to, e.g., which step determines the process rate or how the biochemical reactions can be accelerated. The investigation should be based on knowledge of molecular concepts and laws of chemical and physical kinetics and dynamics. This knowledge can underlie the control of industrial enzyme processes and operation of biosynthesis fermenters.

Biochemical processes at the first three levels differ from the kinetic model of heterogeneous catalytic reactions by the following:

some of the processes are characterized by a complex composition of the reaction mixture;

the system is heterogeneous, multiphase, and multi-component;

biochemical reactions have complex mechanisms;

there can be a multiplicity of states of microorganisms in fermentation, etc.

The kinetics of elementary steps in biological and ordinary catalysis is very similar. An enzyme significantly decreases the entropy component of the activation barrier and, in many cases, the energy component too.

Biocatalytic systems are reactive diffusion systems with nonlinear source functions. Therefore, concepts and methods of nonlinear dynamics should be widely used. In many cases, in fermenters, there is a multiplicity of steady states. At the outset, it is necessary to determine which of the possible steady states are stable and feasible. Then, the steady state that ensures the optimal production conditions should be checked. Next, the attraction region of the chosen steady state should be studied to determine how the startup mode should be organized. Nonlinear dynamics is also necessary to investigate the possible hystereses of the reaction rate as a function of concentrations.

In complex multiply connected enzyme systems, the fermenter efficiency can be considerably increased by periodically varying the control parameters. Forced oscillations of reactant concentrations in complex systems may be useful owing to an increase in the selectivity. This is also a problem of nonlinear dynamics.

To successfully apply methods of nonlinear dynamics to analyzing industrial biochemical processes and to use the diverse experience of industrial catalytic processes for designing fermenters and determining the optimal conditions, it is necessary to study the kinetics, mechanism, and energetics of enzymatic reactions and also process control.

Of considerable interest and practical value is biological nitrogen fixation. In recent years, the price of fertilizers has abruptly increased, and it is necessary to reduce the dependence of the crop on nitrogen fertilizers. Note also that the production of nitrogen fertilizers requires oil and natural gas, whose reserves are limited.

COMBINED PROCESSES IN CATALYTIC REACTORS

One of the methods for improving catalytic process selectivity, increasing the degree of feed conversion, and saving energy is to combine catalytic and heat- and mass-transfer processes. A combination of these processes allows one to increase the intensity of both reactions and heat- and mass-transfer processes and to overcome thermodynamic limitations. Among combined processes are

reactive distillation,

processes in membrane reactors,

processes in chromatographic reactors,

adsorption-catalytic processes, and

catalysis with heat exchange.

In the 1950s, heavy water production involved catalytic isotope exchange between hydrogen and water with simultaneous water distillation [83].

Catalysis on membranes enables one to remove some reaction products from the reaction zone, which increases the degree of conversion and selectivity of reversible reactions. The most widely used are catalytic membranes removing hydrogen at the moment of formation. Dehydrogenation of alkanes and cyclohexane and also alkane dehydrocyclization yield hydrogen. The presence of hydrogen in the reaction zone decreases the reaction rate and the catalyst selectivity. This is determined by the ratio between the forward reaction and side reactions. Membranes from palladium and palladium alloys combine hydrogen permeability with catalytic activity in dehydrogenation of some organic compounds.

The advantage of membrane catalysts is the possibility of performing coupled reactions. Separately performed hydrogenation and dehydrogenation require heat removal and heat supply, respectively, which complicates the design of reactors and requires the creation of systems of circulation of a heat-transfer medium. Coupling of dehydrogenation and hydrogenation on a membrane catalyst with high thermal conductivity overcomes these difficulties. Coupling of reactions allows one to abruptly reduce the energy consumption and decrease the number of process steps. An important advantage of membrane catalysts is a new possibility of improving the selectivity by maintaining the membrane catalyst surface in a state of nonequilibrium with the gas phase in the reaction zone [84–86]. The disadvantage of membrane catalytic reactions is a low output because of low membrane permeability, complex reactor design, and high reactor cost.

In a chromatographic reactor, a catalyst is simultaneously used as a sorbent that can separate the initial reactant and the reaction product (or a necessary adsorbent is added to a catalyst) and the process is performed in a near-chromatographic mode: either the initial reactant is periodically dosed into the reactor in a flow of a continuously fed gas (batch variant) or one of the variants of continuous chromatography is used, e.g., the initial reactant is continuously fed into the reactor with a moving bed of sorbent catalyst. Because of the continuous removal of the reaction products from the reaction zone, the thermodynamic equilibrium continuously shifts toward the formation of the reaction products. This enables one to reach a more complete conversion of the initial feed in a single pass through the reactor (to increase the degree of conversion) or to decrease the reactor temperature and, owing to this, to perform the reaction at temperatures that are otherwise unfavorable because of a low constant of thermodynamic equilibrium. The latter reduces the energy consumption, generally improves the selectivity, and

increases the product quality. It is most expedient to use chromatographic reactors to perform reversible decomposition reactions of the type $A \rightleftharpoons B + C$, e.g., dehydrogenation, dehydration, ester saponification, etc. [87].

An adsorption-catalytic system of reactors is used in fine removal of impurities from diluted gases and in cold starting of car engines.

In tubular catalytic reactors, heat-releasing and heat-exchanging surfaces can be combined. Such reactors enable one to perform highly exothermic reactions without catalyst overheating at near-stoichiometric ratios between reactants [88].

In adiabatic catalyst layers, catalysis and heat recovery can be combined by exchanging the heat of the catalyst with the reaction mixture. The process is performed cyclically by switching the direction of feed of the reaction mixture into the catalyst bed. An exothermic reaction front propagates through the fixed bed; i.e., there is a nonstationary temperature mode. However, this does not mean that the composition of the catalyst surface is nonstationary with respect to the composition of the reaction medium, as Boreskov et al. [89] considered, calling the combined process nonstationary catalysis. The composition of the surface depends on the relaxation times of steps of the catalytic process, is unknown, and cannot be controlled. However, such an engineering technique as the combination of catalysis and heat exchange is useful. A heat front forms, whose width, height, and velocity are determined by the physicochemical characteristics of the process and the hydrodynamics of the flow in the disperse bed. This technique can be used, e.g., in utilization of low-calorie methane-air mixtures from coal mines. The heat from the central, high-temperature, zone of the bed can be used.

AERODYNAMIC MODELING

The experience of operation of catalytic reactors shows that the calculated efficiency of their operation is not always reached. This is because of various nonuniformities of the flow of the reaction mixture as it is fed toward the reactor and moves within the reactor. Ensuring a uniform velocity distribution over a cross section of an industrial reactor presents significant difficulties because of the limited reactor sizes, because of which bends cannot be made sufficiently smooth. But sharp bends and branches may give rise to separation flows. This was noted by Academician M.A. Lavrent'ev in organizing works on aerodynamic modeling at the Institute of Catalysis in the very first years.

The temperature distribution in contact reactors depends on the gas flow distribution over a cross section and, in case of mixing of gases with different temperatures, also on the method of their mixing. In reactors with heat exchangers, the temperature distribution also depends on the heat-exchange conditions, determined by the flow hydrodynamics [90].

To create rational designs of contact reactors, it is necessary to perform aerodynamic modeling before or during design. In modeling of hydrodynamic phenomena, geometric, kinematic, and dynamic similarities should be observed. The observance of geometric similarity means that all the linear sizes of a model being analyzed should be the same number of times smaller than the corresponding sizes of an industrial reactor. Kinematic similarity means that the dimensionless velocity fields in the considered flows are identical. To observe dynamic similarity, it is necessary that the flows should be described by similar differential equations of motion under similar boundary conditions. If two flows are dynamically similar, then the following dimensionless numbers should be equal for these flows:

$$\text{Re} \frac{VL}{\gamma}, \quad \text{Eu} = \frac{\Delta p}{\rho w^2}, \quad \text{F}^2 = \frac{w^2}{y}, \quad \text{and} \quad \text{Sh} = \frac{wt}{L}.$$

The equality of the Reynolds number Re , the Euler number Eu , and the Froude number Fr in similar flows means the equality of the ratios of the viscous forces, the pressure forces, and the body forces to the inertial forces. The similarity conditions for the Strouhal number are used for nonstationary flows.

Aerodynamics plays an important role beginning with the scale of a single catalyst grain as a bed element and at the next scale levels of the reactor. However, as noted above, aerodynamic modeling had a significant effect on solving the problem of designing high-output equipment of increased unit capacity. Currently, distributed-memory multiprocessor systems open up the possibility of modeling the flows of a reaction mixture in apparatuses in industrial catalytic processes using the Navier-Stokes equations. These systems can also model reacting flows. This area of research was called computational fluid dynamics [91-94] and became a new powerful tool of the chemical engineer in analyzing the operation of apparatuses in catalytic processes. Computational experiment on multiprocessor systems in combination with natural experiment offers new possibilities for studying the effect of fluid dynamics on the chemical transformation rate over a wide range of parameters of the flow of reacting substances and determining the contributions of various (including design and geometric) factors to this effect. The necessary scope of a natural experiment abruptly decreases, and it becomes possible to solve problems that cannot be solved by direct experiment.

KHIMREAKTOR ALL-UNION AND INTERNATIONAL CONFERENCES ON CHEMICAL REACTORS [95]

For more than 40 years, conferences on chemical reactors have been systematically held. These conferences have been of great importance for developing the theory of the kinetics of catalytic reactions, processes, and reactors by mathematical modeling.

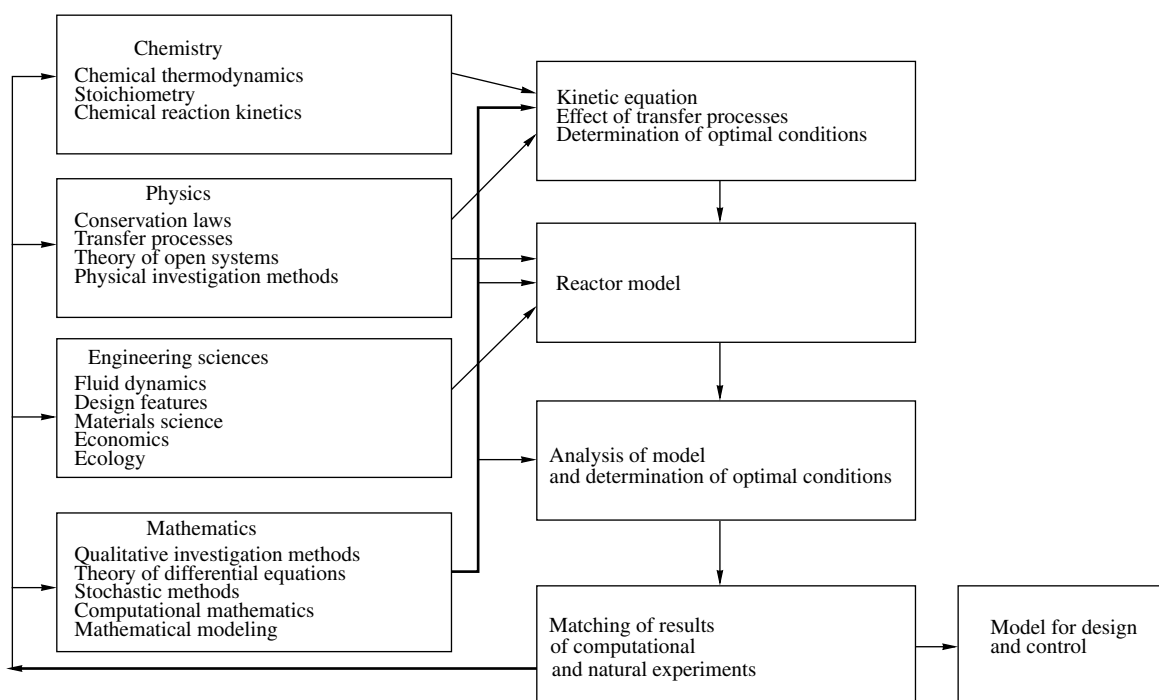


Fig. 2. Methodology of constructing a mathematical model of a catalytic reactor.

The conferences are organized by the Institute of Catalysis and have taken place at many large centers of the chemical, petrochemical, and petroleum refining industries in our country and abroad. The first Khimreaktor conference was held in 1963 in Novosibirsk; the last, in 2006 in Athens.

The proceedings of the conferences on chemical reactors contain the main results of studies performed in our country. The wide range of industrial centers in our country allowed researchers not only to actively propagandize the ideas of mathematical modeling of catalytic reactions, processes, and reactors but also to establish a close relationship with industrial institutes and plants. This favored the development of the method of mathematical modeling on the basis of the optimal combination of natural and computational experiments performed cyclically by an iterative procedure.

Thus, the works on mathematical modeling of chemical reactors were begun in design organizations of the USSR Ministry of Chemical Industry in the 1930s. Mathematical modeling on computers was started in 1958, the year of foundation of the Institute of Catalysis, Siberian Division, USSR Academy of Sciences, Novosibirsk. The basic principles of the functioning of the Siberian Division of the USSR Academy of Sciences—the development of natural sciences and humanities on the basis of physical and mathematical knowledge in unity with practice, solution of large scientific and technical problems, integration of science and education, selection of talented youth, and the accord of scientists of different generations—all this

favored the formation of a scientific collective that generated new ideas but retained the best traditions and a high scientific level of the work done. It became possible to carry out interdisciplinary studies together with the Institute of Mathematics and the Computational Center, Siberian Division, USSR Academy of Sciences, and also to rapidly advance in solving the problems of industrial catalysis together with industrial institutes.

The greatest scientific discovery of our time is the understanding that laws of nature and technology can be written by mathematical expressions. Physics, mathematics, mathematical modeling, and nonlinear dynamics, along with chemistry, form the basis for the theory and practice of chemical engineering, including catalysis. These introduced abstract concepts, many of which lack naive demonstrativeness. Intuition and common sense became a sacrifice to mathematical modeling. The development of mathematical modeling of catalytic processes revealed a large number of unexpected features in the behavior of catalytic reactions, processes, and reactors, e.g., unstable and chaotic modes in industrial reactors. Now, we do not see strange attractors as strange and meaningless. Self-organization and self-organized criticality were also introduced into catalysis by physics and mathematics.

For 45 years, researchers from the Institute of Catalysis have formed a methodology for constructing mathematical models and their analysis (Fig. 2) [35]. The methodology consists of four sets of sciences: chemistry, physics, engineering sciences, and mathematics (using computers). The arrows in Fig. 2 indicate the

participation and role of each set at different steps of constructing models. One of the main advantages of the methodology is the increase in the role of information and intellectual activity, which sharply decreases the time for research, scale-up from the results of laboratory work to industrial conditions, and the determination of the optimal process conditions, i.e., saves the main nonrenewable resource—time. The economic efficiency is also high, although it sometimes cannot be accurately determined since mathematical modeling methods are used to solve problems that were previously considered unsolvable. Ignoring mathematical modeling methods will limit the development of the theory and practice of industrial catalysis and will cause a gap between the achieved understanding of catalytic processes and the method for making decisions in creating and improving catalytic processes and reactors.

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