

BOOK PRESENTATION

THEORETICAL CHEMICAL ENGINEERING

Modeling and Simulation

Chr. Bojadjiev

Bulgarian Academy of Sciences, Institute of Chemical Engineering,
“Acad. St. Angelov” St., Block 103, 1113 Sofia, Bulgaria,
E-mail: chboyadj@bas.bg

MOTTO

The experimenters are striking force of the science. The experiment is a question, which the science put to the nature. The measurement is the registration of the nature's answer. But before the putting of the question to the nature, it can be formulated. Before the using of the measurements result, it must be explained, i.e. the answer can be understood rightly. These two problems are the obligation of the theoreticians.

Max Planck

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INTRODUCTION

1. Quantitative description

Modeling and simulation are principle approaches employed for quantitative descriptions of processes and process systems in chemical and process engineering, for solutions of scientific and engineering problems.

From a scientific point of view, the quantitative process description addresses the process mechanism study. The creation of a hypothesis about the process mechanism is followed by a mathematical model and proof of its adequacy that in fact is proof of the hypothesis.

From an engineering aspect the quantitative description of a process (and process systems too) forms the basis of the engineering optimizations of new chemical plants or control and renovations of older ones, as well.

The recovery of quantitative information concerning processes and process systems through modeling and simulations has some advantages with respect to the physical experiments. The most important of these advantages are:

1. reduction of required material resources;
2. simulations of extreme (or dangerous) conditions give an opportunity to avoid or eliminate the risks;
3. short time simulations of long time technological cycles.

In all the cases, the quantitative description is oriented towards the kinetics of the processes and the systems. The rates of non-equilibrium processes (in accordance with the Onsager approach) depend on the deviations from their equilibrium states. Thus, the quantitative description needs knowledge concerning the process statistics (thermodynamics).

Beside of the variety of the problems mentioned both, the modeling and the simulation follow almost unified approaches including several stages (see Table 0.1). In several particular cases, some stages could be reduced or eliminated.

2. Modeling and simulation

The Association for the advancement of Modeling and Simulation Techniques in Enterprises (AMSE) defines the purpose of **the modeling** as *a schematic description* of the processes and the systems, while **the simulations** are *employments of the models for process investigations or process optimizations without experiments with real systems*.

Obviously, it is easy to realize that modeling addresses the first three stages (see Table 0.1), while the simulations utilizes the last three ones, where the final step means performance of numerical experiments.

On the other hand, the concept of *the mathematical modeling* as a **unified method** employs the assumption that the model build-up and the simulations are steps of it. This approach considers the *mathematical description* as *a model* after the creation of computer-oriented algorithms and codes. From this point of view, the difference between the physical and the mathematical models disappears. The physical modeling replaces the mathematical analogy, while the physical experiment corresponds to the numerical experiment.

The present book addresses **the process modeling** as *a technology concerning selection* (or creation) of *mathematical structures* (the model equations), *parameter identification* (based on data obtained through a physical experiments) and *a check of the model adequacy*. According to the operator definition of the direct and inverse problem solutions, if A and A^{-1} are the direct and inverse operators, the simulation is a direct problem solution, namely:

$$y = Ax, \tag{0.1}$$

Table 0.1. Modeling and simulation stages.

Quantitative description	
M O D E L I N G	Determination of mathematical description structure.
	Identification of parameter estimates in mathematical description using physical experiments.
	Verification of parameters statistical significance and model adequacy.
S I M U L A T I O N	Creating of algorithm for model equations solution.
	Computer realization of solution algorithm.
	Quantitative description obtaining by means of computing (mathematical) experiments.

This implies, obtaining the target (object) function y of the real process (the big apparatus on the book cover) if the model parameters values x are known. Obviously the direct problem solution has an experimental equivalent (the target function is possible to be obtained experimentally).

The modeling is an inverse problem solution. i.e.:

$$x = A^{-1}y_e, \quad (0.2)$$

and addresses obtaining the model parameters value x of the modeled process (the small apparatus on the book cover). The latter implies that the experimental values of the target function y_e are known; in this case finding the inverse problem solution is possible by means of calculation only.

3. Chemical engineering and chemical technology

Employment of modeling and simulation during the quantitative description of processes and systems needs of clear determinations of the **Chemical Engineering** and the **Chemical Technology** problems.

Chemical Engineering is a branch of the chemical sciences concerning implementation the physical chemistry processes at industrial scale in chemical plants. The chemical engineering employs modeling or simulation of processes at issue as principle tool based on an amalgam of fundamentals of chemistry, physics and mathematics. The main target of these investigations is the quantitative descriptions of the process mechanisms and kinetics upon industrial conditions. These descriptions are the first steps of the consequent optimal process design, process control and plant renovations.

The industrial implementation of the physical chemistry processes considers purely chemical and physical phenomena whose performance is affected mainly by the scale of the contacting devices used.

Chemical Technology is a science oriented to the creation of technological schemes including consequences of processes. The flowsheet synthesis provides all the relationships between the processes at the flowsheet sub-levels that needs a systematic approach to be employed. In this context, *the objects of investigations* of the chemical technology are *the technological systems*. The analyses of such systems with the methods of the *system techniques* are in the domain of the **Process System Engineering**. Such an approach is not trivial and it is based on some common suggestions, among them:

Separate chemical and physical (hydrodynamic, diffusion, thermal, adsorption, etc) processes of the chemical technologies are subjects of the **Chemistry** and the **Physics**. The simultaneous perform of these processes in industrial devices is the subject of the **Chemical Engineering**. In this context, the complex interrelated connections between processes of the technological systems are subjects of the **Chemical Technology**. It should note that the system synthesis and optimization are also branches of the Process System Engineering. These standpoints allow describing the chemical technology as a **Chemical Engineering System Technique** employing both the modeling and the simulations as working methods based on the developments of the **Chemical Engineering** and the **Applied Mathematics**. The main goal of studies employing these methods is the quantitative descriptions of the systems and the consequent optimal design, control, and renovations, as well.

It should be noted that optimal reconstruction (retrofit) could be defined as a renovation from a more generalized point of view. Thus, the development of the system towards a better and more efficient (economically) state with respect to the existing situation is the main purpose of the renovation.

4. Theoretical problems and methods

The chemical engineering processes are combinations of basic processes (hydrodynamic, diffusion, thermal, chemical, etc) that occur simultaneously (or consequently) upon imposed conditions by the complex geometry of the industrial contactors. The ordered consequence of separate stages (elementary processes) is the mechanism of the chemical engineering process. From this point of view, the structure of the mathematical description of the process depends on the mathematical description of the elementary processes involved and the interrelations between them. Therefore, the creation of the mathematical description of the elementary processes involved is the first step towards the modeling of the entire chemical engineering process.

The analysis of the separate stages of the modeled process (see Table 0.1) shows that the main step is the creation of the mathematical structures of the model utilizing sub-models of elementary process and the interrelation mechanisms. Obviously, these structures (sub-models) depend on the knowledge available about the process mechanisms.

A very important stage of model development is the parameter identification (based on experimental data) through inverse problem solutions. The main difficulties are related to the inverse problem incorrectness.

The *mathematical structures* developed (structures with identified parameters) *become models* after the evaluation of both, the *parameter significance* and the *model adequacy*.

The model created (before the simulations) can be used for a qualitative analysis of the relation between the process mechanism (and kinetics) and the model parameters values. This allows defining some levels of a hierarchical modeling as well as the scale-up effects of the processes. All these steps permit to facilitate the consequent simulation and *very often, they are required preliminary steps*.

The modeling and simulation of both the processes and the systems are related to many calculation problems. Moreover, there are various approaches of the optimal design, control

and renovations.

A large part of the calculation problems are related to the differential equations solutions. Different analytical (*similarity variables method, Green's functions, Laplace transforms, Sturm-Liouville problem, eigenvalue problem, perturbation method*) and numerical (*finite difference method, finite element method, iterative solution methods*) methods is necessary to be used.

The calculation problems of the model parameters identification need sets, metric spaces, functionals, variational and iterative methods, as well as different methods for functions minimization to be used.

The modeling and simulation of chemical plant systems deal with quite specific calculation problems that should be solved by the help of graphs, matrixes, non-linear, integer and heuristic programming, etc.

5. Physical fundamentals of the theoretical chemical engineering

The theoretical chemical engineering uses physical approximations of the mechanics of continua. Simply, this implies that the material point of the medium corresponds to a volume sufficiently small with respect to the entire volume upon consideration but at the same time sufficiently large with respect to the intermolecular distances of the medium. The modeling in the chemical engineering utilizes mathematical structures (descriptions) provided by the mechanics of the continua.

The principal problem in the theoretical chemical engineering is the necessity of full adequacy mathematical operators in the mathematical models to the physical effects described. This is very important in the theoretical and diffusion type of models and the mass transfer theory is very important example of such problems.

The theoretical analyses employing similarity theory models demonstrate that if the mathematical methods are very simple the formalistic use of the theory could result in wrong results. This note addresses, for example, incorrect formulation of similarity conditions, independent and dependent dimensionless parameters, etc. Physical ideas form the basis of the similarity theory and its mathematical methods. In this context, the correct physical approach might help the use of the similarity theory as a powerful method of quantitative investigations because the correct understanding of the process physics of primary importance.

Part 1. MODEL CONSTRUCTION PROBLEMS

Chapter 1. SIMPLE PROCESSES MODELS

The simple processes in the chemical engineering concern hydrodynamic, diffusion, heat conduction, adsorption and the chemical ones. These are typical non-equilibrium processes and the relevant mathematical descriptions concern quantitatively their kinetics. This gives ground to utilize the laws of the irreversible thermodynamics as mathematical structures building the models of the simple processes [1].

The quantitative description of the irreversible processes depends on the level of detailed processes description. From such point of view, could be defined three basic levels of descriptions – *thermodynamic, hydrodynamic* and *Boltzmann levels*. These different levels of process description form a natural hierarchy. Thus, going-up from a level to level the description becomes richer, i.e. more detailed. This approach allows the kinetic parameters

defined at the lower level to be described through relevant kinetic parameters at the upper level.

The thermodynamic level utilizes quantitative descriptions through *extensive variables* (internal energy, volume and mass). If there is a distributed space, the volume must be presented as a set of unit cells, where the variables are the same but different in different cells.

The hydrodynamics is the next level, where a new extensive variable participates in the processes. This variable is the momentum. Therefore, the hydrodynamic level of description could be considered as a generalization of the lower thermodynamic level. Here, the extensive variables (taking into account their distribution in the space) are mass density, momentum and energy. In the isolated systems, they are conserved and the conservation laws of mass, momentum and energy are used.

The Boltzmann level is the next upper level of description that concerns only the mass density as a function of the molecules' distribution in the space and their momenta.

The hydrodynamic level is a wide applicable in the mechanics of continua. Here, the *material point* corresponds to a sufficiently volume of the medium that is simultaneously *sufficiently small* with respect to the entire volume upon consideration and at the same time *sufficiently large* with respect to the intermolecular distances of the medium.

Modeling in the chemical engineering utilizes *mathematical structures* (descriptions) provided by the mechanics of the continua. The principle reason for this is the fact that these structures sufficiently well describe the phenomena in details. Moreover, they employ physically well-defined models with low number of experimentally defined parameters.

&1.1. Mechanics of continuous media

Scalar and vector fields. Stress tensor and tensor field.

The simple chemical engineering processes in liquids and gases are macroscopic type and must be considered in the continuum approximation [2], i.e. the size of such elementary volume of liquid (gas) is sufficiently large with respect to the intermolecular distances (the elementary volume consists of many molecules).

The simple processes of continua are related to variations of basic physical quantities such as *density* (ρ), *velocity* (\mathbf{u}), *pressure* (p), *concentration* (c) and *temperature* (t):

$\rho = \rho(x, y, z, \tau)$, $\mathbf{u} = \mathbf{u}(x, y, z, \tau)$, $p = p(x, y, z, \tau)$, $c = c(x, y, z, \tau)$, $t = t(x, y, z, \tau)$, where x, y and z are Cartesian co-ordinates and τ is the time. The quantities ρ, p, c and t are *scalars*, while velocity \mathbf{u} is a *vector*. The scalars are determined by numbers, while the vector - by a number and a direction (in mathematics two or more arranged numbers define a vector). The main quantity in hydrodynamics is the stress tensor (nine numbers as a square matrix). That is why the theory of the *scalar, vector and tensor fields* is presented.

&1.2. Hydrodynamic processes

Basic equations. Cylindrical co-ordinates. Boundary conditions. Laminar boundary layer. Two phase boundary layers. Particular processes. Generalized variables. Basic parameters. Rheology. Turbulence.

The base of the hydrodynamic processes models is the Newton law, i.e. the product of the mass per unit volume (*density*) (ρ) and its *acceleration* (\mathbf{a}) equals the sum of both the surface (\mathbf{P}) and the volume (\mathbf{K}) forces acting on it:

$$\rho \mathbf{a} = \mathbf{K} + \mathbf{P}. \quad (1)$$

Here \mathbf{a} is the *substantial* acceleration, i.e., the velocity change with respect to the *space coordinates* and the *time*.

The volumetric (mass) forces are an effect of the influence of *external* forces on the volume (mass) of the medium considered. The latter means that acting on a mass of the particular volume they are produced by external physical fields such as the gravitational force (the body force of gravity), electrical forces (Coulomb forces between charged bodies), centrifugal forces, and buoyant forces.

In the dynamics of continua, the volume forces are usually expressed through the density of their distribution (\mathbf{k}) or, in other words, through the force per unit mass:

$$\delta \mathbf{K} = \rho \mathbf{k} (\delta v), \quad (2)$$

where (δv) is a sufficiently small volume. If (Δv) contains the material point $M(x,y,z)$, the unit vector \mathbf{k} is defined as

$$\mathbf{k} = \lim_{\Delta m \rightarrow 0} \frac{\Delta \mathbf{K}}{\Delta m} = \frac{1}{\rho} \lim_{\Delta v \rightarrow 0} \frac{\Delta \mathbf{K}}{\Delta v}, \quad (3)$$

where Δm is the mass of the volume Δv . When \mathbf{K} is the gravitational force, the density \mathbf{k} is the gravity acceleration \mathbf{g} .

The surface forces differ principally from the body forces. They also act on a particular volume of the medium, but *are not proportional* to its mass. They are *internally* determined forces, i.e., they represent *the reaction of the medium* against the application of the external (to the volume) forces. Thus, they represent the *stressed state* of the medium.

The surface forces \mathbf{P} are described by the *stress vector* \mathbf{p} :

$$\delta \mathbf{P} = \mathbf{p} ds, \quad (4)$$

where ds is an *infinitely small* surface area. If Δs contains point $M(x,y,z)$, the definition of \mathbf{p} is

$$\mathbf{p} = \lim_{\Delta s \rightarrow 0} \frac{\Delta \mathbf{P}}{\Delta s}, \quad (5)$$

where Δs is a small surface area and contains point M . In the above equations, \mathbf{p} is the force acting on a *unit surface* of a plane containing point $M(x,y,z)$ and characterized by its *normal vector* \mathbf{n} , i.e., \mathbf{p} depends on the normal vector components.

For many gases and liquids, there are linear relationships (*experimentally derived laws*) between the stresses and the shear rates (the deformation rate). The using of this Stokes postulation permit to present the components of the stress tensor through the velocity components in (1) and the projections of this vector equation along the coordinate axes gives the so-called Navier-Stokes equations.

The cases, which are strayed from the Stokes postulation, are presented in the *Rheology and Turbulence*.

The velocity distribution near interphase surfaces for high values of Reynolds numbers are presented in the *laminar boundary layer approximations*.

& 1.3. Mass and heat transfer processes

Basic equations. Boundary conditions. Transfer processes rate. Diffusion boundary layer. Turbulent diffusion. Turbulent mass transfer.

Mass transfer processes models are mass transport of component with a local concentration c with a non-uniform distribution over the flowing fluid. They present the mass balance in the elementary volume δv . If the surface δs encloses the volume δv , the mass transfer across this surface will be a result of the molecular diffusion (chaotic motion of the non-uniform distributed molecules) and convection (arranged motion of these molecules with the flow).

The convective mass of the elementary volume ρ by the mass (ρc) of the component with a non-uniform concentration distribution c leads to

$$\frac{\partial}{\partial t}(\rho c) + \text{div}(\rho c \mathbf{u}) = 0. \quad (6)$$

Because of the concentration distribution non-uniformity, the density of the diffusion mass flux across surface δs is

$$\mathbf{q}_c = -D \text{grad}(\rho c) = -D \nabla(\rho c), \quad (7)$$

where the linearity of (7) follows from Onsanger's linear principle for small $\nabla(\rho c)$ and D is the *diffusivity* (molecular diffusion coefficient). Equation (7) is Fick's first law, and for small concentrations $D = \text{const}$.

The diffusion mass flux (7) takes part in the mass balance in the elementary volume δv as $\text{div} \mathbf{q}_c$:

$$\frac{\partial}{\partial t}(\rho c) + \text{div}(\rho c \mathbf{u}) + \text{div} \mathbf{q}_c = 0. \quad (8)$$

The combination of (6) and (7) gives the *convection–diffusion equation*:

$$\frac{\partial}{\partial t}(\rho c) + \text{div}(\rho c \mathbf{u}) = \text{div} [D \nabla(\rho c)]. \quad (9)$$

A similar result could be obtained for the heat transfer if in the mass conservation law (6) we replace the mass (ρc) with the heat, i.e., internal energy $(\rho \mathcal{E})$ of the mass, where

$$\mathcal{E} = c_p T + \varepsilon_\theta. \quad (10)$$

In (10) c_p is the specific heat of the substance at pressure p , T is the absolute temperature, and ε_θ is a nonessential constant.

By analogy to the mass transfer, the heat transfer is a result of conduction and convection. In chemical engineering processes, radiation heat-transfer effects are not so big because these effects are the result of high temperature.

In many cases, the relation between the conductive (molecular) heat flux \mathbf{q}_T and the temperature gradient is linear (the first Fourier law):

$$\mathbf{q}_T = -\lambda \text{grad} T = -\lambda \nabla T, \quad (11)$$

where λ is thermal conductivity.

The convective heat transfer in moving fluids with variable temperature can be obtained from (1.3.2) by replacing the mass concentration with the internal energy concentration:

$$\frac{\partial}{\partial t}(\rho \mathcal{E}) + \text{div}(\rho \mathcal{E} \mathbf{u}) = 0. \quad (12)$$

The conductive heat transfer may supplement the convective one and the convection–conduction equation has the form:

$$\frac{\partial}{\partial t}(\rho \mathcal{E}) + \text{div}(\rho \mathcal{E} \mathbf{u}) + \text{div} \mathbf{q}_T = 0. \quad (13)$$

If ρ , c_p , and λ are constants, from (11) and (12) it follows that

$$\frac{\partial T}{\partial t} + \text{div}(\mathbf{u} T) = a \nabla^2 T, \quad a = \frac{\lambda}{\rho c_p}, \quad (14)$$

where a is the thermal diffusivity.

The concentration distribution near interphase surfaces for high values of Peclet numbers are presented in the *diffusion boundary layer approximations*. The *turbulent diffusion* and the *turbulent mass transfer* are presented, too.

&1.4. Chemical processes and adsorption

Stoichiometry. Mechanism and reaction route. Kinetics of simple chemical reactions. Kinetics of complex reactions. Adsorption processes. Physical adsorption. Chemical adsorption. Heterogeneous reactions.

The main problem in modeling chemical processes is the determination of the kinetic model for simple chemical processes, which is further used in the model description of complex reactions and processes. Since hydrodynamic, diffusion, and heat processes are associated with chemical reactions, it can be done in two different ways:

1. The rate of the complex process determines the rate of the chemical process, accounting for the hydrodynamics and mass transfer effects.

2. The rate of mass transfer, accounting for chemical reaction effects, is considered.

Chemical reactions can be realized in the phase volume or at the boundary of two phases. In the first case, they are called “homogeneous” and their rate is determined by the amount of substance reacted in a unit volume for a unit time. In the second case, they are heterogeneous ones and the rate is determined by the amount of substance reacted on a unit surface for a unit time.

&1.5. Examples

Dissolution of solid particle. Particle radius is constant. Particle radius decreases. Contemporary approach of turbulence modeling.

The examples are based on author’s papers.

Chapter 2. COMPLEX PROCESSES MODELS

Chemical engineering processes are aggregates of simple chemical and physical processes having mathematical descriptions based on fundamental chemical and physical laws. Establishment of a mathematical model of a certain complex process needs information about the interactions between the simple processes involved. The latter simply means that such complex mechanisms have to permit mathematical descriptions consisting of mathematical operators corresponding to the physical and chemical effects contributing to the processes. In accordance with this standpoint, the basic *theoretical models* of mass transfer, for instance, contain equations of hydrodynamics, convection-diffusion, and chemical reactions.

In many cases, the model construction becomes more complicated owing to the complex hydrodynamic situation (turbulence, fluid motion as drops, bubbles, or through a bed of particles, etc.). Using physical analogies (e.g., between turbulent and molecular diffusion) or average velocity and concentration models, one can solve the modeling problems.

Otherwise, if there is a lack of information about the process mechanism, then *similarity theory models can be employed*. In cases when the information about the process mechanism is completely missing, *regression models* allow one to create functional relationships.

& 2.1. Mechanism and mathematical description

Mechanism of physical absorption. Mathematical description. Generalized variables and characteristic scales. Dimensionless parameters and process mechanism. Boundary conditions and mechanism. Kinetics and mechanism.

The significance of the models for science and practice is mainly related to their exactness, which in general addresses the correspondence between the separate mathematical

operators in the model and the physical and the chemical effects in the process. That is why the principal step in the process of model building is the correct theoretical analysis of the process mechanism being considered. This is exemplified by model building concerning a physical absorption process.

The mathematical description of the absorption process contains many parameters, but their number can be reduced if dimensionless parameters are used. Suitable use of these parameters permits to make a qualitative (generalized) analysis of the proposed process mechanism concerning order of magnitude analysis of separate parameters and relevant physical effects. For this purpose, dimensionless (generalized) variables are introduced using characteristic (inherent) scales of the process. These scales have to be selected in a manner allowing the dimensionless (generalized) variables to be of the order of magnitude of unity. Consequently, the order of magnitude of the separate terms in the model equations (separate physical effects) will be equal to the order of magnitude of their dimensionless parameters. On this base is analyzed the relations between *dimensionless parameters and process mechanism, boundary conditions and mechanism, chemical kinetics and mechanism*.

& 2.2. Theoretical models. Mass transfer in film flows

Film with free interface. Effect of chemical reaction. Effect of gas motion. Absorption of slightly soluble gas. Absorption of highly soluble gas.

Many processes in chemical engineering are carried out in gas (vapor)-liquid film flows. In such flows, the effects of different volume (velocity distributions, chemical reactions) and interface (gas motion, surfactants, capillary waves) effects on the mass transfer in liquid film flows [2,3] have to be taken into account in presented theoretical analysis.

The kinetics of gas *absorption of slightly soluble and highly soluble gases is analyzed*.

& 2.3. Diffusion type models

Mass transfer with chemical reaction. Interphase mass transfer. Average concentration models. Airlift reactor.

The analysis of the theoretical models indicates that the main difficulties are related to the hydrodynamic equations of the models. The first problem results from the nonlinearity of the equations, whereas the second one originates from the very complicated or unidentified shape of the interface separating the phases. The first problem can be avoided with the help of advanced numerical codes. The second one is a common problem in columnar devices for performing chemical reactions in gas-liquid and liquid-liquid systems such as airlifts and bubble columns. In all these cases, the formulation of the boundary conditions at the interphase surface is practically impossible and as a result, the velocity distribution in these devices cannot be obtained. The solution of this problem in model theories (the *film theory* of Nernst, Langmuir, Lewis and Whitman; Higbie's *penetration theory*; *surface renewal theory* of Kishinevsky and Danckwerts) results in large discrepancies between the theoretical predictions and the performance of the real processes. A way to overcome these difficulties and to develop solutions of existing problems is the use of diffusion-type models.

Diffusion type models for *mass transfer with chemical reaction and interphase mass transfer are presented. On this base are obtained average concentration models, which are used for modeling of an airlift reactor.*

& 2.4. Similarity theory models

Absorption in packed bed column. Generalized (dimensionless) variables. Generalized individual case and similarity. Mathematical structure of the models. Dimension analysis.

Some errors in criteria models.

The similarity theory model is used for modeling of an *absorption packed bed column*. The use of *generalized (dimensionless) variables* permits to formulate the *similarity of the processes in the generalized individual case*. *Mathematical structure* of the similarity theory models is obtained. Some shortcomings of the *dimension analysis* and *criteria models* are shown.

& 2.5. Regression models

Regression equations. Parameter identification. Least square method.

In the cases of absence of information of the process mechanism, the regression models are used. The main problem of regression models is parameter identification (estimation). The *least square method* is used for solution of this problem.

& 2.6. Examples

Effect of surfactants. Effect of interface waves. Photobioreactor model.

The examples are based on author's papers.

Chapter 3. MASS TRANSFER THEORIES

& 3.1. Linear mass transfer theory

Model theories. Boundary layer theory. Two phases boundary layers.

Two-dimensional mass transfer problem of the linear mass transfer theory within an area with dimensions L and h is Here, $y = 0$ is the surface (interphase surface), through which the mass transfer towards another phase (solid, liquid, and gas) takes place:

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right);$$

$$x = 0, y > 0, c = c_0, x = L, 0 \leq y < h, c = c^* ;$$

$$y = 0, 0 \leq x < L, c = c^*; y = h, c = c_0. \quad (15)$$

Here, $y = 0$ is the surface (interphase surface), through which the mass transfer towards another phase (solid, liquid, and gas) takes place. From (15) the mass transfer rate (J) can be defined through the mass transfer coefficient (k) and the local mass flux (i):

$$J = k(c^* - c_0) = \frac{h}{L} \int_0^L i \, dx, \quad i = -D \left(\frac{\partial c}{\partial y} \right)_{y=0}. \quad (16)$$

This leads to the definition of the Sherwood number:

$$Sh = \frac{kL}{D} = - \frac{1}{c^* - c_0} \int_0^L \left(\frac{\partial c}{\partial y} \right)_{y=0} dx. \quad (17)$$

The principal problem in linear mass transfer theory is the determination of the velocity field since the Navier–Stokes equations are strongly nonlinear.

In the *model theories*, this problem is passed over. In the *film theory* (Nernst, Langmuir, Lewis, and Whitman) the velocity is equal to zero. Higbie's *penetration theory* use constant value of the velocity

In the *boundary layer theory* the linear mass transfer theory problem have the form:

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = v \frac{\partial^2 u}{\partial y^2}, \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0, \quad u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2};$$

$$x = 0, \quad u = u_0, \quad c = c_0; \quad y = 0, \quad u = 0, \quad v = 0, \quad c = c^*; \quad y \rightarrow \infty, \quad u = u_0, \quad c = c_0. \quad (18)$$

For solution of (18) similarity variables are used.

& 3.2. Mass transfer in countercurrent flows

Velocity distribution. Concentration distribution. Comparison between co-current and countercurrent flows.

The theoretical analysis of the countercurrent flow shows, that it is a non-classical problem of mathematical physics, i.e. the parabolic boundary value problem with changing direction of time. It is shown that this non-classical problem can be described as consisting of several classical sub-problems. For solution the similarity variables method is used.

& 3.3. Non-linear mass transfer

Influence of the intensive mass transfer on the hydrodynamics. Boundary conditions of the non-linear mass transfer problem. Non-linear mass transfer in the boundary layer. Two phase systems. Non-linear mass transfer and Marangoni effect.

The theoretical analysis of linear mass transfer shows that such a process exists when the equation of convection-diffusion (3.1.4) is linear, i.e., the velocity (u , v) and the diffusivity (D) are independent of the concentration (c) of the transferred substance. These conditions are valid in systems where the mass transfer does not affect the hydrodynamics and the mass flux is related linearly to the concentration gradient. The linear mass transfer theory, built with these assumptions, has two main outcomes: (1) *the mass transfer coefficient is independent of the concentration and (2) the mass transfer rate is unaffected by the direction of interphase mass transfer.*

Any deviations in experiments apart from these two principal theoretical outcomes indicate that nonlinear effects are taking place. The latter are mainly due to secondary flows caused by high mass transfer rates or concentration effects on transport coefficients such as viscosity and diffusivity. The secondary flows can be caused by a concentration gradient (nonlinear mass transfer), a surface tension gradient (Marangoni effect), a density gradient (natural convection), or a pressure gradient (Stefan flow). Under such conditions, the effect of concentration on both the velocity field and the convection-diffusion equation becomes nonlinear. The secondary flows may affect the mass transfer rate through changes in the velocity field, i.e., the result is a changed ratio of the convective and the diffusive transfer in the convection-diffusion equation. The effect may increase many times when the system becomes unstable as a result of secondary flows and attains a new hierarchical state of self-organization (recall, the systems are dissipative structures).

Theoretical analysis of the *influence of the intensive mass transfer on the hydrodynamics* permit to solve the *non-linear mass transfer problem in the boundary layer approximation* in one and two phase systems. A comparison analysis of the *non-linear mass transfer and Marangoni effect* is presented.

& 3.4. Examples

Heat transfer in the conditions of non-linear mass transfer. Multicomponent mass transfer. Concentration effects. Influence of the high concentration on the mass transfer rate. Non-linear mass transfer in countercurrent flows.

The examples are based on author's papers.

Part 2. THEORETICAL ANALYSIS OF MODELS

Chapter 4. QUALITATIVE ANALYSIS

& 4.1. Generalized analysis

Generalized variables. Mass transfer with chemical reaction. Non-stationary processes. Steady-state processes. Effect of the chemical reaction rate.

The generalized analysis uses generalized (dimensionless) variables, where the characteristic scales are equal to maximum (or average) variables values. As a result dimensionless terms (generalized variables and differential operators) have orders of magnitude of unity, $O(1)$.

Each term in a generalized (dimensionless) variables model represents a physical effect and the order of magnitude of this effect is equal to the parameter value (dimensionless prefactor) in this term. If there is no prefactor, which is actually equal to 1, then the order of magnitude of the entire term is $O(1)$. If the model equation contains dimensionless parameters greater than 1, this equation must be divided by the parameter with maximum value. As a result, all effects in the complicated process are of three types: *main effects* (the terms do not contain dimensionless parameters), *small effects* (the parameter values are in the range $[10^{-2}, 10^{-1}]$), and *negligible effects* (the parameter values are less, than 10^{-2}).

The generalized analysis is used for a qualitative analysis of *mass transfer with chemical reaction, non-stationary and steady-state processes, effect of the chemical reaction rate.*

& 4.2. Mechanism of gas-liquid chemical reactions

Irreversible chemical reactions. Homogenous catalytic reactions. Reversible chemical reactions. Relationships between the chemical and physical equilibrium during absorption.

A theoretical analysis of chemical processes in gas-liquid systems, when chemical reactions take place in the liquid phase, is presented. The effects of the reaction kinetics in the liquid phase on both the mechanism and the rate of the mass transfer across the interphase surface is analyzed. The analysis is addressed to both the linear and non-linear reaction kinetics laws as well as *reversible* and *irreversible* chemical transformations. In all cases, *homogenous catalytic reactions* are considered. *Relationships between the chemical and physical equilibrium during absorption is obtained.*

& 4.3. Comparative qualitative analysis for process mechanism identification

Comparison of the non-linear effects. Non-stationary absorption mechanism. Non-stationary evaporation kinetics.

The existence of experimental data on the process kinetics permits is to decipher the process mechanism. The solution of this problem is made difficult by the possibility of the existence of different physical effects and their combination in the process mechanism (e.g., different nonlinear effects). The comparative qualitative analysis permits us to reject the negligible effects. For example, in many cases there is a big difference between the experimental data and the predictions of the linear mass transfer theory because of nonlinear

effects. These effects are caused by secondary flows, where the velocity is a function of the concentration. The influence of the mass transfer on the hydrodynamics as a result of a big concentration gradient, a surface tension gradient (Marangoni effect), a pressure gradient (Stefan flow), or a vertical density gradient (natural convection), is analyzed.

The theoretical and experimental investigation of the mass transfer between two immovable phases in the case of absorption of pure gases in an immovable liquid shows that under these conditions three processes can take place: natural convection, nonlinear mass transfer, and the Marangoni effect. In these conditions, the Marangoni effect is negligible.

The non-stationary evaporation of a liquid with a moderate partial pressure (water, methanol, ethanol, and isopropyl alcohol) in an inert gas (nitrogen, argon, and helium) is investigated. Under such conditions, the non-stationary mass transfer of the liquid vapors in the gas phase limits the process rate.

& 4.4. Examples

Sulphuric acid alkylation process in a film flow reactor.

The examples are based on author's papers.

Chapter 5. QUANTITATIVE ANALYSIS

& 5.1. Scale-up

Similarity and scale-up. Scale effect. Diffusion model. Scale-up theory. Axial mixing. Evaluation of the scale effect. Hydrodynamic modeling.

The quantitative analysis of the models is the last step before using the models for modeling and simulation of the real processes. The quantitative results obtained from small-scale laboratory models must be "remade" for large-scale real process simulation. This "scale-up" from the models to the real processes is a very important stage in the modeling and simulation.

The scale-up problems related with incompatible similarity criteria and scale-up effect are analyzed. The methods of *evaluation of the scale effect* and *hydrodynamic modeling* are presented

& 5.2. Average concentration model and scale-up

Diffusion type of model. Influence of the velocity distribution radial non-uniformity on the process efficiency. Scale effect. Average concentration model. Scale effect modeling. Scale-up parameter identification.

The founded *diffusion type of models* permit to obtain the *influence of the velocity distribution radial non-uniformity on the process efficiency in column apparatuses and scale effect*. The created *average concentration models* are a base for the *scale effect modeling and scale-up parameter identification*.

& 5.3. Statistical analysis

Basic terms. Statistical treatment of experimental data. Estimates of the expectation and the dispersion. Tests of hypotheses. Dispersion analysis. Significance of parameter estimates and model adequacy. Model suitability. Adequacy of the theoretical models and model theories.

The presented statistical methods are used for statistical analysis of *parameter significance, model adequacy and model suitability* of different type of models.

& 5.4. Examples

Statistical analysis of diffusion type of models.

Chapter 6. STABILITY ANALYSIS

& 6.1. Stability theory

Evolution equations. Bifurcation theory. Eigenvalue problem.

The stability theory is presented on the base of the *evolution equations, bifurcation theory, and eigenvalue problems.*

& 6.2. Hydrodynamic stability

Fundamental equations. Power theory. Linear theory. Stability, bifurcations and turbulence. Stability of parallel flows.

The hydrodynamic stability theory is presented in the cases of big (*power theory*) and small (*linear theory*) perturbations. On this basis, the relation between *stability, bifurcations and turbulence is shown.* The hydrodynamic stability of *parallel flows* is analyzed.

& 6.3. Orr-Sommerfeld equation

Parallel flows. Almost parallel flows. Linear stability and non-linear mass transfer.

The Orr-Sommerfeld equation is used for stability analysis of *parallel flows, almost parallel flows.* A *linear stability analysis in the cases of non-linear mass transfer is presented.*

& 6.4. Self-organizing dissipative structures

Non-linear mass transfer in boundary layer. Gas absorption. Liquid evaporation.

In the cases of supercritical bifurcations ($Re > Re_{cr}$) the amplitudes of the small disturbances (perturbations) increase and reach a stable amplitude. As a result, the mass transfer in the flow is very intensive. These flow regimes are very useful because the energy dissipation is less than that in turbulent flow regimes.

The main problem of the theoretical analysis of self-organized structures is to obtain the amplitude of the disturbances. There are practically two approaches: to use experimental data and to use an additional theoretical condition. A method for *stability analysis of the nonlinear mass transfer processes*, using a balance between kinetic energies of the main flow and the disturbance, is proposed. Self-organizing dissipative structures in the cases of *gas absorption and liquid evaporation* is investigated.

& 6.5. Examples

Gas-liquid system. Liquid-liquid system. Effect of concentration. Effect of temperature.

The examples are based on author's papers.

Part 3. CALCULATION PROBLEMS

Chapter 7. DIFFERENTIAL EQUATIONS SOLUTIONS

& 7.1. Analytical methods

Green's functions. Similarity variables method. Eigenvalue problem. Laplace transformation.

Analytical solutions of the parabolic partial differential equations in the general case, using *Green's functions, similarity variables method, Eigenvalue functions and Laplace transformation, are shown.*

& 7.2. Perturbation methods

Expansions with respect to parameter. Expansions with respect to coordinate. Non-uniform expansions (method of Poincaré-Lighthill-Ho).

Some of the perturbation methods for solving of mass transfer problems are presented.

7.3. Numerical methods

Finite differences method. Finite elements method.

The *finite differences* and *finite elements methods* are demonstrated as fundamental numerical methods.

& 7.4. Examples

Green's functions application. Sturm-Liouville problem.

Different analytical solutions are shown.

Chapter 8. PARAMETERS IDENTIFICATION (ESTIMATION)

& 8.1. Inverse problems

Direct and inverse problems. Types of inverse problems. Incorrectness of the inverse problems.

The inverse problem is the process of *parameter identification*. It allows to calculate the parameter values for known experimentally determined values of both the independent variables and the objective function. In contrast to the forward problems, the inverse problems can be solved through calculation only. Obviously, the inverse problem solution strongly depends on the mathematical structure of the model considered.

Most chemical engineering models (hydrodynamic equations, convection–diffusion equation, convection–conduction equation) are used in the boundary layer approximation, i.e., in the form of parabolic partial differential equations. A characteristic peculiarity of these equations is the presence of a small parameter (viscosity, diffusivity, conductivity) at the highest derivate. In these conditions the direct operator is fully continuous (fully bounded), whereas the corresponding inverse operator is not continuous and the *inverse problems is incorrect (ill-posed)*.

& 8.2. Sets and metric spaces

Metrics. Linear spaces. Functional. Operator. Functional of the misfit. Some properties of the direct and inverse operators.

The specific features of the inverse problems are relevant to the theory of functions and the functional analysis considered in & 8.2.

& 8.3. Incorrectness of the inverse problems

Correctness after Hadamard. Correctness after Tikhonov.

The mathematical analysis show, that the problems that are incorrect after Hadamard is possible to be solved through conditionally correct methods (correctness after Tikhonov).

& 8.4. Methods of solving of incorrect (ill-posed) problems

Method of selections. Method of quasi-solutions. Method of the substitution of the equations. Method of the quasi-reverse.

& 8.5. Methods for solving of essentially ill-posed problems

Regularization operator. Variational approach. Stabilizing functional. Smoothing functional. Iterative approach. Gradient methods. Uniqueness of the solution. Approximate equations. Criteria for stopping the iterations.

& 8.6. Parameter identification in different types of models

Regression models. Selection methods. Variational regularization. Similarity theory models. Diffusion type of models. Determination of the heat conductivity coefficients in inverse heat transfer problem. Iterative algorithm. Theoretical models and model theories.

In & 8.4, & 8.5 and & 8.6 different methods are presented for solving *incorrect* and *essentially incorrect* problems and its applications for parameter identification in different types of models

& 8.7. Least square function minimum

Incorrectness of the inverse problem. Incorrectness of the least square function method. Regularization of the iterative method for parameters identification. Iteration step determination and iteration stop criterion. Iterative algorithm. Correct problem solution. Effect of the regularization parameter. Incorrect problem solution. Essential incorrect problem solution. General case. Statistical analysis of model adequacy. Comparison between correct and incorrect problems.

Incorrectness of the inverse problem is possible to be illustrated using a simple one-parameter model:

$$\varepsilon y'' + y' = 0; \quad x = 0, \quad y = 1; \quad y' = b = \varepsilon^{-1}, \quad (19)$$

where ε is small parameter at the highest derivate. The solution of (19) is

$$y = 1 - \exp(-bx) \quad , \quad (20)$$

i.e., the dependence of y on ε (for big values of b) is similar to the cases of the diffusion-type models.

Figure 1 shows the relationship between the objective function y and the parameter b for a constant value of the independent variable $x = x_0 = 5$. Such a type of relationship is typical for a number of models of heat or mass transfer processes.

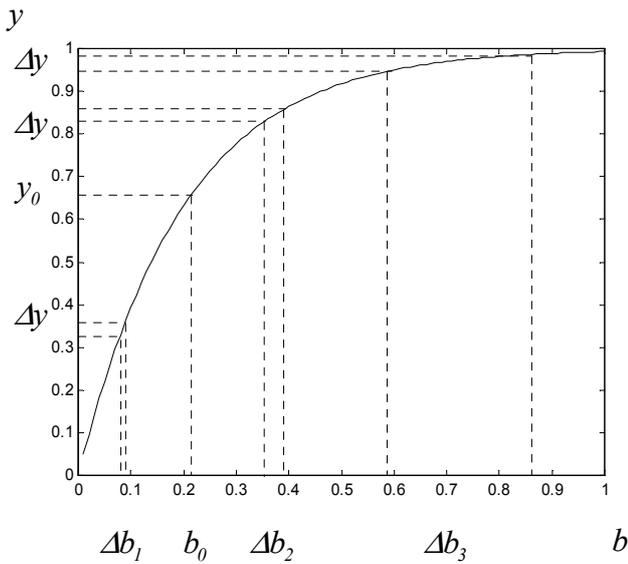


Fig. 1 Objective function y for different values of the model parameter b at $x = x_0 = \text{const}$.

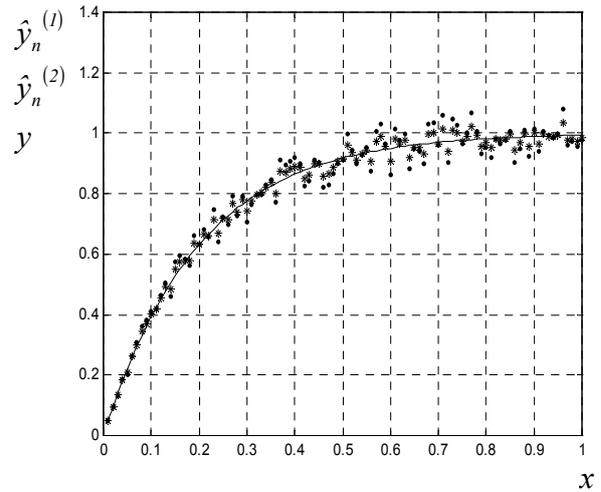


Fig. 2 Mathematical model and “experimental” data: asterisks $\hat{y}_n^{(1)}$, values of y with a maximum “experimental” error of $\pm 5\%$; circles $\hat{y}_n^{(2)}$, values of y with a maximum “experimental” error of $\pm 10\%$; line $y = 1 - \exp(-5x)$

The plot in Fig. 1 permits us to obtain the objective function y_0 if the value of the parameter b_0 is known, which is a *direct problem solution*. However, an *inverse problem* looks for the value of the parameter b_0 if experimental values of the objective function y_0 are known.

Consider Δy as the experimental error of the objective function. Fig. 1 shows that the error of the parameter identification depends on the magnitude of the objective function y . For small values of the objective function, there are small error Δb_1 , which shows the inverse identification problem is the *correct* one. However, if the objective function values are large, the corresponding values of Δb_2 are large too and the inverse problem is *incorrect*. In cases of the parameter identification of the models describing elementary processes, extremely large objective function values are utilized and enormous errors Δb_3 occur, which classify the inverse identification problem as *essentially incorrect*.

The results shown in Fig. 1 indicate that the incorrectness of the inverse problem is not a result of the size of the error of y and the cause is the parameter sensitivity with respect to the experimental errors of the objective function.

8.8 Incorrectness of the Least Squares Function Method

Consider the two-parameter model

$$\varepsilon y'' + y' = 0; \quad x = 0, \quad y = 1 - b_1, \quad y' = -b_1 b_2^2, \quad b_2 = \varepsilon^{-1}. \quad (21)$$

The solution of (21) is

$$y = 1 - b_1 \exp(-b_2 x), \quad (22)$$

where $\bar{b}_1 = 1$ and $\bar{b}_2 = 5$ are the exact values of the parameter.

The parameter identification problem will be solved with help of artificial *experimental data* provided by a random number generator:

$$\hat{y}_n^{(1)} = (0.95 + 0.1A_n)y_n, \quad \hat{y}_n^{(2)} = (0.9 + 0.2A_n)y_n, \quad (23)$$

where A_n are random numbers within the interval $[0, 1]$. The values of y_n are obtained from the model (22) for $x=0.01n$ ($n=1, \dots, 100$). The maximum relative errors of these “experimental” data ($\Delta\hat{y}$) are ± 5 and $\pm 10\%$. The values of $y_n, \hat{y}_n^{(1)}$, and $\hat{y}_n^{(2)}$, are shown in Fig. 2. Comparison of Figs. 1 and 2 shows that when $0 < x < 0.30$ the inverse identification problem is *correct*, whereas in the case of $0.30 < x < 0.65$ it is *incorrect*. The problem becomes *essentially incorrect* when $0.66 < x < 1.00$.

The artificial *experimental data are used for to be* obtained least-squares function:

$$Q(b) = \sum_{n=1}^N (y_n - \hat{y}_n)^2, \quad y_n = f(x_n, b), \quad n = 1, \dots, N, \quad (24)$$

where n is the experiment number.

If the experimental data in the separate intervals $0 < x < 0.30$, $0.30 < x < 0.65$, and $0.66 < x < 1.00$ (in the cases of $\pm 5\%$ relative experimental errors) are used, the least-squares function (24) yields horizontal lines (Figs. 3–5) when the inverse problem is correct (Fig. 3), incorrect (Fig. 4), or essentially incorrect (Fig. 5). These results show that when the difference between the exact parameter values and the determined value (the point of the function minimum) is very small, the least-squares method is correct (Fig. 3). In cases of remarkably large differences between the exact parameter values and the minimum of the least-squares function, the inverse problem is incorrect (Fig. 4). In the extreme case when the least-squares function has no minimum, the inverse problem is essentially incorrect (Fig. 5).

The results presented show that in the cases of incorrect inverse problems minimization procedures of least-squares functions do not provide solutions, i.e., *the minimum of the least-squares function is not a solution of the incorrect inverse problem*.

Consider a gradient method for a minimum search. If the iterative procedure is convergent, at each step the difference between the iterative solution and the exact one will decrease towards the minimum of the least-squares function. However, there is a step after some iteration where this difference begins to increase. *The number of this last iteration is an additional condition, the iterative procedure must stop, and the last point is the solution of the incorrect inverse problem*.

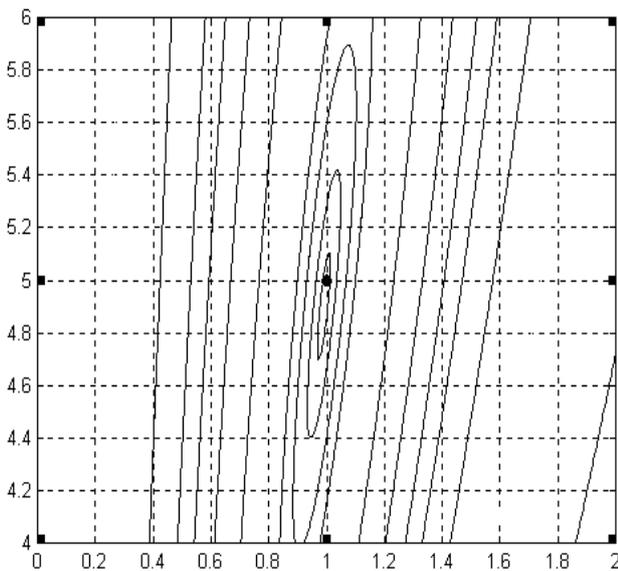


Fig. 3 Horizontals of the least-squares function Q ($n=1-30$; $\Delta\hat{y}[\%]=\pm 5$); circle $b=[1,5]$.

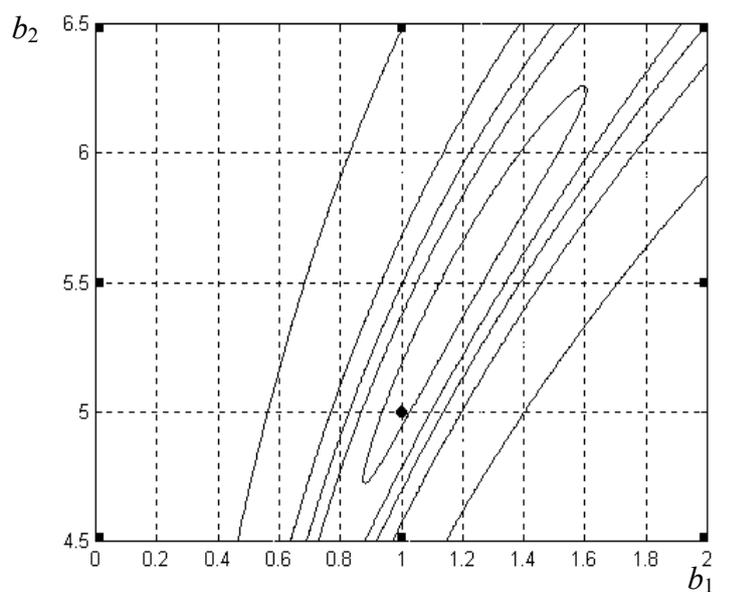


Fig. 4 Horizontals of the least-squares function Q ($n=31-65$; $\Delta\hat{y}[\%]=\pm 5$); circle $b=[1,5]$.

& 8.8. Multiequation models

Problem formulation. Fermentation system modeling. Experimental data. Zero order approximations for the model parameters. First order approximations of the parameters.

The kinetics of many chemical, biochemical, photochemical, and catalytic reactions is very complex, i.e., the kinetic model consists of many equations. The number of parameters of the separate equations is not large, but the total number of parameters is very large [34].

Model parameter identification in these cases is very difficult because of the multiextremal least-squares function or because of the fact that some minima are of ravine

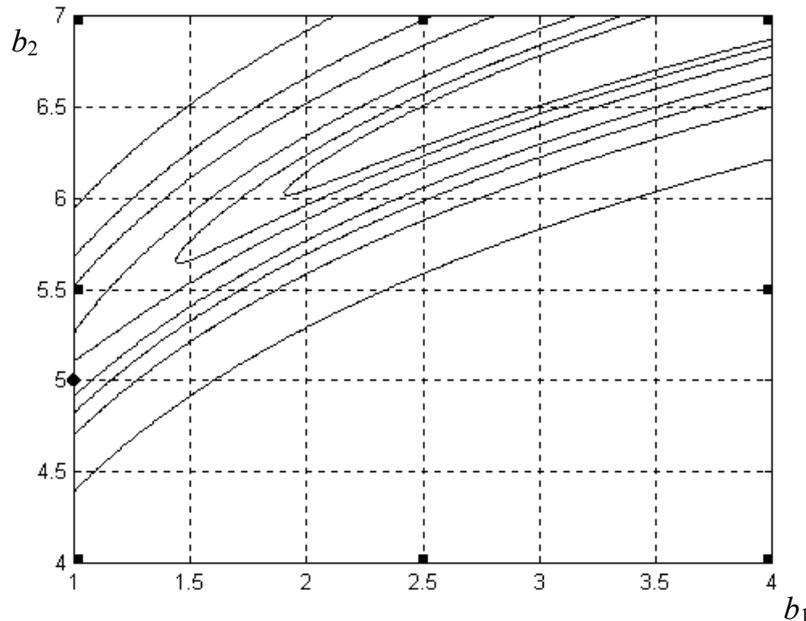


Fig. 5 The horizontals of the least-squares function Q ($n=66-100$; $\Delta y[\%] = \pm 5$); circle $b = [1, 5]$

type. The solution of this problem needs very good initial value approximations for the parameters (in the attraction area of the global minimum) for the minimum searching procedure. This main problem in the multiextremal function minimization is solved on the basis of a hierarchical approach, where the experimental data for the objective functions (concentrations) are represented using polynomial approximations.

& 8.9. Experiment design

Experimental plans of modeling. Parameters identification. Significance of parameters. Models adequacy. Randomized plans. Full and fractional factor experiment. Compositional plans.

The experiment design is used for regularization of the incorrect inverse problem of the model parameter identification

& 8.10. Examples

Regression models. Statistical analysis of the parameter significance and model adequacy of the regression models. Clapeyron and Antoan models. Incorrectness criterion. Exactness increasing of the identification problem solution. Incomplete experimental data cases.

The examples are based on author's papers.

Chapter 9. OPTIMIZATION

& 9.1. Analytical methods

Unconstrained minimization. Constraints minimization. Calculus of variations. Solution of set of nonlinear equations.

& 9.2. Numerical methods

Linear programming. Nonlinear programming.

& 9.3. Dynamic programming and principle of the maximum

Functional equations. Principle of optimality. Principle of the maximum.

& 9.4. Examples

Problem of the optimal equipment change. A calculus of variations problem.

In & 9.1–& 9.4 different optimization methods are presented.

Part 4. CHEMICAL PLANTS SYSTEMS

Chapter 10. SYSTEMS ANALYSIS

& 10.1 Simulation of CPS

Model of CPS. Simulation methods. Sequential-module (hierarchical) approach. Acyclic. Cyclic CPS. Independent contours. Breaking sets. Optimal order.

& 10.2. Simulation at specified outlet variables

Zone of influence. Absolutely independent influence. Independent influence. Combined zones.

& 10.3. Models of separate blocks

Types of modules. Heat transfer. Separation. Chemical processes.

In & 10.1–& 10.3 are presented methods for simulation of chemical plants systems with specified inlet or outlet variables and models of separate blocks.

Chapter 11. SYNTHESIS OF SYSTEMS

& 11.1. Optimal synthesis of chemical plants

Optimization. Optimal synthesis. Main problems. Methods of synthesis. Optimal synthesis of a system for recuperative heat transfer.

Different methods of *optimal synthesis and optimal synthesis of a system for recuperative heat transfer* are presented.

& 11.2. Renovation of CPS

Mathematical description. Mathematical models. Main problems. Renovation by optimal synthesis of CPS. Renovation by introduction of high intensive equipment. Renovation by introduction of high effective processes.

A problem of renovation of chemical plants systems is formulated.

CONCLUSION

The book does not address to most common topic of *distillation column modeling*. The modeling of distillation devices in plate columns use the approach “from plate to plate”: the model equations relevant to each plate are mass and heat balance equations, where the parameters of mass and heat transfer kinetics are replaced by efficiency coefficients. To this end, the thermodynamic liquid-vapor equilibrium at each plate has to be calculated, too. All these parameters depend on the types and concentrations of the components in both the liquid and the vapor phases. The use of iterative methods to solve the model equations at each plate requires very effective thermodynamic methods allowing repeatedly calculations of the liquid-vapor equilibria. The models of distillation plate columns contain many equations, but every equation contains few variables. This leads to model equations with *scarce matrices and to use of special mathematical software to solve them* is necessary. Obviously, the modeling of the distillation plate column is more thermodynamic and mathematical one without involving hydrodynamic background. Solutions of such problems are commonly performed by especially developed codes (ChemCad, for example).

The basic reason of this book is to provide correct formulations and solutions of theoretical problems in chemical engineering by involvement of the modeling and simulation methods allowing to solve practical problems.

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