

Equilibrium Thermodynamic Modeling of Dissipative Macroscopic Systems

B.M. Kaganovich, A.V. Keiko*, and **V.A. Shamansky**

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Melentiev Energy Systems Institute SB RAS, Irkutsk, Russia
Translated from Russian by M.V. Ozerova and V.P. Ermakova

* Corresponding author.
E-mail address: keiko@isem.sei.irk.ru

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Abstract

The possibility is substantiated to model open and closed systems as well as reversible and irreversible processes on the basis of classic equilibrium thermodynamics statements. The consideration is given to new modifications of the model of extreme intermediate states (MEIS) built originally in the mid-1980s. They include constraints on irreversible macroscopic kinetics presented in a thermodynamic form, i.e., without the time variable. MEIS is compared with models of chemical kinetics and irreversible thermodynamics from two viewpoints: (1) the range and versatility of application areas, and (2) the simplicity and self-descriptiveness of computational experiments. The potential of equilibrium modeling is explained on the examples of analysis of chemical systems and hydraulic circuits.

1. INTRODUCTION

The subject of the studies to be discussed is modeling of macroscopic dissipative systems on the basis of the classical equilibrium thermodynamics principles. The modeling tool is the model of extreme intermediate states (MEIS) suggested in the mid-1980s at the Melentiev Energy Systems Institute of Siberian Branch of Russian Academy of Sciences ([Antsiferov et al., 1987](#); [Gorban et al., 2001, 2006](#); [Kaganovich et al., 1989, 1993, 1995](#)) and which, unlike the traditional thermodynamic models intended for search of the final equilibrium point, allows one to study the entire attainability region from a given initial state of the studied system and find a point of partial or complete equilibrium that corresponds to the extreme value of a property the researcher is interested in (for example, concentration of target or harmful products of the processes that may

occur in the system). Various modifications of MEIS have been created over the past years. They include the constraints on irreversible macroscopic kinetics that are written in thermodynamic form (without time variable) (Gorban et al., 2006; Kaganovich, 2002; Kaganovich et al., 2004, 2005a, 2005b, 2006a, 2006b, 2006c).

The equilibrium modeling of reversible and irreversible processes has been a traditional approach for studies in the natural science (and since the mid-19th century in the social and economic sciences as well). The theoretical foundations of this approach were laid by Galileo whose principles of equilibrium, relativity, and inertia showed that the motion could be represented as a sequence of states of rest (equilibrium). The formalized analysis of equilibrium models was mostly carried out in the 18th century, first of all in the works by Euler and Lagrange. Lagrange using his equilibrium equation gave a single mathematical description for the entire Newton mechanics (Lagrange, 1997). Revealing the interrelations between the models of motion and rest resulted in creation of mathematical disciplines and methods related to the solution of variational and extreme problems: the method of multipliers, the theory of optimal equilibrium trajectories—calculus of variations and, later, the modern mathematical theory of extreme equilibrium states—mathematical programming (MP).

In the 19th century the variational principles of mechanics were extended to the analysis of nonconservative, nonholonomic, and nonscleronomous systems. However, the greatest progress in equilibrium modeling in the century before last is certainly connected with the science about equilibrium—the thermodynamics—created by Clausius, Helmholtz, Maxwell, Boltzmann, and Gibbs. Owing to thermodynamics the extreme principle—the principle of entropy increase (the second law of thermodynamics) came into physics. It is more general compared with the principles of virtual work and of least action that were formulated in mechanics. Boltzmann explained this law in two ways (Boltzmann, 1878; Polak, 1987): (1) from the motion trajectory analysis (kinetic) formulated as the H-theorem and (2) from the immediate consideration of possible states of a system and determination of the most probable among them. This explanation facilitated further analysis of interrelations between the models of motion and rest as interrelations between kinetics and thermodynamics. The assumptions on the Markov random behavior of processes of motion toward entropy maximum and on existence of the thermodynamic Lyapunov functions (without using the corresponding terms, of course), which had been made by Boltzmann in his research even before Markov and Lyapunov, became the foundation for the development of equilibrium modeling of diverse processes including irreversible natural ones.

However, with successful penetration of equilibrium models into physics, chemistry, biology, and social sciences in the 20th century, largely because of the need to study various nonlinear effects (self-oscillations,

self-organization), special sciences started to develop: the theory of dynamic systems (Arnold, 1989; Katok and Hasselblatt, 1997), nonequilibrium thermodynamics (Glansdorff et al., 1971; Kondepudi et al., 2000; Prigogine, 1967), synergetics (Haken, 1983, 1988) and others which are intended either completely or partly for the analysis of nonequilibrium irreversible processes. The “seizure” of a considerable part of the application area of equilibrium thermodynamics by other sciences was fostered by two conditions: First, is it due to the contradiction in the Boltzmann explanation of the second law which lies between the following suppositions: on the one hand, reversibility of the individual interactions among micro particles and, on the other hand, irreversibility of the final result of all these interactions in the aggregate (the Boltzmann paradox). Second, it is because of a wide discussion of the mentioned contradiction which unfolded at the turn of the 20th century. Now the opinion that “Classical thermodynamics gives a complete quantitative description of equilibrium (reversible) processes,... for nonequilibrium processes it establishes only the inequalities which indicate the direction of these processes (for example, the Clausius inequality)” (Zubarev, 1998) has become widespread.

The MEIS developers relying on the capabilities of modern computers and computational mathematics started the work which resulted in an essential expansion of the application area of “good, old” classical thermodynamics and in the possibility to study (using thermodynamics) any states on all possible motion trajectories of a nonequilibrium system. In other words, they put forward the goal to use the models of equilibrium not only to determine the directions of irreversible processes but to estimate the attainability of desired and undesired states on these directions.

The works on equilibrium modeling of dissipative systems include four natural components:

1. substantiation of the possibility to describe irreversible processes in terms of equilibrium;
2. creation of quite a representative set of models (modifications of a general equilibrium model) to enable the analysis of a wide range of problems interesting in terms of theory and application;
3. comparison of advantages and disadvantages of equilibrium and nonequilibrium models and differentiation of the areas of their effective applications;
4. solving as many as possible specific problems and analysis of the modeling experience gained.

The above four topics of studies are subsequently discussed below. In creation of MEIS its authors have used as a base the ideas of their colleagues in studies of equilibria—those by Bykov, Gorban, and Yablonsky (Gorban, 1979, 1984, 1986; Yablonsky et al., 1991), as well as works by Horn (1964; Horn and Jackson, 1972), Feinberg (1972, 1999; Feinberg and

Hildebrant, 1997; Feinberg and Horn, 1974), Shinnar (1988; Shinnar and Feng, 1985) and other scientists who dealt with thermodynamic analysis of macroscopic systems kinetics and attainable states and areas research. In development of the latest MEIS modifications intended for modeling of irreversible processes we have utilized the equilibrium trajectory interpretations suggested by Gorban (2007; Gorban and Karlin, 2005; Gorban et al., 2001), which in turn are based on elaboration of Ehrenfest's idea on coarse-graining phase spaces (Ehrenfest, 1959). Besides, the study being presented has been strongly influenced by the works by Gorban on "Model Engineering"—a new scientific discipline formulated in Gorban and Karlin (2005) and further unfolded in Gorban (2007; Gorban et al., 2007). Whereas mathematicians often use formalized statements of problems that were suggested in other sciences and, then, based on the study of mathematical features develop the methods of their solution, the "Model Engineering" supposes the choice of the initial models which are most suitable in terms of both analysis and computation. The research area presented below fits naturally into this new discipline and represents a limit case of reduction, i.e., the transformation of models of motion into models of rest (equilibrium).

2. SUBSTANTIATION OF THE EQUILIBRIUM THERMODYNAMICS CAPABILITIES FOR DESCRIBING IRREVERSIBLE PROCESSES

2.1 The experience of classics

Great experience in equilibrium modeling of irreversible processes was gained even in the classical mechanics. Lagrange, analyzing the specific features of the equilibrium search problems (Lagrange, 1997), stated that if the left-hand side of his equation of the mechanical system equilibrium represents a total differential of some function, then the solution to the problem of determining the equilibrium corresponds to the solution to the problem of finding the extremum of this function. Thus, he assumed that the cases were possible where the equilibria are attained between non-differentiable variables. The assumption on the equilibrium of mechanical systems that was made by him in a formalized description of the Newton mechanics appeared to be more general than the assumption on the conservatism of these systems that was in fact used by Newton and Leibniz for creation of the differential calculus. While the conservatism is a sufficient but not necessary condition of the possibility to describe the system behavior with the help of differential equations, the equilibrium is a necessary condition for admissibility of such a description. Indeed, the nonequilibrium systems cannot be described by intensive macroscopic

parameters which are the functions of states and the notion of the function differential for such systems loses its sense.

In the 19th century the variational principles of mechanics that allow one to determine the extreme equilibrium (passing through the continuous sequence of equilibrium states) trajectories, as was noted in the introduction, were extended to the description of nonconservative systems (Polak, 1960), i.e., the systems in which irreversibility of the processes occurs. However, the analysis of interrelations between the notions of “equilibrium” and “reversibility,” “equilibrium processes” and “reversible processes” started only during the period when the classical equilibrium thermodynamics was created by Clausius, Helmholtz, Maxwell, Boltzmann, and Gibbs. Boltzmann (1878) and Gibbs (1876, 1878, 1902) started to use the terms of equilibria to describe the processes that satisfy the entropy increase principle and follow the “time arrow.”

The principle of entropy increase was explained by Boltzmann in two ways: (1) by analyzing the feasible paths (H-theorem) and (2) by considering the possible attainable states of thermodynamic system and searching for the most probable ones among them. In both explanations he made assumptions on the independence of the considered states from the attainment prehistory and the possibility of their full description on the basis of functions, determined exclusively by the probability of fulfillment, and changing monotonously in the process of transitions from state to state. Using modern terms we can say that Boltzmann presupposed the Markov behavior of processes taking place and the existence of the Lyapunov functions. In turn the possibility to represent the states by a set of quantity related only to the probability of attainment implies that such a state can be interpreted as partial or complete equilibria. Indeed, fixing some quantity (function) can be easily explained by equilibrium of the forces tending to change it. This makes clear both the equilibrium of the Boltzmann trajectories of attaining the entropy maximum and the “equilibrium” of the Boltzmann descriptions of irreversible processes. Boltzmann’s explanations reveal to a great extent the interrelations between thermodynamics and kinetics and the possibilities of thermodynamic equilibrium analysis of kinetic equations, i.e., the equations of motion.

Gibbs in his system explanation of macroscopic thermodynamics (Gibbs, 1876), which had been made before he and Boltzmann formulated the principles of statistical mechanics, relied on the Lagrange equilibrium description of mechanical systems. However, instead of the single Lagrange equilibrium equation, which, according to Krylov, included all Newton mechanics, Gibbs, in order to derive all thermodynamic relationships, used four fundamental equations written for different combinations of independent parameters. Thus, not ordinary but partial differential equations became the mathematical apparatus of thermodynamics unlike mechanics. Owing to thermodynamics, a more general, compared with the

mechanical principles, the extreme principle, i.e., the second law of thermodynamics, appeared in the science. For trajectories it determined the entropy nondecrease instead of action minimization (according to the least action principle) and for states—instead of the virtual work principle the entropy maximum: global for complete equilibrium and conditional (under the condition of braking all the processes that can continue after the given state is attained)—for partial equilibria.

Gibbs conducted the specific studies on the basis of mathematical relations obtained. These studies focused on the complex systems, subjected to the action of various forces (chemical, electrical, gravitational, surface tension, and elastic), and the systems in which there can be substance transformations and phase transitions along with energy transformations. In these studies Gibbs used the method of potentials which supposed equilibrium trajectories of attaining the sought equilibrium states. Gibbs, without using time variable, distinguished the approximate equilibria which settle fast and the final equilibrium which is slowly attained. Not considering the computational problems proper he foresaw the relations between physical stability and uniqueness of the final equilibrium point. In terms of the art of equilibrium modeling of irreversible processes the analysis of the process of hydrogen burning in oxygen (Gibbs, 1876) is particularly impressive. Gibbs, without information on thermodynamic properties of substances and without computers, managed to draw a complete qualitative picture of this process. Discussing potential solutions to the system of equations he explained the decrease in reaction temperature due to water dissociation and the presence of constrained explosibility and ignition regions. Certainly, he could not find the chain mechanism of the considered reaction but the probable results of the studied processes for different conditions under which these processes occur Gibbs showed absolutely correctly.

Discussing the period when the thermodynamic equilibrium descriptions of various irreversible phenomena started one cannot but point out the papers on the theory of electric circuits that are of explicitly thermodynamic character. These had been written by Kirchhoff (1848, 1882) before the works by Clausius and Boltzmann, which made the second law the property of science. In his work (Kirchhoff, 1848)(yet in 1848!) Kirchhoff proved the theorem on minimum heat production in the open passive (without electromotive force sources) electric circuit for the case of isothermal motion of charges. It is easy to ascertain that this theorem represents a particular case of the nonequilibrium thermodynamics theorem on minimum entropy production that was proved by Onsager and Prigogine approximately 100 years after Kirchhoff. In the 1870s Rayleigh suggested the principle of the least energy dissipation (Rayleigh, 1873).

Following the founders of thermodynamics, Planck and Einstein presented vivid illustrations of the possibilities to analyze irreversible

processes in terms of equilibrium. Taking into consideration the condition of equilibrium between substance and radiation and the condition of equilibrium energy transfer, they derived the laws of light radiation, propagation, and absorption. As is known their works were the development and brilliant completion of the radiation thermodynamics works by Kirchhoff and Boltzmann. In the papers dedicated to the Brownian motion Einstein, proceeding from the equations of equilibrium between the Brownian particle and carrying fluid, derived the law of Fick for a principally irreversible process, i.e., diffusion. In the theories of fluctuations and opalescence Einstein “broke into” the fields of applications of modern nonequilibrium thermodynamics. He introduced the notion of partial equilibria (in his terms “incompletely determined in the phenomenological sense of the word”) in the analysis of opalescence phenomenon and used this notion to explain the irreversible process of light diffusion, considering, in fact, a set of attainable states.

In the second half of the 20th century it is precisely the classical equilibrium thermodynamics that became a basis for the creation of numerous computing systems for analysis of irreversible processes in complex open technical and natural systems as applied to the solution of theoretical and applied problems in various fields. The methods of MP, i.e., the mathematical discipline that emerged from the Lagrange interpretation of the equilibrium state, were a main computational tool employed for the studies.

2.2 New interpretations of equilibrium and reversibility

In order to clearly explain the possibilities of describing nonequilibrium irreversible processes in terms of equilibrium it is certainly necessary to define quite accurately the notions of equilibrium and reversibility, nonequilibrium and irreversibility. It is clear that their interpretation, as well as the interpretation of other scientific notions, changes with the development of respective theories, models, and methods. Since the work touches upon the issues of interrelations between the competing models in a historical profile it is desirable that the appropriateness of various interpretations of the said notions be assessed in this profile. Making no pretence of the systematic presentation of the issue we will only touch upon some points that are important for understanding the text¹ below.

Mechanics emerged as a science studying reversible processes that are symmetrical relative to time. Euler, in his “thesis” on the least action

¹ A rich material for the comprehension of the evolution of basic notions in the course of development of variational principles and principles of equilibrium and extremality in physics can be found in remarkable books by L.S. Polak (1987, 1960).

principle, wrote that this principle did not hold for the systems with friction. Lagrange took the equilibrium equation as a basis for the formalization of mechanics and simultaneously made equilibrium a most important property of mechanical systems as well. This property appeared to be essentially more general than conservatism which is still believed to be the main feature that determines the obedience of studied system to the classical mechanics laws. Relying on the Lagrange idea of equilibrium the mechanics (Hamilton, Gauss, Ostrogradsky et al.) started to gradually expand the area of their science applications to nonconservative systems, allowing, obviously, some analysis errors. Boltzmann related the possibilities of equilibrium descriptions with the possibilities of describing irreversible processes. The Boltzmann trajectories of motion to the entropy maximum that meet the conditions of Markov behavior of the studied processes and the existence of the Lyapunov functions, as well as the Euler–Lagrange–Hamilton trajectories, can be represented by a continuous series of equilibrium states. It is convenient to characterize these states (points on trajectories) with the help of local potentials and to describe the trajectories themselves by autonomous equations of the form

$$\dot{x} = f(x).$$

However, unfortunately, the definitions of equilibrium processes that relate them with the notion of irreversibility did not arise from the Boltzmann description of irreversible processes by equilibrium trajectories. This was possibly to some extent a result of the discussion related to Boltzmann’s paradox, mentioned in the “Introduction.” To the contrary, in the 20th century the idea about the identity of equilibrium and reversible processes grew strong. In the workbooks on macroscopic thermodynamics equilibrium processes were interpreted as infinitely slow, in the course of which, at each time instant, equilibrium has time to settle within the system and between the system and the environment. If to implement such a process after attaining the final state in the reverse direction to the initial state, nothing will change in the system and in the environment, i.e., the results of the direct process will appear to be reversible. Such interpretation of equilibrium processes fits harmoniously into the theories and models associated with the efficiency analysis of various technical systems. Indeed, any deviation of the system parameters from the equilibrium values leads to additional potential differences between the system and the environment and additional work or heat loss, i.e., to a decrease in the working (target) process efficiency.

However, the presented interpretation of equilibrium processes turns out to be unsatisfactory for the analysis of possibility to use equilibrium descriptions for irreversible phenomena. The interpretation of interrelations between equilibrium and reversibility that was given by

Gorban et al. in their works (Gorban, 2007; Gorban et al., 2001, 2006) seems to be more comprehensive for our discussion. The works unfolded the idea of the Ehrenfests (1959) on the isolated system tending toward the Boltzmann equilibrium trajectory as a result of “agitations.”

Figure 1, taken with some changes from Gorban et al. (2001), illustrates the processes that occur in the isolated systems where the number of particles is so large that the statistical regularities take place. Closed curves represent the levels of entropy S . Dotted straight lines show the sets of states with constant values of macroscopic parameters. The contact points of the curves with straight lines are the equilibrium points that meet the equilibrium distributions. At these points entropy has its maximum value on a corresponding tangent. The set of these points forms the equilibrium trajectory S^* , along which the system moves toward the point of global maximum of entropy S^{\max} . Curve arrows stand for isentropic (reversible) processes that occur as a result of reversible (elastic) interactions of particles. Straight arrows show the system “agitations” that are explained by deviations of part of the interactions from reversibility and that push the system toward an equilibrium trajectory.

According to the given interpretation of the equilibrium processes they differ principally from the reversible ones and represent at the limit (with the intervals between agitations and, hence, the distances $S_1^* - S_2^*$, $S_2^* - S_3^*$, etc., tending to zero) a continuous sequence of local entropy maxima.

The above statement on the identity of equilibrium and reversible processes is also consistent to some extent with the Gorban interpretation only in the assumption on the limiting coincidence of nonequilibrium states, located on the trajectories $S = \text{const}$, with equilibrium ones—on the Boltzmann trajectory. In this case the entire set of possible states in Figure 1 is reduced to the curve $S_1^* - S^{\max}$.

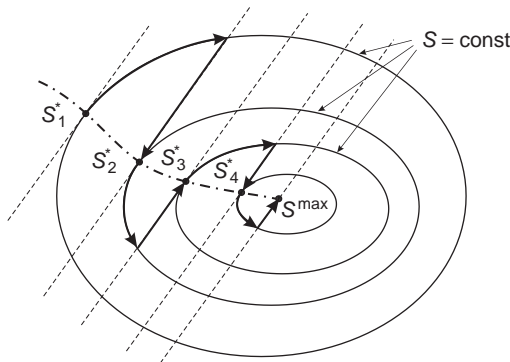


Figure 1 Dynamics of a system with periodic agitation.

It will apparently be possible to provide coordination between the capabilities of equilibrium models in (1) the analysis of perfection of the energy and substance transformation processes and (2) the analysis of different irreversible phenomena on the basis of dual interpretation of equilibrium processes as being both reversible and irreversible at a time. In the first case they are convenient for interpretation as reversible in terms of the system interaction with the environment and in the second case—as irreversible in terms of their inner content according to Gorban. It is clear that to explain the dual interpretation it is necessary to extend the analysis by Gorban to the nonisolated thermodynamic systems with other characteristic functions to be used along with entropy.

Concurrently with the joint analysis of the notions “equilibrium” and “irreversibility” we must determine in our discussion the meaning of and the extent to which the notion “nonequilibrium” and word combination “far from equilibrium” affect the requirements for the models employed. There are three meanings assigned to the indicated word combination in different contexts in Gorban (1984). Firstly, it is assigned to the systems in which distribution of some microscopic variables (for example, energy of particle translational motion) differs from the equilibrium distribution so much that the evolution of macroscopic variables cannot be described by the first-order differential equations (autonomous, if the environment is stationary). Secondly, the closed system with equilibrium environment (or isolated one) is supposed to be far from the equilibrium if its relaxation from the given state toward a small neighborhood of the equilibrium continues for a long time, during which various nonlinear effects can be observed (self-oscillations, spatial ordering, etc.). The third use of the word combination “far from equilibrium” refers to the open systems that exchange mass and energy with the environment which is not in the state of thermodynamic equilibrium.

Normally the apparatus of equilibrium thermodynamics can be used for the remoteness in the second and third sense and a corresponding choice of space of variables, though in each specific case this calls for additional check. Because for the spaces that do not contain the functions of state (in the descriptions of nonequilibrium systems these are the spaces of work–time or heat–time) the notion of differential loses its sense, and transition to the spaces with differentiable variables requires that the holonomy of the corresponding Pfaffian forms be proved. The principal difficulties in application of the equilibrium models arise in the case of remoteness from equilibrium in the first sense when the need appears to introduce additional variables and increase dimensionality of the problem solved.

In some cases where it is impossible to strictly substantiate the feasibility of equilibrium descriptions we have to be content with equilibrium approximations. Such approximations are considered below in Section 2.4.

2.3 Equilibrium interpretations of the basics of nonequilibrium thermodynamics

We can specially show that the main principles of nonequilibrium thermodynamics (the Onsager relations, the Prigogine theorem, symmetry principle) and other theories of motion (for example, theory of dynamic systems, synergetics, thermodynamic analysis of chemical kinetics) are observed in the MEIS-based equilibrium modeling. In order to do that, we will derive these statements from the principles of equilibrium thermodynamics.

First of all relying directly on the second law we will try to give the interpretation of the Prigogine theorem. Taking into account that the traditional variables of equilibrium thermodynamics are the parameters of state and, wishing to reveal the formalized relations between both thermodynamics, let us consider two situations sequentially: (1) when some parameters of interaction that hinder the attainment of final equilibrium between the open subsystem and other parts of the isolated system that contains this subsystem are set; (2) when flows are taken constant for the flow exchange between the open subsystem and the environment. It is obvious that both situations can be reduced to the case of fixing individual forces which is normally considered in the nonequilibrium thermodynamics.

Studying the first situation let us assume, for example, that temperature T and pressure P are set. The state of the final equilibrium of the isolated system corresponds to

$$\max \left[S_{\text{is}} = S_{\text{os}} + \frac{H_{\text{os}}^{\text{in}} - H_{\text{os}}}{T} + \text{const} \right] = S^{\text{eq}}, \quad (1)$$

where H —enthalpy; indices “is,” “os,” “in,” and “eq” refer to isolated system, open subsystem, initial state, and final equilibrium, respectively. The second term in the right-hand side of the equality in square brackets stands for entropy transferred from the open subsystem to the environment.

Taking into account that

$$S_{\text{os}} = \frac{H_{\text{os}} - G_{\text{os}}}{T},$$

where G —the Gibbs energy, and multiplying (1) by T , we obtain a transformed criterion of equilibrium

$$\max [TS_{\text{is}} = -G_{\text{os}} + H_{\text{os}}^{\text{in}}].$$

Since $H_{\text{os}}^{\text{in}}$ is constant, we find that $\max S_{\text{is}}$ corresponds to $\max(-G_{\text{os}})$ and, hence, to $\min G_{\text{os}}$. In turn, attainment of the minimum possible value of the Gibbs energy means the largest feasible useful transformation and the minimum dissipation of the total energy, i.e., the minimum (in this case a zero one) entropy production in the open subsystem.

If owing to the external conditions the point of final equilibrium in this subsystem is not attained and the subsystem passes into one of possible partial equilibria the change in the Gibbs energy reduces as compared to $(G^{\text{in}} - G^{\text{eq}})$ but remains maximum for the newly established conditions, which is explained by the reasoning similar to those presented above. Accordingly, the entropy production appears to be minimum.

Derivation of the expression for the minimum production of S in the systems with constant T and V (volume) differs from the one above only by replacement of enthalpy by internal energy (U) and the Gibbs energy by the Helmholtz energy in the equations. When we set S and P or S and V dissipation turns out to be zero according to the problem statement. In the case of constant U and V or H and P , the interaction with the environment does not hinder the relaxation of the open subsystem toward the state $\max S_{\text{os}}$.

Let us discuss the second situation taking the isolated system shown in Figure 2 as an example. The open system (os) exchanges flow J with the environment through boundaries 1 and 2. The constant value of the flow is maintained owing to the source of thermodynamic potential μ_1 situated to the left of 1. With the increasing energy dissipation and constant μ_1 the value of thermodynamic potential on boundary 2 decreases (to do the same amount of the effective work (useful effect) requires greater difference in potentials).

Entropy production in the isolated system (is) can be expressed by the equation

$$\Delta S_{\text{is}} = \int_{T(\mu_1)}^{T(\mu_2)} \frac{\varphi(\mu)}{T(\mu)} dT + \int_{T(\mu_2)}^{T^{\text{eq}}} \frac{\varphi(\mu)}{T(\mu)} dT, \quad (2)$$

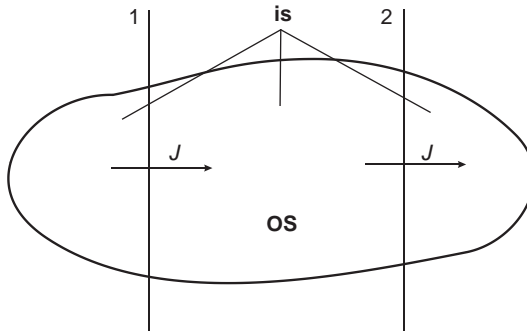


Figure 2 Isolated system (is) and open subsystem (os) with minimum entropy production.

where the first and second integrals in the right-hand side denote productions of S in os and part of its environment located to the right of boundary 2, respectively (production of S to the left of boundary 1 can be assumed constant). With decrease in the difference $(\mu_1 - \mu_2)$ the second integral increases faster than the first decreases. Indeed, to the right of boundary 2 entropy is generated at lower values of thermodynamic potential than in os. However, the flow with a larger value of μ heats a certain amount of substance to the higher temperature than the flow with lower μ . Therefore, if the infinitely small change in the potentials of these flows occurs the dissipation of energy and, hence, entropy generation

$$J \frac{d\mu}{T} = \frac{dq}{T}$$

appears to be lower for larger μ , i.e.,

$$\frac{\partial(\Delta S)}{\partial \mu} \leq 0. \quad (3)$$

From this follows the tendency of the isolated system toward the distribution of energy dissipation among its parts so that the share of the total dissipation in the open system with fixed flows was ultimately small.

The simplest and vivid example of such a distribution of entropy generation is the case of fixed heat flow from the open subsystem to the environment. For this case equality (2) takes the form:

$$\Delta S_{\text{is}} = \int_{T_1}^{T_2} \frac{dq}{T} + \int_{T_2}^{T^{\text{eq}}} \frac{dq}{T}.$$

It is clear that even at partial transformation of heat into work in open subsystem the maximum entropy of the isolated system will be reached at the largest value of T_2 .

Probably the presented equilibrium interpretation of the Prigogine theorem cannot be considered as its strict or general proof. At the same time this interpretation reveals the possibilities to automatically observe the principle of the least entropy production at equilibrium modeling of a wider spectrum of physicochemical processes.

From a satisfactory, to a certain extent, explanation based on the second law of the Prigogine theorem we can pass to an absolutely macroscopic explanation of the Onsager reciprocal relations by changing the order of proofs accepted in the nonequilibrium thermodynamics (in the nonequilibrium thermodynamics the Prigogine theorem is derived from the Onsager relations).

Let us consider an elementary system with two acting forces F_1 and F_2 and two flows J_1 and J_2 caused by them. If the forces are not constant then in the equilibrium state both the flows and the Onsager kinetic coefficients— L_{11} , L_{12} , L_{21} , L_{22} —turn out to be equal to zero. The equality to zero of these coefficients follows from the absence of flows at the initial moment of applying the forces that cause deviation of the system from its equilibrium. If either force (for example, F_2) is fixed then the equalities hold:

$$(\Delta S)^{\text{eq}} = L_{11}F_1^2 + (L_{12} + L_{21})F_1F_2 + L_{22}F_2^2, \quad (4)$$

$$\frac{\partial(\Delta S)^{\text{eq}}}{\partial F_1} = 2L_{11}F_1 + L_{12}F_2 + L_{21}F_2 = 0,$$

and

$$L_{11}F_1 + L_{12}F_2 = J_1 = 0,$$

since J_1 is caused by the nonfixed force and is absent at equilibrium.

Hence,

$$L_{11}F_1 + L_{21}F_2 = 0$$

and

$$L_{12} = L_{21}. \quad (5)$$

It is obvious that using the properties of homogeneity and additivity of thermodynamic functions it is easy to obtain the Onsager relations in a general form

$$L_{jk} = L_{kj}.$$

We have managed to interpret the theorem of minimum entropy generation and the Onsager relations on the basis of the second law; therefore, we can additionally explain the Curie symmetry principle in terms of equilibrium. Let us suppose that far from the equilibrium between flows and forces there are nonlinear relationships

$$J_{jk} = L_{jk}F_k^\alpha \quad (6)$$

(a change in the form of this relationship does not affect the result of the reasoning below). Then for the case of two forces and two flows

$$\Delta S = L_{11}F_1^{\alpha+1} + L_{12}F_1^\alpha F_2 + L_{21}F_1 F_2^\alpha + L_{22}F_2^{\alpha+1},$$

$$\frac{\partial(\Delta S)}{\partial L_{12}} = F_2^\alpha F_1 \quad \text{and} \quad \frac{\partial(\Delta S)}{\partial L_{21}} = F_1^\alpha F_2.$$

It is clear that equality (5) with available relationship (6) will be attained only in the limit at the tendency of a toward unity near the point “eq.” Hence, in the course of relaxation toward equilibrium the number of system symmetry elements should increase (or at least not decrease).

In order to reveal the generality of equilibrium thermodynamic models it seems to be useful to interpret the least action principle (PLA) as a corollary to the second law. Each equilibrium flow that occurs in the isolated system between states (or time instants) 1 and 2 can be considered as an open subsystem. At any infinitely small time interval energy dissipation in this subsystem takes minimum possible value (the flow goes through a continuous sequence of equilibrium states). Accordingly, integration with respect to time from the initial to the final state determines the minimum of a quantity with a dimension of the product of energy by time, i.e., action. Historical interrelations between the PLA and the second law of thermodynamics and futile efforts of deriving the latter from the former are considered in detail in Polak (1960).

Besides, let us note the automatic observance (certainly with correctly set initial data) and, hence, needlessness of the formalized descriptions in equilibrium modeling of such important regularities of macroscopic system behavior as the Gibbs phase rule, the Le Chatelier–Brown principle, mass action laws, the Henry law, the Raoult law, etc.

2.4 Equilibrium approximations

In Section 2.2 we mentioned the impossibility to strictly substantiate the equilibrium descriptions for all cases of life and the need to apply equilibrium approximations in some situations. The vivid examples of the cases, where the strongly nonequilibrium distributions of microscopic variables are established in the studied system and the principal difficulties of its description with the help of intensive macroscopic parameters occur, are fast changes in the states at explosions, hydraulic shocks, short circuits in electric circuits, maintenance of different potentials (chemical, electric, gravity, temperature pressure, etc.) in some spatial regions or components of physicochemical composition; interaction with nonequilibrium and sharply nonstationary state environment.

A known method of overcoming these difficulties and passing to the equilibrium terms is the introduction of additional variable forces balancing the differences in potentials in the description of the modeled phenomenon. A good example of using similar method is given in Einstein’s paper related to the quantum theory of radiation (Einstein, 1914) in which he presented a chemically homogeneous gas as a mixture of different components that are characterized by their values of mole energy, found the law of energy distribution among them from the condition of chemical

equilibrium, and relying on this distribution, derived the Planck formula for the monochromatic radiator. Einstein's derivation demonstrates the efficiency of equilibrium descriptions and also shows nontriviality of the method of their construction. Indeed, the constraints on attainability of the final complete equilibrium can be caused both by different processes of transfer or chemical transformations within the system and by specific features of the system interaction with the environment. The diverse conditions of nonequilibrium appearance make it hardly possible to imagine the development of a single algorithm for transition from nonequilibrium to equilibrium modeling.

Along with the difficulties associated with searching for a principal idea of this algorithm there are complications related to the "damnation of dimension." A rapidly growing dimension of the solved problem certainly affects the time and stability of the computational process convergence, however, even to a greater extent, it affects the volume of the initial data preparation and difficulty to formalize the numerous constraints to be set. Unfortunately, so far the authors have managed to overcome the problems of equilibrium approximations only in solving several specific problems. Some of them are discussed in Sections 4 and 5.

3. MODELS OF EXTREME INTERMEDIATE STATES

3.1 MEIS with variable parameters

Currently the authors are developing three classes of models of extreme intermediate states (MEIS): (1) with variable parameters; (2) with variable flows, and (3) those describing spatially inhomogeneous systems. All these classes of the models are formulated and analyzed in terms of MP, which, in the authors' opinion, can be defined as a mathematical theory of equilibrium states. It is natural to start the analysis of the created modifications with the MEIS with variable parameters, which is the closest in character to the traditional equilibrium thermodynamics models.

With fixed T , P , and initial composition of the components y of physicochemical system this model will take the form:

find

$$\max \left[F(x) = \sum_{j \in J^{\text{ext}}} c_j x_j \right] = F(x^{\text{ext}}) \quad (7)$$

subject to

$$Ax = b, \quad (8)$$

$$D_t(y) = \{x : x \leq y\}, \quad (9)$$

$$\varphi_r(x_r, z_r) \leq \psi_r, r \in R^{\text{lim}}, \quad (10)$$

$$G(x) = \sum_j G_j(x)x_j, \quad (11)$$

$$x_j \geq 0, \quad (12)$$

where $x = (x_1, \dots, x_n)^T$ —a vector of mole quantities of the system components; the vector of the initial composition $y \subset x$; c_j —a coefficient, ranging the property of the j -th component x (usefulness or harmfulness) of interest for a researcher; J^{ext} —a set of indices of the components, with the extreme concentration of their mixture to be determined; A —the $(m \times n)$ matrix of element contents in the system components; b —a vector of mole quantities of elements; $D_t(y)$ —the region (the set) of thermodynamic attainability from y ; φ_r and ψ_r —the constrained kinetic function of the r -th component x or (and) any other parameter z_r and its limit value, respectively; R^{lim} —a set of indices of constraints on macroscopic kinetics; G and G_j —the Gibbs energies of the system and its j -th component; x^{ext} —the point with extreme value of the system property of interest to a researcher. The sign \leq in expression (9) is understood in the thermodynamic sense suggested by Gorban: $x \leq y$, if it is possible to pass from y to x along the continuous trajectory, along which $G(x)$ does not monotonously increase.

The objective function (7) in accordance with the general purpose of MEIS that was mentioned in the introduction, i.e., finding the state with extreme value of the system property of interest to a researcher, in this case determines the extreme concentration of the given set of substances. Equality (8) represents a material balance. Expression (9) represents the region of thermodynamic attainability from point y . It is obvious that in $D_t(y)$ the inequalities are satisfied: $G(x^{\text{eq}}) \leq G(x) \leq G(y)$, where x^{eq} —the final equilibrium point. Inequalities (10) are used to set the constraints on macroscopic, including irreversible, kinetics. Presence of this constraint makes up principal difference of the model (7)–(12) from previous modifications of parametric MEISs. The choice of equations for the calculation of individual terms under the sign of sum in the right-hand side of equality (11) depends on the properties of the considered system.

Writing model (7)–(12) we use two main assumptions following from the previous text:

1. all points of the set $D_t(y)$ are the points of equilibria; partial equilibria within $D_t(y)$ possess all the properties of the complete final equilibrium provided any processes to occur in them are inhibited.

2. each of these points can be attained from y along the equilibrium, in a general case irreversible, trajectory along which the condition of monotonous change in the characteristic thermodynamic function is met (as applied to the described case—the Gibbs energy).

An important specific feature of model (7)–(12) consists in the fact that, unlike the models of chemical kinetics, nonequilibrium thermodynamics or equilibrium thermodynamics, in the case of applying the law of mass action, this model, does not employ the complete representation of mechanism (a list of stages) of the studied process (chemical reactions and transfers of energy, impulses, substance, charges) but sets the lists of components of physicochemical composition x and parameters z . The need to indicate individual stages may arise only in the description of constraints (10) on the rates of change in some components of the vectors x and z . Eliminating or considerably reducing the list of stages in the model description and retaining in the description only the list of sought variables make essentially easier the preparation of initial information, which is particularly important for solution of the applied large-dimensional problems.

Note that when setting the list x_j , $j = 1, \dots, n$, the authors deviate from the classical Gibbs definition, understanding by the system components not individual substances but their quantities contained in a certain phase. For example, if the water in reaction mixture is in gaseous and condensed phases, its corresponding phase concentrations represent different parameters of the studied system. Such expansion of the space of variables of the problem solved facilitates its reduction to the problems of convex programming (CP).

System (7)–(12) does not include the formalized condition of meeting the Gibbs phase rule. This is related to the fact that this rule may appear to be untrue, for example, when finding part of the studied system components in the states close to critical, however, if it is true it should be observed automatically (with accuracy depending on the errors in calculations) due to meeting the equilibrium and conservation principles. The requirement for equality of phase potentials is also not set in the MEIS version presented due its obvious automatic satisfiability. The mentioned “omissions” in the description of the modeled phenomena reflect general advantages of the extreme approach that are well known in physics and reveal additional advantages of the equilibrium models discussed.

Along with the model with fixed T and P the authors also suggested MEIS versions for other classical conditions of interaction between systems and the environment, i.e., for fixed: T and V , S and V , S and P , U and V , H and P . The model has been created to simultaneously search for x^{ext} and optimize the initial set of reagents y .

The MEIS written in form (7)–(12) does not determine unambiguously the character of the mathematical problem solved, whether it belongs to convex or concave programming. However, to date when specifying this model as applied to the solution of numerous theoretical and applied problems it has always been reduced to the CP problem, which facilitated enormously to the development of computational algorithms and the computational experiments.

The examples of specifying the representation of individual expressions in system (7)–(12) and application of MEIS with variable parameters are presented in Section 5.

3.2 MEIS with variable flows

Development of the “flow” MEIS with the form reminding the models of nonequilibrium thermodynamics seems to be a very promising direction in equilibrium modeling of physical and chemical systems. Application of these models opens prospects for simpler analysis and solution of many complex problems related to the calculations of processes considered to be irreversible in principle. Certainly the flows in MEIS are interpreted statically as the coordinates of states. Thermodynamic interpretations are naturally extended to the kinetic coefficients that relate these flows with forces. Correctness of such interpretations is confirmed by the application of MP, being the theory of equilibrium states, as the terms for MEIS description.

The flow modifications created can be divided into two groups: (1) the models of systems with real flows that are distributed on the schemes in the form of graphs and (2) the models of systems with conditional flows that undergo some certain chemical transformations or transfer processes. The modifications of the first group, in turn, are divided into parts that are related, respectively, to stationary and nonstationary flow distribution. The main object of modeling on the basis of the first group of the flow MEIS are hydraulic (heat-, water-, oil-, gas supply, etc.) (Gorban et al., 2001, 2006; Kaganovich et al., 1997) and electric networks. However, there can be other applications of such models as well. For example, Kaganovich et al. (1997) show their use to describe the distribution of harmful substances in the vertical column of the atmospheric air.

MEIS of stationary isothermal flow distribution in a closed (without sources and sinks) multi-loop hydraulic circuit has the form:

find

$$\max \sum_{i=1}^n P_i^{\text{br}} x_i \quad (13)$$

subject to

$$Ax = 0, \quad (14)$$

$$\sum_{i=1}^n P_i^{\text{mov}} x_i - \sum_{i=1}^n P_i^{\text{br}} x_i = 0, \quad (15)$$

$$\varphi_r(x) \leq \psi_r, \quad r \in R^{\text{lim}}, \quad (16)$$

$$P_i^{\text{br}} = f_i(x_i), \quad i = 1, \dots, n. \quad (17)$$

In (13)–(17) P_i^{br} and P_i^{mov} —friction pressure loss and effective pressure (created by a pump or gravitational), respectively, on the i -th branch of the circuit; $x = (x_1, \dots, x_n)^T$ —the vector of volumetric flows in branches; $A = [a_{ij}]$ —the $(m-1) \times n$ —matrix of incidence of independent nodes and branches; $a_{ij} = 1$, if the flow in the i -th branch in accordance with the direction set in advance nears the j -th node; $a_{ij} = -1$, if the i -th flow goes from the j -th node, and $a_{ij} = 0$, when node j does not belong to the branch i ; $j = 1, \dots, m$; functions φ_r and their limiting values ψ_r in this case can be determined by setting values of regulated pressures at individual nodes or flow rates in the individual branches of the circuit.

The objective function (13) representing the total dissipation of kinetic energy of the flows at isothermal motion of fluid is proportional to the entropy production in the circuit and its transfer to the environment, i.e., proportional to the entropy accumulated by the isolated system (interconnection of the circuit and environment). The matrix equation (14) describes the first Kirchhoff law, which, as applied to hydraulic circuits, expresses the requirement for mass conservation. Equality (15) represents a balance between the energy generated and consumed in the circuit.

Using system (13)–(17) it is possible to describe the hydraulic circuits with lumped, with regulated, and with distributed parameters (Gorban et al., 2001, 2006). It stands to reason that depending on the type of circuits the types of functions $f_i(x_i)$ in equalities (17) (closing relations) will change. In Gorban et al. (2001, 2006) and Kaganovich et al. (1997) system (13)–(17) was modified as applied to the description of flow distribution in the heterogeneous circuits in which flows in branches undergo chemical transformations and phase transitions. In the analysis of such circuits the extreme thermodynamic approach reveals to a greater extent its advantages relative to the use of closed systems of equations. In particular, it turns out to be the simplest for practical implementation.

Using model (13)–(17), it is possible to identify the extremality criteria for different cases of interaction between the circuit and environment and reveal the reducibility of the problem of calculating the stationary flow distribution to the CP problem. Let us suppose that for the circuit with lumped parameters the closing relations have the form:

$$P_i^{br} = \gamma_i x_i^\beta, \tag{18}$$

where γ_r —a constant coefficient and exponent $\beta \geq 1$. In this case the Lagrange function of the circuit is

$$L = \sum_{i=1}^n \gamma_i x_i^{\beta+1} - \sum_{j=1}^{m-1} \lambda_j \sum_{i \in I_j} a_{ij} x_i + \lambda_m \left(\sum_{i=1}^n \gamma_i x_i^{\beta+1} - \sum_{i=1}^{n1} P^{mov} x_i \right), \tag{19}$$

where λ_j and λ_m —the Lagrange multipliers; I_j —a subset of branches incident to node j .

It can be shown (Gorban et al., 2001, 2006) that the second partial derivatives of L with respect to x_i

$$\frac{\partial^2 L}{\partial x_i^2} = -(\beta + 1) \gamma_i x_i^{\beta-1} \leq 0. \tag{20}$$

Hence, the solution to problem (13)–(17) in this case corresponds to the maximum $L = f(x)$ and maximum of the objective function (13). The possibility of existence of the maximum point at the function convexity and nonlinearity of the system of constraints is illustrated in Figure 3a.

The extreme thermodynamic model of passive circuit (without effective pressure sources) is obtained by transforming model (13)–(17). Toward this end let us mentally isolate a passive fragment with n_p

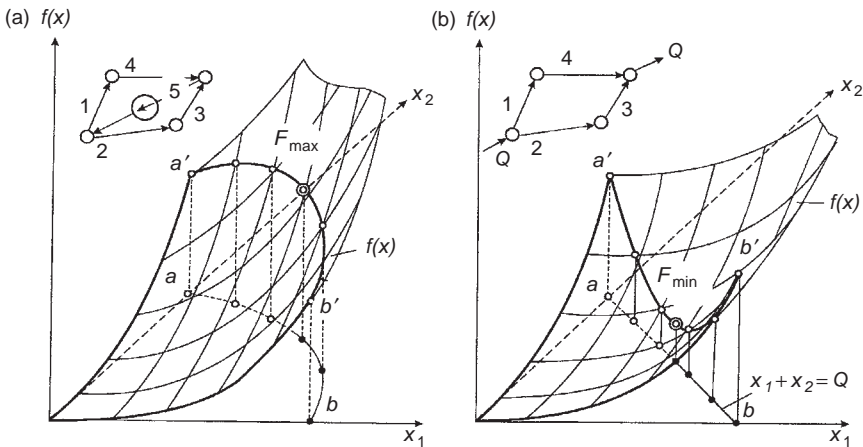


Figure 3 An objective function and extreme points on nonlinear (a) and linear (b) set of constraints.

branches and m_p nodes from the active circuit. The variables $x_i (i = n_{p=1}, \dots, n)$ on the branches of the rejected circuit part include flows that determine the directions and magnitudes of sources and sinks $Q_j (j = 1, \dots, m_p)$ in the isolated fragment. Then condition (15) is excluded and model (13)–(17) is replaced by the model that corresponds to the Kirchhoff theorem of minimum heat production (Kirchhoff, 1848):

$$\begin{array}{l} \text{find} \\ \left. \begin{array}{l} \min \sum_i P_i^{\text{br}} x_i \\ Ax = Q, \quad P_i^{\text{br}} = \gamma_i x_i^\beta, \quad i = 1, \dots, n_p. \end{array} \right\} \end{array} \quad (21)$$

In this case the second derivatives of the Lagrange function

$$L = \sum_{i=1}^{n_p} \gamma_i x_i^{\beta+1} - \sum_{j=1}^{m-1} \lambda_j \left(\sum_{i \in I_j} a_{ij} x_i \right)$$

with the above supposition on the form of closing relations

$$\frac{\partial^2 L}{\partial x_i^2} = \beta(\beta + 1) \gamma_i x_i^{\beta-1} \geq 0. \quad (22)$$

Hence, the extremum $L(x)$ is the point of minimum. Thus, the problem of entropy maximization is transformed into the problem of heat minimization; and the Kirchhoff and Prigogine theorems result from the extension of the second law to the passive isothermal circuits. The graphical interpretation of problem (21) is given in Figure 3b.

In the work by Gorban et al., (2001, 2006) the extremality criteria and corresponding MEIS modifications were presented for different cases of interaction between hydraulic circuits and the environment.

Let us write the model of nonstationary flow distribution as applied to the problem of search for the maximum pressure rise at a given node of the hydraulic circuit at a fast cut off of the flow in one of its branches (or the largest drop at pipe break) provided that there is an isothermal motion of viscous incompressible fluid subjected to the action of the pressure, friction, and inertia forces (Gorban et al., 2006).

find

$$\text{ext} \left(P_s = e P_m + P_q^{\text{br}} - P_q^{\text{mov}} \right) \quad (23)$$

subject to

$$Ax^k = 0, \quad (24)$$

$$\sum_{i=1}^n P_i^{\text{mov}} x_i^k - \sum_{i=1}^n P_i^{\text{s.br.k}} x_i^k l_i = 0, \quad (25)$$

$$D_i(y) = \left\{ x^k : \sum_{i=1}^n P_i^{\text{br.k}} \left(\gamma_i^{\text{br}} P_i^{\text{s.br.k}} - \gamma_i^{\text{fr}} (x_i^k)^2 \right) \geq 0 \right\} \quad (26)$$

$$\Phi_r(x_r^k) \leq \Psi_\rho, \quad r \in R^{\text{lim}}, \quad (27)$$

$$P = eP_m - \bar{A}_q^{-1} (P_q^{\text{br}} - P_q^{\text{mov}}), \quad (28)$$

where P —a vector of pressures at nodes; P_m —the fixed pressure at node $j = m$; $P_i^{\text{s.br}}$ —the specific (per length unit) pressure loss; P_q^{br} and P_q^{mov} —vectors of pressure losses and effective pressures in branches of the “circuit tree” q comprising the paths from nodes $j = 1, \dots, m-1$ to the node m , \bar{A}_q^{-1} —a matrix of “paths” corresponding to this tree, which is obtained by inversion of the submatrix of matrix A for branches which belong to this tree; γ_r^{br} and λ_i^{fr} —coefficients; e —a unit vector; s —an index of the node for which we find the extreme pressure; k —the index of computational process iteration.

Further development of MEIS for nonstationary flow distribution is related to the possibility of many new problem statements and their attractiveness. The obvious objects to be studied in the future are changes and deviations from the required values of sources and sinks at nodes and flow rates in the branches of circuits under normal and emergency operating conditions. The problem of calculating the emergency operating conditions seems to be the most important. The emergency operating conditions result from the disturbances that are too fast for the friction forces to manifest themselves, and we have to consider the propagation of shock waves in the ideal fluid. The starting points for the thermodynamic description of this problem can be the “equilibrium” derivation of the formula for hydraulic shock in an individual pipe (Gorban et al., 2001, 2006) and the work of several authors on modeling of hydraulic shocks in pipeline systems on the basis of traditional (nonthermodynamic) methods of hydraulic circuit theory (for example, Balyshev and Kaganovich 2003; Balyshev and Tairov 1998).

The experience gained with construction of the flow models of hydraulic systems was applied to create the models that are based on the graph representation of mechanisms of chemical reactions (sets of elementary reactions) and transfer processes. In the work by Kaganovich et al. (1989, 1993) and Kaganovich and Filippov (1995), the advantages of setting a list

of substances (components of a system) versus setting mechanisms as initial information have been discussed. Setting of substances appears to be immeasurably simpler, for example, in the analysis of coal combustion processes where the list of reactions includes thousands of units. However, in many cases, the use of the mechanism notion can be useful either for a quite complete elucidation of specific features of the studied process or for the choice of the analyzed mechanism which can be implemented by selecting catalysts or by specially arranging the course of reactions that constitute the process.

Construction of the flow models of the second group (with conditional flows) will be exemplified by the MEIS of chemical system with constant T , P , and y that has the form:

find

$$\max \left[Fx((\xi)) = \sum_{j \in J^{\text{ext}}} c_j x_j(\xi) \right] = F(x(\xi^{\text{ext}})) \quad (29)$$

subject to

$$x_j = y_j + \sum_i \nu_{ij} \xi_i, \quad j = 1, \dots, n, \quad i = 1, \dots, m, \quad (30)$$

$$D_t(y) = \{\xi : x(\xi) \leq y\}, \quad (31)$$

$$\Phi_r(x_r(\xi), z_r) \leq \Psi_r, \quad r \in R^{\text{lim}}, \quad (32)$$

$$G(x(\xi)) = \sum_j G_j(x(\xi)) x_j, \quad (33)$$

$$x_j \geq 0, \quad 0 \leq \xi_i \leq 1, \quad (34)$$

where $\xi = (\xi_1, \dots, \xi_m)^T$; ξ_i —the degree of completeness (a coordinate) of the i -th reaction; ν —a stoichiometric coefficient.

Equation (30) describes the material balance of transformations of the j -th system component. The kinetic constraint (32) is similar to (10), but it includes the relationships between the constrained functions (rates of reactions, the most attainable concentrations of reagents, etc.) and the degrees of completeness of reactions.

Model (29)–(34) determines the chemical process mechanism which is optimal from the stand point of the formation of a sought extreme concentration of the given set of substances $(\sum c_j x_j)$ that are ranked in terms of

importance. Here a specific formulation of constraint (32) seems to be even simpler than that of condition (10) since “kinetics” determines the rates of reactions that are already contained in the “prekinetic” system (29)–(31), (33), and (34) and requires a comparatively small amount of additional information for its description.

Currently the flow MEISs are less developed and used than the MEISs with variable parameters. Some examples of their use were presented in the works by Gorban et al. (2001, 2006) and Kaganovich et al. (1997). The problems of further equilibrium modeling evolution on the basis of flow models are discussed below.

3.3 MEIS of spatially inhomogeneous systems

A generalized description of spatially inhomogeneous systems seems to be rather complicated. Indeed, various natural and technical systems can possess a very diverse specific inhomogeneity. In some cases the inhomogeneous system can be divided into parts with fixed spatial coordinates that differ from one another by the values of intensive parameters, phase, and component composition. In the other cases parts of the system with macroscopic nonzero volumes that possess different thermodynamic properties get constantly mixed up with each other and change spatial coordinates. The original modifications of MEIS with spatial inhomogeneity were constructed as applied to the first cases and, in particular, to describe the distribution of harmful substances in the atmospheric air (Gorban et al., 2001, 2006; Kaganovich et al., 1997) and combustion of fuels in fixed-bed, fluidized-bed, and torch furnaces (Kaganovich et al., 2004, 2005a, 2006a, 2006c). Modeling of the exchange processes between some zones was based on the construction of flow distribution graph (Figure 4).

Let us write the MEIS of spatially inhomogeneous system with intensive parameters changing only along the vertical axe, and with fixed y and, in each k -th zone, T and P has the form:

find

$$\max \left[F(x) = \sum_{j,k \in \text{ext}} c_{jk} x_{jk} \right] = F(x^{\text{ext}}) \quad (35)$$

subject to

$$Ax = b, \quad (36)$$

$$A^{\text{in}} \sigma^m = Q, \quad (37)$$

$$\Delta h_1 P_1 \sigma_k T_k - \Delta h_k P_k \sigma_1 T_1 = 0 \quad (38)$$

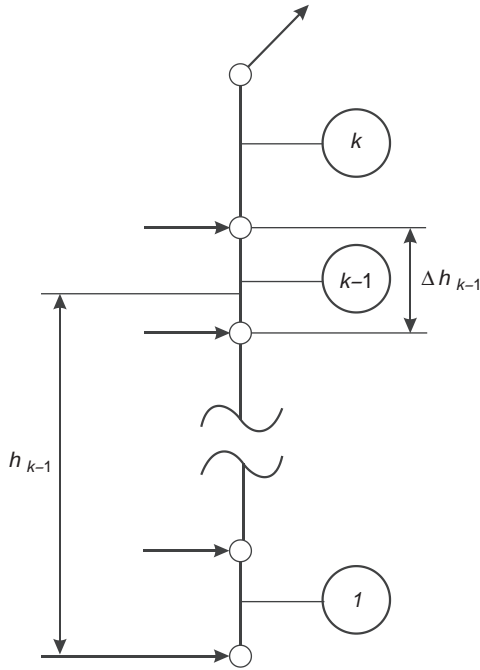


Figure 4 A graph of spatially inhomogeneous system.

$$D_t(y) = \{x : x \leq y\}, \quad (39)$$

$$\varphi_r(x_{rk}, z_{rk}) \leq \psi_r, \quad r \in R^{\text{lim}}, \quad (40)$$

$$E(x) = \sum_{j,k} E_{jk}(x) x_{jk}, \quad (41)$$

$$E_{j(q)k} = G_{jk}^0(T_k) + RT_k \ln \left(P_k \frac{x_{jk}}{\sigma_k} \right) + M_j g h_k, \quad (42)$$

$$E_{j(c)k} = G_{j(c)k}^0(T_k) + \frac{2\alpha_j \nu_j}{r_{jr}}, \quad (43)$$

$$x_{jk} \geq 0, \quad z_{rk} \geq 0, \quad (44)$$

where A^{in} —a matrix of incidences (connections) of independent nodes to branches (arcs) of the graph mapping the system structure; $\sigma^m = (\sigma_1^m, \dots, \sigma_k^m)^T$, $\sigma_k^m = \sum_j x_{jk} \mu_j$; μ_j —the mole mass of the j -th system component; Q —the vector of external sources and sinks; h_k and Δh_k —an average level and thickness of the k -th zone, respectively; σ_k —the mole quantity of gaseous components of the k -th zone; E and E_{jk} —energy functions of the system and its jk -th component, respectively; R —the universal gas constant; g —the free fall acceleration; α —the surface tension; ν —molar volume; r —a radius of condensed particle; index 1 refers to the zone with minimum h ; indices g and c refer to the gaseous and condensed phases, respectively.

Model (35)–(44) includes two material balances: the first of them (36) represents the condition of conservation of element quantity in chemical reactions and phase transitions; the second balance (37) is the expression of the first Kirchhoff law (in this case the law of mass conservation at substance motion along branches of the system graph). Equation (38) is based on the assumption that the gas phase in each zone is ideal. Expression (40) is the constraint on macroscopic kinetics. Energy functions E represent the sums of chemical (the Gibbs energy), gravitational, and surface (related to interphase formation) components. Derivation of formulas (42, 43) is given in Kaganovich et al. (1997). Here we will only note that Equation (43) unlike (42) does not include the member $M_j g h_k$ that reflects the action of the gravity forces that are balanced for the condensed phase by resistance forces whose field is not a potential. Therefore it is difficult to associate the solution to the equilibrium problem of these two types of forces with the solution to the extreme problem. At the same time their equilibrium does not affect the other equilibria that occur in the heterogeneous system and can be excluded from consideration.

On the whole model (35)–(44) includes the features of both parametric (the main sought variables are system parameters) and flow (the flow distribution graph is used) MEISs and can be considered as their combination in some respects.

For the time being the MEIS of spatially inhomogeneous systems (without kinetic constraint (40)) has found the use only in solving the problem of harmful substance distribution in the vertical air column of isothermal atmosphere (Gorban et al., 2001, 2006; Kaganovich et al., 1997). Extension of this model application to every new problem even provided that the system can be divided into zones with different spatial coordinates is associated with considerable difficulties due to specific character of the studied object. It is natural that these difficulties increase greatly with inclusion of the macroscopic kinetics constraints into the model. The main difficulties are: division of a modeled system into zones, determination of a set of limiting processes, and choice of mathematical formulations for corresponding constraints taking into account sensible accuracy of calculations.

3.4 Variants of kinetic constraints formalization

The section addresses the problem of specifying constraints (10), (16), (27), (32), and (40) on macroscopic kinetics as applied to various problems. Formalization of these constraints as well as constructions of MEIS are on the whole based on the Boltzmann assumption on the equilibrium of “kinetic” trajectories of motion toward point x^{eq} and the possibility to describe them by autonomous equations of the form $\dot{x} = f(x)$.

The problems of including kinetic blocks into thermodynamic models vary in their significance and, hence, differ by the level of complexity for the MEIS types considered. In the flow and “spatial” models even initial, basic relations reflect to a certain degree the kinetics, and additional description of special kinetic constraints can affect insignificantly the computational process. The experience in applying the models of form (7)–(12) and preliminary analysis of problems to be studied in the future show that taking into account kinetics in MEIS with variable parameters, in many cases, leads to a sharp change in the mathematical character of the studied problems and, hence, to the need to modify the computational algorithms employed. Therefore, the discussion presented below refers largely to the parametric MEISs.

The “translation” of kinetics into thermodynamic terms which is necessary for constraint (10) to be organically included in the MEIS and which suggests exclusion of time variable from this constraints is, of course, a nontrivial problem. The optimal solution of the latter, which determines the formalized problem statement providing comparative simplicity and accuracy of computing experiments, refers to the newly formed scientific discipline “Model Engineering” (Gorban, 2007; Gorban and Karlin, 2005; Gorban et al., 2007).

Three approaches can be outlined to choose the formalized thermodynamic description of the kinetic block of model (7)–(12): (1) the thermodynamic approach, with additional thermodynamic relations that limit some stages of the studied process mechanism, to be written; (2) the approach related to the transformation of right-hand sides of the kinetic equations and transition from the space of sought variables of the solved problem to the space of thermodynamic potentials, and (3) the approach based on direct use of these sides.

Applicability of the first approach suggested by Keiko and Zarodnyuk is based on the unity of thermodynamics and kinetics which explain differently the same physical regularities. As was said above this unity was brilliantly revealed by Boltzmann in his “kinetic” and “thermodynamic” explanations of the second law. In our case, setting, for example, a constraint on the equilibrium constant value of an individual reaction $\sum \nu_j x_j = 0$ within complex chemical process and writing this constraint in l one of the possible forms:

$$K_p = \prod_j p_j^{\nu_j} = \exp\left(-\frac{\Delta G^0}{RT}\right) = \frac{\prod_j x_j^{\nu_j}}{\prod_j y_j^{-\nu_j}}, \quad (45)$$

we indirectly impose the constraints on the rate of this reaction which determines attainable concentrations of its final products. (In (45) ΔG^0 —the difference between the total Gibbs energies of products and initial substances.) The constraints similar to (45) allow the mechanism of processes to be taken into account in the thermodynamic studies and do not require the complete knowledge of the mechanism and corresponding formalized description. Instead of the equalities of type (45) one can compose an auxiliary MEIS intended to search for the extreme values of constrained variables and substitute them into the initial model. It is obviously most expedient to set thermodynamic constraints on individual stages as applied to fast variables whose formation to a great extent determines further course of the process studied. For example, the fast formation of harmful substances can complicate the production of target products. Derivation of formulae for additional thermodynamic constraints disregarding the permissible time of chemical reactions and transfer processes narrows the area of effective application of the given approach. Nevertheless, some possibilities of its effective application are demonstrated in Section 5.3. The usefulness of this idea undoubtedly deserves further scrutiny.

The second method of excluding time variable from (10) is based on thermodynamic analysis of kinetic equations suggested by Horn (1964; Horn and Jackson, 1972), Feinberg (1972, 1999; Feinberg and Hildebrant, 1997; Feinberg and Horn, 1974), Gorban, and other authors. We consider the technique used in the work by Gorban (1984), which implies the transformation of right-hand sides of kinetics equations, i.e., replacement of coordinates by potentials and further substitution of the transformed sides into the expression for the derivative of the total characteristic function of the considered system with respect to time τ . In the work by Gorban (1984) according to Boltzmann it was supposed that this function possessed the properties of the Lyapunov functions.

We will explain this method on the example of setting the constraint on the rate of the i -th chemical reaction. Let the rate equation of this reaction have the form:

$$w_i = \frac{dx_i}{d\tau} = k_i \prod_j x_j^{\nu_j}, \quad (46)$$

where k —the rate constant. Independence of the right-hand side of Equation (46) from τ makes possible the transformation (47) and the

representation of derivative of the characteristic function (48) with respect to time in the form (49):

$$k_i \prod_j x_j^{\nu_j} \rightarrow \varphi_i \exp \left(\sum_j \nu_j \mu_j \right), \quad (47)$$

$$G = \sum_i \int \mu dx, \quad (48)$$

$$\dot{G} = \sum_i \sum_j \varphi_i \mu_j \exp \left(\sum_j \nu_j \mu_j \right), \quad (49)$$

where μ —a chemical potential.

The set of thermodynamic attainability $D_t(y)$ can be described in MEIS by either using the nonpositivity condition of the right-hand side of Equation (49), or writing the constraint on the sign of derivative of (48) with respect to x . Both methods as applied to MEIS are associated with great difficulties that can be explained by the fact that the constraints on rates are set only for part of the stages of the studied process mechanism. Therefore, the representations of the components of vector x , which take part in the constrained reactions and influence the values of this function only through their concentrations in the sequential states, should be matched in the formulation of monotonicity condition of the system characteristic function (in description of the set $D_t(y)$). Due to these difficulties to date the authors, despite the theoretical effectiveness of the second approach, have used mainly the third of the above methods for excluding time variable from MEIS to specify the kinetic constraints.

The simplest situation in the use of the third method is when the constraint on the process rate is determined only by one reaction, for example, of form (46). In this case to find the limiting concentration (or another parameter of the r -th component) we can write the inequality:

$$dx_r \leq k_r \prod_j x_j^{\nu_j} d\tau. \quad (50)$$

When the mechanism of formation x_r includes several reactions, (50) is replaced by a more complex expression

$$dx_r \leq \sum_i \left(k_{ir} \prod_j x_j^{\nu_j} \right) d\tau. \quad (51)$$

With integration of (50) or (51) the considered time interval τ_b is taken equal to either the duration of the components stay in whole reactor or in a zone where the limiting stage of the process occurs. The values x_j , here, are very often set constant. Depending on the statement of the problem solved, sometimes they can be taken equal to the values of corresponding components of vector y , and sometimes they can be calculated on the basis of search for the extremum of the objective function on the auxiliary MEISs. It is clear that by replacing all variables in the integrals of the form

$$\int_0^{\tau} \sum_i \left(k_{ir} \prod_j x_j^{\nu_j} \right) d\tau$$

by constant constraints (10) reduce to linear inequalities

$$x_r \leq \sum_i \left(k_{ir} \prod_j x_j^{\nu_j} \right) d\tau \quad (52)$$

and their inclusion into MEIS does not affect the reducibility of the latter to the CP problems.

Unfortunately it is not always possible to use only linear inequalities. In further studies we will have to include into the kinetic constraints both the equations of nonlinear chemical kinetics and the nonlinear equations of transfer processes. Nonconvexity of the problem solved and possible multi-valuedness of its solutions, in case the constraints on radiant heat exchange are included into MEIS, are shown in the work by Kaganovich et al. (2005a).

The MEIS modifications including the constraints on macroscopic kinetics have already revealed their high efficiency in the analysis of environmental characteristics of the fuel combustion processes (Kaganovich, 2002; Kaganovich et al., 2004, 2005a, 2006a, 2006b, 2006c, Shamansky, 2004). Their application enriched the explanations of the equilibrium model capabilities for studying the irreversible phenomena of different nature with vivid examples. Simultaneously it is shown that the account taken of the macrokinetic constraints reduces appreciably the thermodynamic attainability region studied with the help of MEIS and hence enhances the accuracy of thermodynamic estimations of the limiting characteristics of processes. Specific examples of formulation and use of kinetic blocks of MEIS are considered in the Section 5. Along with the merits of the new equilibrium model modifications serious difficulties of their construction and application were revealed. First of all these difficulties are related to the above change in the mathematical character of the

problems solved: convexity violation of the system of constraints or an objective function, multivaluedness of solutions, etc.

The difficulties emerging are certainly surmountable. However, thorough studies are necessary to overcome them. The discussion of prospects for MEIS application includes, in addition, the issue on the optimally complete description of constraints on macroscopic kinetics. A normal desire here is to include into the unified model the constraints on maximum possible number of stages that limit the results of the total process. The “uniting” tendency should undoubtedly manifest itself in thermodynamic modeling. At the same time creating comprehensive descriptions of chemical kinetics and transfer processes one should remember that overcomplication of thermodynamic models leads to the loss of their comparative advantages over kinetic ones: loss of comparative easiness of setting the initial information (first of all about the process mechanism) and simplicity of the mathematical apparatus employed.

3.5 Geometrical interpretations

Graphical interpretation of MEIS first will be given for a parametric model of elementary reaction of isomerization. Let us suppose that the reaction proceeds with constant T and P , $y = (1,0,0)$, the maximum value of the third isomer is found and MEIS has the form:

find

$$\max x_3 \quad (53)$$

subject to

$$x_1 + x_2 + x_3 = y, \quad (54)$$

$$D_t(y) = \{x : x \leq y\}, \quad (55)$$

$$G(x) = \sum_1^3 \left(G_j^0 + RT \ln \left(P \frac{x_j}{\sigma} \right) \right) x_j, \quad (56)$$

$$x_j \geq 0. \quad (57)$$

Model (53)–(57) does not include kinetic constraint that corresponds to constraint (10) in the general model (7)–(12). Graphical illustrations of the efficiency of including constraints on macroscopic kinetics into MEIS are given in Section 5. This section focuses on the geometrical explanation of

comparative advantages of using traditional space of kinetic variables (rates, flows, and time) and thermodynamic space of characteristic functions and parameters of state in physicochemical modeling.

Let us explain the specific features of model (53)–(57) using Figure 5. The equilateral triangle $A_1A_2A_3$ in Figure 6a is a material balance polyhedron $D_t(y)$, which is determined by equality (54) and inequality (57). The vertices correspond to the states in which the mole content of one of the components equals an absolute value of y , which for simplicity and without loss of generality can be assumed equal to unity and the remaining two—equal to zero. Index at the symbol of vertex A coincides with the index of the corresponding component. The interior points of the edges represent the reaction mixture compositions in which the concentration of only one reagent is zero and the total mole quantity of the remaining two makes up unity (in case the above possible supposition is assumed). On the area of the triangle you can see the points x^{eq} and x^{ext} , lines $G = \text{const}$ as well as dashed zones of thermodynamic unattainability from y by condition (55) near the vertices A_2 and A_3 . Correspondingly the nondashed part of the triangle represents $D_t(y)$. The two trajectories of motion from y to x^{ext} are shown: the one that meets (a continuous line) and the one that does not meet (a dot-and-dash line) the requirement for the Gibbs energy monotony. The point \tilde{x}^{ext} represents approximately the maximum concentration of x_3 . It is obtained at motion from y along the edge A_1A_3 to the point minimum value of Gibbs energy and succeeding transfer to the curve $G = G_{A_1A_3}^{\text{min}}$ tangent to the edge.

Figure 5b presents the surface (in this case it is plane) of the objective function $F(x) = x_3$ and two closed sets that represent a feasible set of solutions on the surface of function $G(x)$ and in the space of variables x . The set x is represented by the projection of the triangle $A_1A_2A_3$ (Figure 5a) to the horizontal plane x_2Ox_3 . Point O , the beginning of coordinates, coincides with the projection of vertex A_1 to this plane, which corresponds to the corresponding initial composition of reagents y . The points x^{eq} and x^{ext} , the lines $G = \text{const}$, and the feasible and unfeasible trajectory of transition from y to x^{ext} are shown on the plane of compositions x_2Ox_3 , and on the surface of function $G(x)$, and on the objective function plane.

Even Figure 5 prompts some thoughts about the convenience of using thermodynamic variables. The form (topology) of the surface of function $G(x)$ helps find the feasible directions of motion to the point $G(x^{\text{ext}})$, which maps the point $F(x^{\text{ext}})$ in the thermodynamic space. These directions are invariant with respect to the second law of thermodynamics and lead to the extremum of the characteristic thermodynamic function of the system (in case, shown in Figure 5, to the minimum G , i.e., to $G(x^{\text{eq}})$).

The projection of the motion trajectories to the manifolds that are invariant with respect to the second law represents one of the components of the method for reducing the physical and chemical kinetics models, which is developed by Gorban and Karlin (2005). The specific feature of

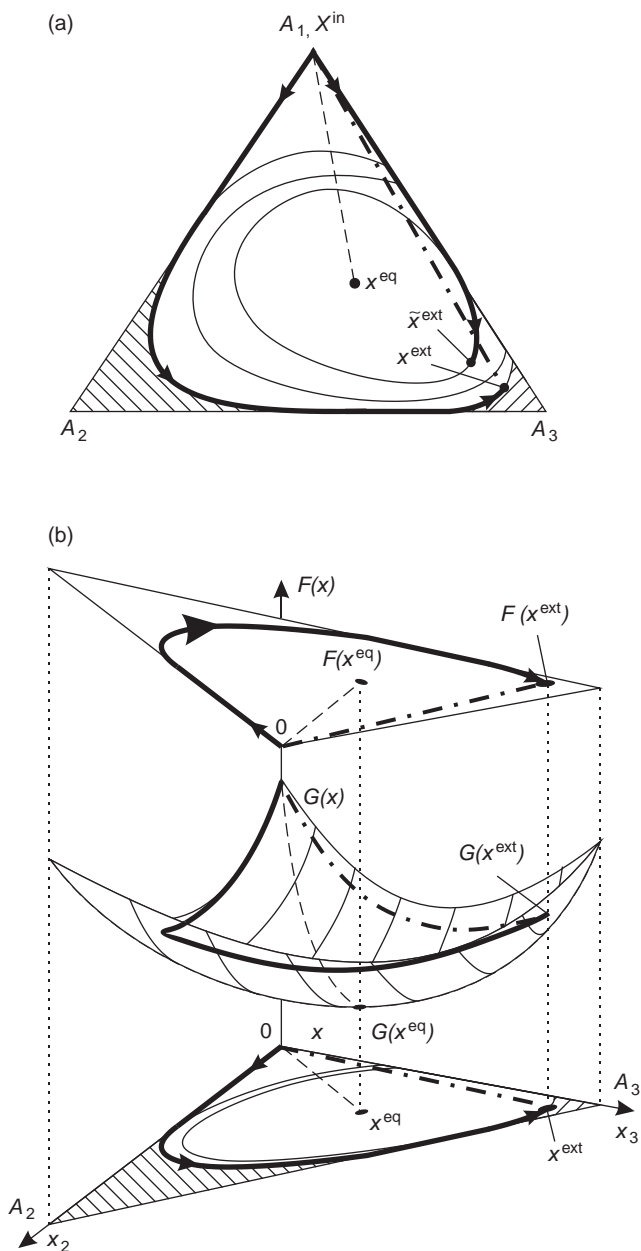


Figure 5 A graphical interpretation of the model of extreme intermediate states.

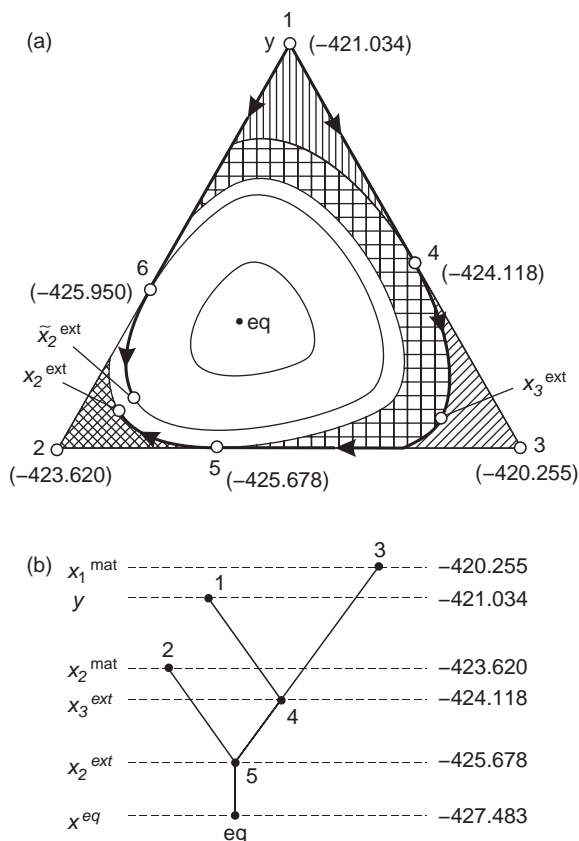


Figure 6 Polyhedron of material balance (a) and thermodynamic tree (b) of hexane isomerization reaction. $T = 600$ K, $P = 0.1$ MPa.

the MEIS-based approach lies in the fact that it envisages the projection (mapping) of sets of possible states rather than trajectories.

A remarkable advantage of the optimization models based on the use of thermodynamic space consists in the possibility, in case of reducing these models to CP problems, to transform the region of feasible solutions into a one-dimensional set (a graph in the form of a tree) and to study the specific features of the studied system behavior on this graph—"a thermodynamic tree."

The notion of thermodynamic tree (the graph, each point of which represents the set of thermodynamically equivalent states) was introduced by Gorban (1984) where he also revealed the possibilities of applying this notion for analysis of the chemical kinetics equations. In the work by Gorban et al. (2001, 2006) the authors consider the problems of employing thermodynamic tree to study the physicochemical systems using MEIS.

Let us exemplify the effectiveness of the idea of tree in equilibrium thermodynamic modeling again by isomerization, using the calculations of transformations of three hexane isomers: *n*-hexane (x_1), 2-methylpentane (x_2), and 3-methylpentane (x_3) at $T = 600$ K and $P = 0.1$ MPa. Graphical interpretation of the analysis is presented in Figure 6a and b.

Figure 6a presents the same triangle of material balance as in Figure 5a, but with some additional details included. It shows the feasible trajectories of motion toward the points of extreme values of both x_3 and x_2 . Different shadings denote five components of the arcwise connectedness (Gorban, 1984), i.e., regions, in each of which any two points can be connected by thermodynamically feasible trajectories. Figure 6b shows a thermodynamic tree with the branches connected with the regions highlighted in Figure 6a by one-to-one correspondence. Each point on the tree represents a section of the curve $G = \text{const}$ that belongs to a corresponding component of connectedness (a set of thermodynamically equivalent states). The points of this section obey the linear balance: $\sum G_j x_j = G = \text{const}$.

The constructed tree which replaces the thermodynamically attainable set $D_t(y)$ allows one to study the behavior of both the characteristic thermodynamic function (in this case the Gibbs energy) and the objective function $F(x)$. The feasible trajectories of the motion from point $y = (1,0,0)$ to the points x_3^{ext} and x_2^{ext} are shown in Figure 6a represented on the tree by paths 1–4 and 1–4–5, respectively. Motion from point 4 to point 3 (the maximum feasible value x_3 according to the condition of material balance x_3^{mat}) and from point 5 to point 2 (x_2^{mat}) turns out to be impossible due to the Gibbs energy increase. Points 4 and 5 are levels of G (isopotential surfaces: $G = -424.118$ kJ/mol and $G = -425.672$ kJ/mol), at which the extreme compositions x_3^{ext} and x_2^{ext} should be located.

Though in formulations of MEIS of type (7)–(12) or the particular form (53)–(57) the possibility of projecting the space of thermodynamic variables to a tree is not shown, the knowledge of principal possibility to reduce the set $D_t(y)$ to the tree makes the analysis of capabilities and comparative merits of the model of extreme intermediate states essentially easier, clearer, and more convincing.

Using the tree we can analyze the situations when the solution of the problem posed appears to be degenerate. As applied to the considered example of isomerization such a situation occurs when we search for $\max(x_2 + x_3)$. In this case all points of edge 2–3 of the material balance triangle that belong to $D_t(y)$ are the points of the objective function maximum. Let us make a natural supposition that the two extreme cases (1) $x_2 = 1, x_3 = 0$ and (2) $x_2 = 0, x_3 = 1$ are equally satisfactory and, hence, we can seek to attain both vertex 2 and vertex 3. In the first case the sought level of the Gibbs energy will be $G = G_5$, and in the second— $G = G_4$. In Figure 6a the found range of levels G_4 – G_5 corresponds to the part of edge 2–3, which is located between the point of its intersection with the curve $G = G_4$ and the

point of contact with the curve $G = G_5$. In Figure 6b the range of possible solutions is represented by the branch of tree 4–5.

The idea of tree is rather effective for solving and analyzing the problem of determining $G(x^{\text{ext}})$ and when its solution is unique. The difficulty of developing relevant computational algorithms is to a great extent related to the implicit form of setting the constraints on the Gibbs energy in MEIS (expressions (9), (26), (39)) (Gorban et al., 2001, 2006; Kaganovich and Filippov, 1995; Kaganovich et al., 1989, 1993). The methods of overcoming the difficulty that have been used so far lead often to the algorithmic (not related to the accuracy of computer computations) error in computations. The use of the tree notion allows it to be used to develop accurate algorithms for the calculation of $G(x^{\text{ext}})$, or substantiate the applicability and assess the accuracy of alternative algorithms. The issues of constructing the algorithms intended for solving the problem of search for $G(x^{\text{ext}})$ and related to the direct application of thermodynamic tree were considered in the work by Gorban et al. (2001, 2006).

When setting the constraints on macroscopic kinetics in MEIS the idea of tree is useful even from the viewpoint of interpreting the applied method for formalization of these constraints. It (the idea) can help represent even the deformation of the region of feasible solutions in the thermodynamic space and the deformation of extremely simple representation of this region (a thermodynamic tree), and the projection of limited kinetic trajectories on the tree. In other words the use of the tree notion helps reveal the interrelations between kinetics and kinetic constraints, on the one hand, and thermodynamics, on the other.

Geometrical illustrations of the efficiency of thermodynamic description of the stationary flow distribution problems as applied to the analysis of closed active and open passive hydraulic circuits were already presented in Section 3.2. The geometrical interpretation of the general models for the nonstationary flow distribution in the hydraulic circuit ((23)–(28)) and chemical systems with the set redundant mechanism of reaction ((29)–(34)) is still to be carried out which will obviously require a number of nontrivial problems to be solved.

4. COMPARISON OF MEIS WITH THE MODELS OF NONEQUILIBRIUM THERMODYNAMICS

4.1 Introductory notes

Feasibility of applying the models of equilibrium thermodynamics to the analysis of nonequilibrium irreversible processes were described in Section 2 of this chapter. This section discusses the comparative efficiency of such application to solve diverse theoretical and applied problems.

Nonequilibrium thermodynamics was chosen as a main object for comparison, though an essential part of conclusions drawn below is useful in MEIS comparison with the models of chemical kinetics, synergetics, theory of dynamic systems and other models, model engineering and theories of motions. Comparison is made from two standpoints: (1) a scope of areas of effective applications and (2) simplicity and fruitfulness of computing experiments.

4.2 On the areas of effective applications of equilibrium and nonequilibrium thermodynamics

First of all, we will touch a widely believed misunderstanding about impossibility of using the second law of thermodynamics in the analysis of open systems. Surely, the conclusion on inevitable degradation of isolated systems that follows from the second law of thermodynamics cannot be applied to open systems. And particularly unreasonable is the supposition about thermal death of the Universe that is based on the opinion of its isolation. The entropy production caused by irreversible energy dissipation is, however, positive in any system. Here we have a complete analogy with the first law of thermodynamics. Energy is fully conserved only in the isolated systems. For the open systems the balance equalities include exchange components which can lead to the entropy reduction of these systems at its increase due to internal processes as well.

The courses of chemical and technical thermodynamics, as the whole applied thermodynamics, are devoted, in their vast majority, to the efficiency analysis of open systems (heat engines, chemical reactors, metallurgical furnaces, etc.) and based in this analysis primarily on the second law. The fundamental Gibbs equations that describe behavior of open and closed systems for different cases of interaction with the environment are devised from the second law. And correspondingly numerous computing algorithms and systems (employing the equations) that were developed in the late 20th century to solve different problems of energy, chemical technology, metallurgy, cosmonautics, geology, ecology, and other spheres of science and technology satisfy it. From the viewpoint of our discussion it is worth noting that all these computing systems are based on the concepts of exactly equilibrium thermodynamics. Therefore, the statement that the nonequilibrium thermodynamics forms a “theoretical base for studying open systems” (Zubarev, 1998) arouses surprise.

The next sphere of competition between equilibrium and nonequilibrium thermodynamics is the analysis of irreversible trajectories. A popular opinion about the possibility for the equilibrium thermodynamics only to determine admissible directions of motion for nonequilibrium processes was already mentioned in Introduction. However, the more

than 20-year experience of MEIS application has revealed the possibility of analyzing any probable states in the admissible directions. This possibility follows directly from two approaches of the second law substantiation by Boltzmann (see "Introduction"): (1) from the analysis of trajectories and (2) from the analysis of states. It is natural to assume that permutation of axioms and theorems allows the methods for search and analysis of any attainable states of the thermodynamic system to be devised from the second law. Reduction of the models of motion to the models of rest, analysis of trajectories to analysis of states is the specific feature of the approach developed by the authors, which determines its role in "Model Engineering" (Gorban, 2007; Gorban and Karlin, 2005; Gorban et al., 2007). This specific feature stipulates to a great extent its comparative computational simplicity and efficiency.

The third, and probably the most complex, area with respect to comparative analysis of equilibrium and nonequilibrium approaches is the modeling of mechanisms of the studied processes. As was described above, the parametric MEISs were constructed on the basis of the lists of substances (system components) rather than the lists (mechanisms) of reactions. However, there is a wealth of experience gained in consideration of both individual stages with the help of parametric models and the complete mechanisms based on the flow models of hydraulic and chemical systems. For the hydraulic systems it is possible to choose not only physical mechanism (flow distribution over branches of the given redundant scheme that provides the minimum energy consumption for fluid transportation), but also "technical" (distribution of resistances of branches depending on their technical characteristics) and "economic" mechanisms (distribution of economic expenditures over branches that minimizes production of "economic" entropy, being a measure of useless irreversible spending of money).

A partial inclusion of mechanisms (their individual stages) by means of Equations (10), (16), (27), (32), and (40) is clear to some extent from the above said and its efficiency is illustrated by examples in Section 5. Here we explain the possibilities of choice by the equilibrium models of complete mechanisms.

Prior to discussion of modeling the complete mechanisms of chemical systems on the basis of MEIS (29)–(34), we will present capabilities of the approximate analysis of the efficiency of such mechanisms by MEIS (7)–(12) with variable parameters. This possibility was studied in Kaganovich and Filippov (1995; Kaganovich et al., 1993). Let us consider a process during which some initial composition a should be used to get the maximum quantity of products b . Let the point y in Figure 7 denote an initial state of the reactive system. The point m corresponds to the maximum thermodynamically admissible concentration of b . The points l and k represent states of a chemical system with the use of catalysts that provide

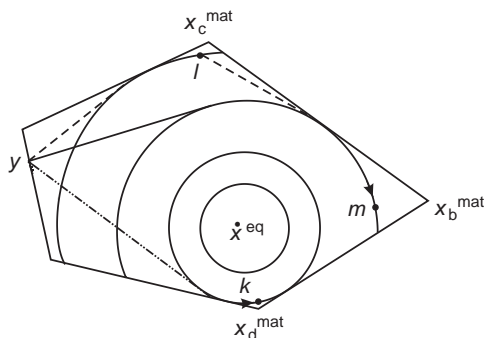


Figure 7 Catalyst impact on the attainable state.

appropriate mechanisms of processes. [Figure 7](#) shows that the mechanism connected with motion through the point l is more effective, since the Gibbs energy monotonically decreases on the curve ylm . From the point k that is passed at the competing mechanism of the process the state m proves to be unattainable.

Comparative assessment of the indicated mechanisms can be obtained on the basis of the multivariant calculations on model (7)–(12). At first we must solve the problems of maximization of sets of the substances c and d that correspond to the main components of compositions of the reactive mixtures l and k . Then taking the obtained extremal states as initial the problems of maximizing b must be solved.

The use of MEIS (29)–(34) allows the comparison of mechanisms based on the single-variant calculation. For this purpose a redundant graph of the process (complete mechanism) is constructed and the “unnecessary” branches are automatically excluded from the scheme during optimization. In this case the constraints on the reaction rates (inequality (32)) are also taken into consideration. An example of the redundant graph as applied to hexane isomerization (see Section 3.5) is given in [Figure 8](#). Preliminary analysis of the efficiency of using the flow MEIS to study mechanisms of chemical reactions (on the basis of the final equilibrium model only and without kinetic constraints) is described in the works by [Gorban et al. \(2001, 2006\)](#), [Kaganovich and Filippov \(1995\)](#), and [Kaganovich et al. \(1993\)](#).

Possibility of equilibrium thermodynamic modeling of fluid transportation mechanisms will be discussed on the example of optimal synthesis problem of multiloop hydraulic systems that was stated by [Khasilev](#), the founder of the theory of hydraulic circuits ([Khasilev, 1957, 1964, 1966](#); [Merenkov and Khasilev, 1985](#)) and was studied in many works (see, for example, [Kaganovich \(1978\)](#); [Kaganovich and Balyshv \(2000\)](#); [Merenkov et al. \(1992\)](#); [Sumarokov \(1976\)](#)). We will formulate this problem as a MEIS

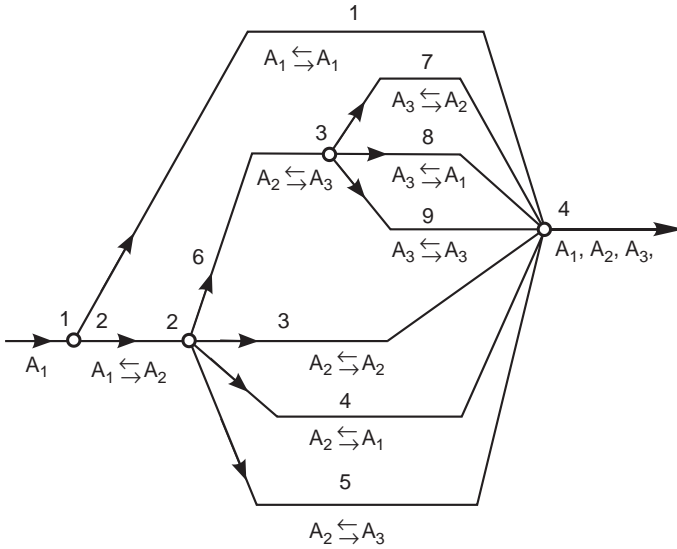


Figure 8 A graph of hexane isomerization reaction.

modification that represents development and generalization of the model of stationary isothermal flow distribution (13)–(17):

find

$$\min \left[F(x, P^{\text{br}}) = \sum_i F_i(x_i(x), P_i^{\text{br}}) \right] = F(x^{\text{ext}}) \quad (58)$$

subject to

$$Ax = Q, \quad (59)$$

$$\sum_{i=1}^n P_i^{\text{mov}} x_i - \sum_{i=1}^n P_i^{\text{br}} x_i = 0, \quad (60)$$

$$D_t(y) = \{x : x \leq y\}, \quad (61)$$

$$\varphi_r(x) \leq \psi_r, \quad r \in R^{\text{lim}}, \quad (62)$$

$$P_i^{\text{br}} = \gamma_i x_i^\beta, \quad i = 1, \dots, n, \quad (63)$$

in $\beta = 2$ (turbulent flow)

$$\gamma_i = \frac{8\lambda\rho l_0}{\pi^2 d^5}, \quad (64)$$

$$F_i = ax_i(x)P_i^{\text{br}} + bx_i^\theta(x)/(P_i^{\text{br}})^\zeta + c, \quad (65)$$

where F and F_i —the cost (economic) characteristics of the whole network and its i -th branch; γ —a coefficient of the i -th branch resistance; λ —a coefficient of friction; ρ —the fluid density; l_i and d_i —the pipeline length and diameter of the i -th branch, respectively; a , b , and c —coefficients; θ and ζ —exponents depending on the exponent value at x_i in (63)

$$k = a_k + b_k d^z. \quad (66)$$

The first term in the right-hand side of (65) is proportional to the energy consumption to move fluid, the second is proportional to capital investments (pipe diameters for the pipeline network), and the third represents a fixed part of expenditures.

Figure 9 gives an insight into the potential objects of studies by model (58)–(65). It shows a scheme of the main double-pipe water heat network of the heat supply system for a large urban district. The optimal synthesis problem for this network consists in the determination of flow distribution

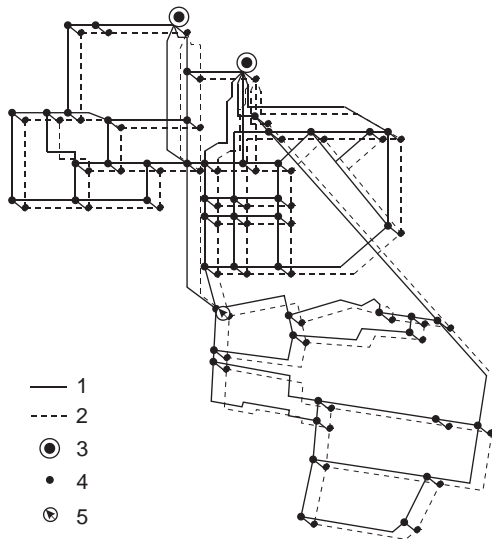


Figure 9 The scheme of heat supply system in a “double-line” representation 1, 2—sections of supply and return pipelines, 3—heat source, 4—nodes of consumer connection; 5—pumping station.

over the scheme branches (the zero-flow branches are excluded from the scheme) and pipeline diameters. Hence, it includes a hydrodynamic (physical) and a technico-economic component. Herewith, in addition account can be taken of the requirements to heat supply reliability (e.g., by specifying the condition of two-sided supply of individual consumers) and ecology (e.g., by specifying the constraints on loading a less environmentally sound heat source).

Interrelations between the simultaneously solved problems of hydrodynamic (calculation of x_i) and technico-economic (choice of diameters d_i) optimization of the network are revealed by taking as initial the empirical Darcy–Weisbach equation

$$P^{\text{br}} = \frac{\lambda \rho w^2}{2d} l = \frac{8\lambda x^2}{\pi^2 d^5} l, \quad (67)$$

from which formula (64) was obtained to determine γ . In (67) w is the fluid speed.

When Khasilev studied mathematical properties of the problems on choosing the vectors x and P^{br} (d) (Khasilev, 1957), he varied the type of equations (67) based on the exponent change at w and x from unity (a laminar mode of fluid flow) to two (a turbulent mode). He established that the functions F and F_i are concave along the axes x_i and convex along the directions P_i^{br} (on the assumption that $0 \leq \zeta \leq 1$ and $0 \leq \theta \leq 1$). Hence, problem (58)–(65) does not belong to the CP.

Since with the fixed value of vector P^{br} and the lack of constraint (62) the admissible region of solutions is a polyhedron, F reaches its minimum at one of its vertices. With the rank of matrix A equal to $m-1$ and n unknowns the reference solution contains no less than $n-(m-1)$ zero components, which equals the number of chords of the system of independent loops of the network graph. In this case the graph tree is a polyhedron vertex and the optimal variant should be among the set of trees of a redundant scheme.

The problem of choosing P^{br} with the fixed x is a problem of CP. Khasilev carried out an interesting analysis of the problem with respect to the properties of $F(P^{\text{br}})$ (disregarding (62) Khasilev, 1957). To do this he applied dimensionless characteristics

$$e = \frac{P^{\text{br}}}{(P^{\text{br}})^{\text{ext}}}, \quad \sigma = \frac{(F - F^{\text{ext}})}{(F - c)}. \quad (68)$$

Transforming (65) based on (68) Khasilev devised the equation

$$\sigma = \frac{\varphi \varepsilon}{(1 + \varphi)} + \frac{1}{\varepsilon^{\varphi}(1 + \varphi)} - 1, \quad (69)$$

where the value of the constant φ is determined by the exponent value at x in (63) and the relationship between capital investments in pipelines and their diameters (66). Analysis of (69) in the context of our discussion is of interest, first of all because it reveals independence of σ , i.e., the relative change of economic cost characteristics of the system, from the coefficients a , b , and c and hence, independence from such technico-economic indices determining these coefficients as specific costs of electricity used for fluid pumping, specific capital investments in pipelines with different diameters, depreciation and repair charges, etc. (naturally, these indices determine absolute values of costs and their variations at pressure loss deviation from the optimum). The only factor that influences the shape of the curve $\sigma = f(\varepsilon)$, i.e., mathematical features of the economic optimization problem of pressure loss distribution over the hydraulic network branches in the form of a tree, is the exponent value at x in the hydrodynamic relation (67).

Specifically, from Equation (69) follows the property of exceptionally great flatness of σ near the optimum point ($\varepsilon = 1$). For example, for the turbulent fluid flow ($\zeta = 0.19$) a twofold pressure loss in comparison to the optimal value increases transportation cost by 4.6% and a twofold reduction of loss decreases the cost only by 3.8%. For the linear electric networks (Equation (69) is also true for them) the corresponding figures are much higher and account for 8.3 and 25.0%. The revealed property of economic function flatness allows a reasonable simplification of the pressure loss optimization methods.

Before discussing of the general method to solve problem (58)–(65) (joint optimization of x and P^{br}) it should be noted that the pressure losses and pipe diameters in branched networks with different constraints, including those of type (62), can be effectively optimized by the dynamic programming method (Kaganovich, 1978; Merenkov and Khasilev, 1985; Merenkov et al., 1992). It is applicable to parameter optimization only in the tree-like schemes. For the closed multiloop networks $x_i = f(x)$ and correspondingly, the cost characteristics of individual branches $F_i = \psi(x)$, i.e., the minimized economic characteristic of the network as a whole, prove to be nonadditive, which does not allow the use of dynamic programming.

The method of coordinatewise optimization was proposed for simultaneous choice of flow rates and pressure losses on the closed redundant schemes (Merenkov and Khasilev, 1985; Merenkov et al., 1992; Sumarokov, 1976). According to this method motion to the minimum point of the economic functional $F(x, P^{\text{br}})$ is performed alternately along the concave ($F(x)$) and convex ($F(P^{\text{br}})$) directions. The convex problem is solved by the dynamic programming method and the concave one reduces to calculation of flow distribution. The pressure losses in this case are optimized on the tree obtained as a result of assumed flow shutoff at the end points of some branches. The concave problem is solved on the basis of entropy

maximization of an isolated system including a hydraulic network and its environment. As was shown in Section 3.2, the sought maximum corresponds to the minimum of entropy production (the minimum energy dissipation) in the open subsystem, i.e., in the network.

From the “physico-economic” standpoint convergence of the chosen method can be explained by the fact that it naturally represents the tendency of an open system with fixed conditions of interaction with the environment to equilibrium, which corresponds to minimum production of both physical and economic entropy. Optimization for the obtained “technico-economic mechanism” determines flow distribution corresponding to the minimum energy consumption, i.e., a physical mechanism. Thus, in this case the model of equilibrium thermodynamics—MEIS solves the problem of self-organization, ordering of the “physico-economic” system that is referred as a rule to the area of applications of nonequilibrium thermodynamics or synergetics.

Note that the coordinatewise optimization method has already found numerous practical applications to optimization of heat, oil, water, and gas supply systems (Merenkov and Khasilev, 1985; Merenkov et al., 1992; Sumarokov, 1976). As a matter of fact, in the algorithms used for applied problems the flow distribution was calculated not on the base of entropy maximization, but with the help of the closed system of equations of the first and second Kirchhoff laws. However, because of equivalence of approaches that are based on the principle of conservation and equilibrium (extremality) the Kirchhoff equations can be strictly replaced by thermodynamic relations. And the extreme thermodynamic approach in many cases should be preferable owing to the known low sensitivity of the extremal methods to variation of the space of variables.

4.3 Comparison of computational efficiency of equilibrium and nonequilibrium approaches

Comparative simplicity of MEIS-based computing experiments is due primarily to the simplicity of the main initial assumption of its construction on the equilibrium of all states belonging to the set of thermodynamic attainability $D_t(y)$ and the identity of their physico-mathematical description. These states belong to the invariant manifold that contains trajectories tending to the extremum of characteristic thermodynamic function of the system and satisfying the monotonic variation of this function. The use of the mentioned assumption consistent with the second thermodynamics law allows one, as was noted, not to include in the formulation of the problem solved different more particular principles, such as the Gibbs

phase rule, Raoult's and Henry's laws for diluted solutions, principles of the linearity of motion equations, etc.

The lacking special description of the Gibbs phase rule in MEIS that should be met automatically in case of its validity is very important for solution of many problems on the analysis of multiphase, multicomponent systems. Indeed, without information (at least complete enough) on the process mechanism (for coal combustion, for example, it may consist of thousands of stages), it is impossible to specify the number of independent reactions and the number of phases. Prior to calculations it is difficult to evaluate, concentrations of what substances will turn out to be negligibly low, i.e., the dimensionality of the studied system. Besides, note that the MEIS application leads to departure from the Gibbs classical definition of the notion of a system component and its interpretation not as an individual substance, but only as part of this substance that is contained in any one phase. For example, if water in the reactive mixture is in gas and liquid phases, its corresponding phase contents represent different parameters of the considered system. Such an expansion of the space of variables in the problem solved facilitates its reduction to the CP problems.

Errors in the description of nonequilibrium processes in the linear nonequilibrium thermodynamics (Glansdorff et al., 1971; Kondepudi et al., 2000; Prigogine, 1967; Zubarev, 1998) are caused primarily by the assumptions (unnecessary at MEIS application) on the linearity of motion equations. One of the main equations of this thermodynamics has the form

$$J_j = L_{jk}F_k, \quad (70)$$

that relates flows with the forces creating them. The assumption on linearity of differential equations describing fluctuations underlies derivation of the Onsager relations and the Prigogine theorem. These assumptions cause inaccuracy of the formulas for the Onsager kinetic coefficients L . Below are some of them (Kondepudi et al., 2000):

$$L_{qq} = kT^2, \quad (71)$$

$$L_{ee} = \frac{T}{r}, \quad (72)$$

$$L_{11} = D_1 T \left[\left(1 + \frac{\nu_1 n_1}{\nu_2 n_2} \right) \frac{\partial \mu_1}{\partial \mu_2} \right]^{-1}, \quad (73)$$

$$L_{11} = \frac{D_1 n_1}{R}, \quad (74)$$

$$L = \frac{R_{f,eq}}{R} = \frac{R_{r,eq}}{R}. \quad (75)$$

The formulas refer: (71) to thermal conductance; (72) to electric current; (73) to diffusion in the two-component mixture; (74) to dissolution in the ideal solution; (75) to the single-stage chemical reaction. In the formulas k is a coefficient of thermal conductance; r is the electric resistance per unit of conductor length; D_1 is a coefficient of diffusion of substance soluble; v and n are the specific volume and the number of moles, respectively; $R_{f,eq}$ and $R_{r,eq}$ are the rates of the forward and reverse reactions in the equilibrium state.

Analysis of formulas (71)–(75) shows that the Onsager coefficients are connected with the constants of the corresponding processes (k , r , D) through the quantities (T , v , n , μ , R_f , R_r) that vary during relaxation to the equilibrium state. It is clear that T will change essentially in the thermal conductance process; v , n , and μ —during diffusion and dissolution; R_f and R_r —in chemical reactions. Therefore, the Onsager coefficients are constant only close to the equilibrium state. This fact causes errors in calculations even in the quantitative analysis of the simplest ideal systems. Analysis of complex large-dimensional real systems firstly, requires that the whole mechanism of the process modeled be known (which is usually impossible) to derive formulas similar to (71)–(75) and construct the equality of type (4). Secondly, it proves to be feasible only at the essential approximation of the obtained analytical relations. This makes clear the difficulty of applying the nonequilibrium thermodynamics models to solution of sophisticated computational problems because of inevitable low accuracy of the obtained results in many cases.

Surely, despite the absence of requirements to linearity of any relations the application of linear approximations providing convenient (from the computational viewpoint) statement of the problem solved at MEIS-based modeling is admissible.

Simplicity of the initial assumptions in MEIS construction stipulates to a great extent both comparative simplicity of the mathematical apparatus applied and easiness of initial information preparation. Simplification of mathematical descriptions concerning kinetics and nonequilibrium thermodynamics is seen first of all in the transition from differential to algebraic and transcendent equations that provides sharp decrease in the number of used complex analytical dependences (for example, similar to (73)).

Decrease of the initial information volume directly and largely depends on the fact that there is no need to know a complete detailed mechanism of the studied process. The use of MEIS with variable parameters (7)–(12) calls for the information on individual limiting stages only. Substitution of the assignment of the list of reactions by the assignment of

the list of substances is a main computational advantage of this modification of MEIS.

Certainly, determination of the composition of vectors x and y is also connected with solution of a series of complex problems. Appreciable errors in calculations can be caused by the incomplete list of the vector x components. If the modeled system has a gas phase, theoretically this list can reach astronomic sizes, since in this case x^{eq} is an interior point of the polyhedron of the material balance², which in a general case implies a complete set of substances formed from the elements of components y . Composition and sizes of the assigned list determine the possibility for revealing superequilibrium contents of the sought set of substances, which is shown in (Gorban, 1984).

Quantitative estimates of errors in the determined numerical values of substance concentrations at points x^{eq} and x^{ext} as a function of the structure and dimension of x and y are obtained with great difficulty. It is only clear that when we are interested in the detailed composition of products, it is desirable to increase this dimension with thorough choice of the set of components x_j and y_j based on the whole preliminary knowledge about specific features of the studied process. Such an increase will be limited by the possibility to analyze numerous results. However, despite the great sophistication of the problem of specifying a list of substances, it is solved much easier than the problem of specifying a process mechanism. Both the list of elementary reactions (that can include many hundreds and even thousands of elements) and the constants of their rates are hard by far to determine than the list and thermophysical properties of reactants of the studied system.

Simplification of the solution or complete exclusion of the problem of dividing the variables into fast and slow is a great computational advantage of MEIS in comparison with the models of kinetics and nonequilibrium thermodynamics. The problem is eliminated, if there are no constraints in the equilibrium models on macroscopic kinetics. Indeed, the searches for the states corresponding to final equilibrium of only fast variables and states including final equilibrium coordinates of both types of variables with the help of these models do not differ from one another algorithmically. With kinetic constraints the division problem is solved by one of the three methods presented in Section 3.4, which are applied in the majority of cases to slow variables limiting the results of the main studied process.

On the whole, simplicity of the initial assumptions and correspondingly comparative simplicity of the mathematical formulation of MEIS allows one to include in it rather easily descriptions of the most diverse conditions of great influence on the results of the studied process. In

² If the components of x are substances, rather than their phases.

particular, it becomes possible to take into consideration comprehensively enough constraints on kinetics; transfer and exchange of energy, mass and charges; fixing the parameters of the environment and in different zones of the modeled system. More detailed representation of the model, in turn, makes the comprehensive and deep analysis on its base more feasible and enriches both theoretical understanding of the considered phenomena and applied knowledge for a technologist, designer or constructor.

5. EXAMPLES OF MEIS APPLICATION

5.1 Introductory notes

In the works devoted to study and development of MEISs numerous examples on their application to the analysis of various problems were certainly presented. They are formation of harmful substances during fuel combustion and cleaning of combustion products from these components, fuel processing, atmospheric pollution with anthropogenic emissions, stationary and nonstationary flow distribution in hydraulic systems, etc. These examples should illustrate practical efficiency of MEISs, their capabilities for revealing specific features of the modeled process and determining directions of its improvement.

This Section deals with the problem of MEIS comparison with the models of motion that was studied in the previous Section. However, whereas comparison was performed there on the basis of purely theoretical analysis, here it was made on the examples of specific objects. Compared are the attainable completeness and significance of the results of computing experiments, and the possibility of using these results, accuracy of the obtained estimates for the sought characteristics of the modeled system, laboriousness of calculations and preparation of initial information.

5.2 Isomerization

In the works devoted to MEISs isomerization became a “through” example for explanation of their specific features and efficiency. The example is simple and very obvious, since the isomerization reaction at any mechanism is described by the same material balance because of invariable amounts of substances and elements. This fact essentially facilitates both analytical and graphical interpretations.

Here the comparative analysis of MEIS characteristics will be made on the example of the simplest mechanism: $x_1 \rightarrow x_2$, $x_2 \rightarrow x_3$ that was considered in Section 3.5. But the applied model is supplemented with the

constraint on the rate of the second reaction stage, i.e., the studied problem is represented in the form:

find

$$\max x_3 \quad (76)$$

subject to

$$x_1 + x_2 + x_3 = 1, \quad (77)$$

$$D_t(y) = \{x : x \leq y\}, \quad (78)$$

$$kx_2 \leq \psi, \quad (79)$$

$$x_j \geq 0. \quad (80)$$

Obviously, model (76)–(80) does not require any comments. The problem of determining the constant ψ was discussed in Section 3.4 and is not treated additionally here.

The stated problem is presented graphically in Figure 10. The thermodynamically unattainable zones from y subject to (78) are indicated by the hatched area of the triangle $A_1A_2A_3$ of the material balance. Besides, the triangle contains the points x^{eq} for final equilibrium, \tilde{x}^{ext} for maximum concentration of x_3 without constraint (79) and x^{ext} for the largest attainable value of the third isomer concentration with a complete system of constraints (77)–(80). The straight line $kx_2 = \psi$ representing kinetic constraint (79) makes unattainable the part of $D_t(y)$ to the left of it. Owing to

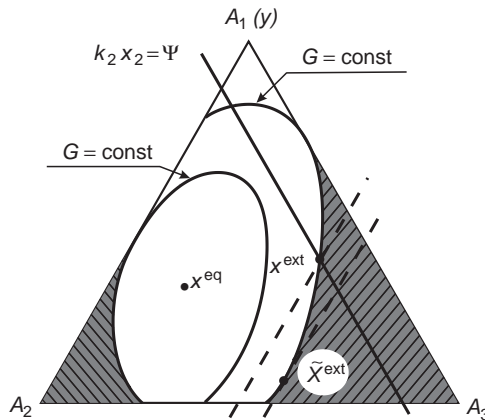


Figure 10 Graphical interpretation of isomerization process.

this constraint solution to problem (76)–(80) shifts from \tilde{x}^{ext} to x^{ext} (intersection of the straight line $kx_2 = \psi$ with the boundary of the unattainability zone near the vertex A_3). It is seen by sight that x^{ext} is somewhat distant from the vertex A_3 (the point of maximum concentration of x_3 with the only constraint of the material balance) than \tilde{x}^{ext} and hence the mole content of the target product in x^{ext} is lower than in \tilde{x}^{ext} .

Even very short interpretation of the problem allows a most important advantage of MEIS to be indicated, namely its capability to choose and determine the value of the subjective parameter of order (Klimontovich, 1997) of the modeled system. In this case the state with the maximum possible content of the target product of the process— x_3 and correspondingly, with the lowest content of “waste”, i.e., useless substances contaminating a produced required “valuable” commodity, is naturally thought to be the most ordered one. In parallel with assessment of the maximum concentration the computing experiments on MEIS determine conditions for its achievement and reveal the factors having the greatest influence on the results of modeled process. This becomes possible owing to the MEIS description in MP language (the theory of extremal problem solution) and capabilities of the computational mathematics as a whole (in particular, capabilities of making multivariant calculations with variation of both the values of initial parameters, and applied dependences between the parameters, including those specified in the nonanalytic form, and presenting calculation results in a convenient tabular and graphical forms). The example of MEIS-based analysis of the “physico-economic” self-organization problem was treated in Section 4.2. The MEIS advantages in detailed analysis of attainability of the ordered states and limiting values of the order parameters are examined in the next Section on an example of nitrogen oxides formation during fuel combustion.

Isomerization will be used as an example to explain to some extent the issues of comparing laboriousness of computing experiments and their accuracy. For the assumed process mechanism the kinetic model has the form:

$$x_1 + x_2 + x_3 = 1,$$

$$\frac{dx_1}{d\tau} = -k_1x_1,$$

$$\frac{dx_2}{d\tau} = -k_2x_2 + k_1x_1,$$

$$x \geq 0.$$

Solution to this system (integrals of differential equations) is:

$$x_1 = \exp(-k_1\tau),$$

$$x_2 = \frac{k_1}{k_2 - k_1} [\exp(-k_1\tau) - \exp(-k_2\tau)],$$

$$x_3 = 1 - \frac{k_2}{k_2 - k_1} \exp(-k_1\tau) + \frac{k_1}{k_2 - k_1} \exp(-k_2\tau),$$

In [Figure 11](#) the curves corresponding to these equations at $k_1 = 1c^{-1}$ and $k_2 = 0.5c^{-1}$ (the values are chosen for the purposes of illustration, the real values of rate constants for the monomolecular reactions can be by many orders of magnitude higher). As is seen from [Figure 11](#), at $\tau \rightarrow \infty$ $x_3 \rightarrow 1$ and $x_1 \rightarrow 0$, which is not allowed by thermodynamics (see [Figure 10](#)). The results of kinetic and thermodynamic analysis could surely be coordinated by including the reverse reactions in the considered mechanism: $x_2 \rightarrow x_1$ and $x_3 \rightarrow x_2$ and assigning for both stages the values of rate constants strictly corresponding to thermodynamics. For complex problems concerning the studies of multistage processes such a growth of dimensionality can sharply increase laboriousness of computing experiments and cause great difficulties in preparation of initial information. The mentioned difficulties will increase still further, if the constraints on rates of transfer and exchange processes are inserted in MEIS in parallel with the constraints on chemical kinetics. In this case it will be necessary to harmonize the values of reaction rate constants and the values of constant coefficients in the equations of Fourier, Fick, Navier-Stokes, etc.

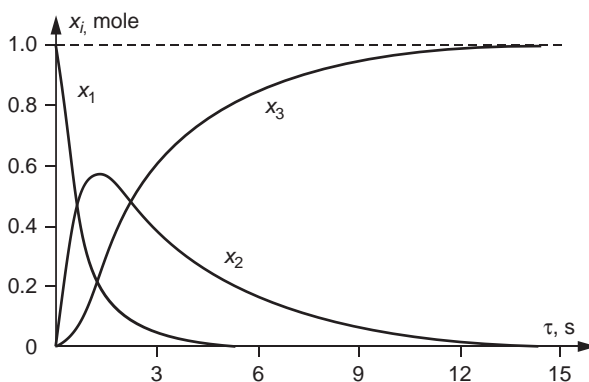


Figure 11 Curves of the kinetic equations for isomerization process.

If we refuse to excessively increase dimensionality and laboriousness of kinetic descriptions, their accuracy can turn out to be lower than the accuracy of the MEIS-based estimates. This was just the case for the considered example, when the results of solving kinetics equations proved to be contradictory to the thermodynamics laws. Needless to say that the accuracy of thermodynamic modeling can be improved unlimitedly by increasing the number of constraints on the macroscopic kinetics. Figure 10 shows that solely constraint (79) in model (76)–(80) sharply decreased $D_i(y)$. However, it should be understood that the increase in accuracy leads to partial or complete loss of such a traditional advantage of thermodynamics as simplicity and possibility of constructing geometrical interpretations of the models applied.

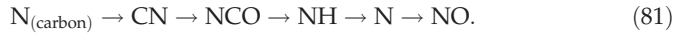
While assessing comparative advantages of the equilibrium thermodynamic modeling, one should remember that with any possible and obligatory expansion of the area of thermodynamics applications and the increasing fruitfulness of thermodynamic modeling it can never substitute and make useless the motion models which determine the rate and time of process course in physicochemical and engineering systems. Kinetics will be always a significant element in designing and constructing diverse engineering objects and studying natural processes.

5.3 Formation of nitrogen oxides during coal combustion

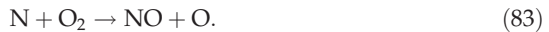
This example belongs to a highly complex physicochemical system. It reveals capabilities of equilibrium thermodynamic modeling of such a purely irreversible process as coal combustion. The calculation using the traditional MEIS (Gorban et al., 2001, 2006; Kaganovich et al., 2006c) shows that the global equilibrium reached by such a system gives rise to formation of a great amount of NO. In practice, however, such amounts of nitrogen oxides are not formed and this fact is indicative of the system transition only to the intermediate equilibrium state because of kinetic factors (bonds). Hence, model (7)–(12) is applicable to study this system. In the model condition (10) for kinetic constraints should be written in the thermodynamic form by using time as a parameter that is determined by technological characteristics of the system (length of the reaction path, flow rates) and the scales of microscopic inhomogeneities of the reaction space. For this purpose it is sufficient to analyze only limiting stages of all basic mechanisms out of numerous chemical reactions that participate in NO formation during coal combustion. Note that by virtue of their significance these processes are studied in sufficient detail and the information on kinetic coefficients is most reliable (Warnatz et al., 2001). The basic mechanisms of NO formation will be described below in short.

Fuel Nitrogen Oxides, according to the current views, are produced from nitrogen-containing compounds of coal in the initial section of torch

at the temperature 900–1,000 K. Transformations of the fuel nitrogen in the process of thermal destruction of the nitrous substances of the organic coal mass (OCM) can be represented by a simplified scheme:



All these transformations take place in the region beyond the surface layer of the coal particle, where the gas phase is enriched with oxygen owing to intensive turbulent mixing. The final stage in the chain is NO formation from the monatomic nitrogen by the reactions:



In the oxidizing medium they are more preferable than other reactions bonding active nitrogen (for example, $\text{N} + \text{NH} \rightarrow \text{N}_2 + \text{H}$). Therefore, according to some data in (Warnatz et al., 2001) up to 70% of fuel nitrogen is converted to NO by this scheme, which makes up on the average 5–7 kg per ton of fuel burnt. The competitive reaction decreasing nitrogen oxide formation in this region is:



The process, in the course of which volatile nitrogen-containing components of OCM leave the coal particle and break down to the nitrile radicals, is a limiting stage of this mechanism. This process is presented in scheme (81) as $N_{(\text{carbon})} \rightarrow \text{CN}$.

Thermal Nitrogen Oxides start to form virtually in the same reaction space region as the fuel ones during fuel combustion. According to the Zeldovich mechanism formation of fuel nitrogen oxides includes elementary reactions (82) and (83) and reactions of active nitrogen generation in this region from atmospheric nitrogen:



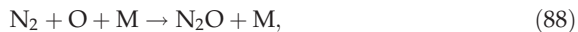
Reaction (85) is limiting in this mechanism and has high activation energy (about 318 kJ/mole (Warnatz et al., 2001)) because of the strong triple bond in the nitrogen molecule. For this very reason the probability of reaction (84) reverse to (85) is high (activation energy is some 27 kJ/mole (Warnatz et al., 2001)), which causes the NO content in the low temperature zones to decrease.

Prompt Nitrogen Oxides emerge because of the lack of oxidizer in the reaction medium. Their formation (Fenimore mechanism) is based on the following reactions:



When burning coal and volatiles, by virtue of diffusion limitations on delivery of oxygen molecules to the reaction surface the oxidizer deficit occurs close to the coal particle surface, which leads to formation of a considerable amount of CH radicals. In parallel the atmospheric nitrogen appears in this region, which favors the course of reaction (86). In the case of strong turbulization of the reaction space the rate of molecular diffusion limits oxygen (as well as nitrogen) access into the turbulent vortex of volatile hydrocarbons, whose size is 10^{-4} m. Therefore, reaction (86) can be supposed to proceed basically in the surface layer, where generation of the CH particles from the volatile components of OCM to the reaction region will be a limiting stage. The products of this reaction pass to the gas phase, where hydrogen cyanide is oxidized in accordance with (87) with a low potential barrier and the nitrogen radical N can participate in reactions (82)–(84).

NO Formation from Dinitrogen Oxide (Nitrous Oxide) takes place during combustion of gaseous hydrocarbons of volatiles in the case of lean mixtures. In accordance with this mechanism at first the dinitrogen oxide N_2O is formed by the termolecular reaction:



(M—any particle), then the molecule N_2O interacts with the oxygen atom:



This mechanism of NO formation is believed to be basic for burning lean mixtures, when the Fenimore mechanism is already inefficient because of absence of CH radicals. Reaction (88), being termolecular, notably accelerates at high pressures and is considered to be limiting in this case. Relatively low activation energies of reactions (88) and (89) make this mechanism responsible for nitrogen oxides formation at low temperatures and pressure of several MPa, when the thermal nitrogen oxides are not virtually formed. Since coal is burnt, as a rule, at the pressure close to atmospheric, this mechanism may not be considered below.

The presented brief survey of basic mechanisms of NO formation during coal combustion allows the MEIS construction with their simultaneous inclusion in the kinetic constraints. Kinetic constraints can be formulated according to the third way among those considered in Section 3.4.

However, several general principles in derivation of multifactor constraints in MEIS should be underlined.

Different limiting processes in the form of kinetic constraints in one thermodynamic model can be taken into account by representing the modeled system as two subsystems—slow and fast. A slow subsystem naturally includes all the limiting stages of different mechanisms and the related processes in the form of a closed system of autonomous kinetic equations. As far as there are usually few limiting processes even in complex physicochemical or other modeled objects, construction of such a system and its solution (analytical or numerical) generally causes no difficulties. Moreover, since we consider conditions for limitation of the thermodynamic attainability region, part of kinetic equations can be substituted by algebraic ones based on the upper (lower) estimates of some variables. This procedure is even necessary, if the kinetic curves of any components are nonmonotonic. Separate points of the phase trajectory of the slow subsystem (i.e., its states) that is obtained by solving the equations correspond to some time parameters of a real object, e.g., the time of passage of the reaction mixture through the flow reactor or the time of diffusion through the boundary layer in the heterogeneous process. If we take these time parameters on the phase trajectory as constant, i.e., limit it on the path to attaining a global equilibrium as a system of inequalities (10) in model (7)–(12), the region of thermodynamic attainability will be constrained for the whole system. In this case several points of constraints for different components of the slow subsystem that correspond to different time scales of the limiting processes can be analyzed simultaneously on one phase trajectory. Thus, for the kinetic limitation of the thermodynamic attainability region MEIS applies separate states of the slow subsystem that belong to its phase trajectory.

Based on the above said, MEIS intended for study of nitrogen oxides formation in the process of torch combustion of coal at constant P and T can be written as follows:

find

$$\max x_{\text{NO}} \quad (90)$$

subject to

$$Ax = b, \quad (91)$$

$$D_t(y) = \{x : x \leq y\}, \quad (92)$$

$$G = \sum_j G_j x_j, \quad (93)$$

$$x_j \leq \psi_i, \quad (94)$$

$$x_j \geq 0. \quad (95)$$

Expression (94) in this model is a system of kinetic constraints for components of the reaction medium.

Constraints (94) will be determined through the rates of NO and N formation on the basis of reactions (82)–(87). Here account will be taken of the above assumption that in the mechanism of forming prompt nitrogen oxides reaction (86) proceeding under oxidizer deficit in the surface layer of the coal particle is limiting and further all the hydrogen cyanide converts to NO beyond this region at oxygen excess. This assumption is sound owing to the low activation barrier of reaction (87) ($E \sim 25.6$ kJ/mole).

$$\frac{dx_{\text{NO}}}{d\tau} = k_{(82)}x_{\text{N}}x_{\text{OH}} + k_{(83)}x_{\text{N}}x_{\text{O}_2} + k_{(85)}x_{\text{O}}x_{\text{N}_2} + k_{(86)}x_{\text{CH}}x_{\text{N}_2} - k_{(84)}x_{\text{N}}x_{\text{NO}}, \quad (96)$$

$$\frac{dx_{\text{N}}}{d\tau} = k_{(85)}x_{\text{O}}x_{\text{N}_2} + k_{(86)}x_{\text{CH}}x_{\text{N}_2} - k_{(82)}x_{\text{N}}x_{\text{OH}} - k_{(83)}x_{\text{N}}x_{\text{O}_2} - k_{(84)}x_{\text{N}}x_{\text{NO}}, \quad (97)$$

Since generation of the atomic nitrogen is a limiting stage in the process of NO formation in these conditions, we can suppose that in terms of other faster reactions the equilibrium condition $d\bar{x}_{\text{N}}/d\tau = 0^3$ is satisfied for it (\bar{x}_{N} here is some equilibrium value of nitrogen radical content in the reaction region). Then the rate of nitrogen oxide formation (96) can be written as the equality:

$$\frac{dx_{\text{NO}}}{d\tau} = 2\bar{x}_{\text{N}}(k_{(82)}x_{\text{OH}} + k_{(83)}x_{\text{O}_2}). \quad (98)$$

System (97)–(98) comprises the following unknowns: x_{NO} , \bar{x}_{N} , x_{OH} , x_{CH} , x_{O_2} , x_{N_2} . Hence, four equations more should be added to make it closed. The relations for the molecular nitrogen and oxygen are most easily represented as an estimate of the upper boundary of their amount:

$$x_{\text{O}_2} \leq y_{\text{O}_2} \quad (99)$$

and

$$x_{\text{N}_2} \leq y_{\text{N}_2}. \quad (100)$$

Assuming that under high humidity of the reaction mixture the OH content is controlled by the reaction:



³This condition is also true for other short-lived radicals: O, ON, SN, etc.

that belongs to the “fast” subsystem, one more equality can be added to Equations (97)–(98):

$$x_{\text{OH}} = (K_{p(101)} x_{\text{H}_2\text{O}})^{0.5}, \quad (102)$$

and the relation

$$x_{\text{H}_2\text{O}} \leq y_{\text{H}_2\text{O}}. \quad (103)$$

Let us note that Equations (102), (103), and (107) supplement the immediate use of kinetic equations for formulation of inequality (94) with a “thermodynamic approach” (see Section 3.4).

The quantities \bar{x}_{N} and x_{CH} will be determined based on the following facts. In the sequence of fuel nitrogen oxides formation (81) all the stages, except for the first, proceed without the activation barrier and as a first approximation they can be taken as fast with respect to the rate of volatiles burning. Assuming that under these conditions according to reactions (85) and (86) the key supplier of active nitrogen to the gas phase is nitrogen-containing components of coal organic matter and CH radicals, we will write the relations for the rates of forming \bar{x}_{N} and x_{CH} ⁴:

$$\frac{d\bar{x}_{\text{N}}}{d\tau} = \frac{dx_{\text{N}(\text{carbon})}}{d\tau} + k_{(85)} x_{\text{O}} x_{\text{N}_2} + k_{(86)} x_{\text{CH}} x_{\text{N}_2}, \quad (104)$$

$$\frac{dx_{\text{CH}}}{d\tau} = \frac{dx_{\text{CH}(\text{carbon})}}{d\tau}. \quad (105)$$

In these expressions the quantities $x_{\text{N}(\text{carbon})}$ and $x_{\text{CH}(\text{carbon})}$ are active nitrogen and CH radicals supplied to the reaction from organic matter of coal, the second term in the right-hand side of (104) corresponds to the mechanism of forming the thermal (85) and prompt (86) nitrogen oxides. Since one more unknown x_{O} appears in Equation (104), the system should be supplemented with the relation determining it. It can be obtained from the fast reaction:



which can limit the number of O radicals as a first approximation. Then:

$$x_{\text{O}} = (K_{p(106)} x_{\text{O}_2})^{0.5}. \quad (107)$$

Integration of (98), (104), and (105) with an account of (99), (100), and (103) results in the following system of inequalities:

⁴These rates are not equal to zero at the time intervals less than τ_D (see below).

$$\left. \begin{aligned} x_{\text{NO}} &\leq 2\bar{x}_N (k_{(82)} x_{\text{OH}} + k_{(83)} y_{\text{O}_2}) \Big|_0^{\tau_f} \\ \bar{x}^N &\leq x_{\text{N}(\text{carbon})} + (k_{(85)} x_{\text{O}} y_{\text{N}_2} + k_{(86)} x_{\text{CH}} y_{\text{N}_2}) \Big|_0^{\tau_D} \\ x_{\text{OH}} &\leq (K_{p(101)} y_{\text{H}_2\text{O}})^{0.5}; x_{\text{O}} \leq (K_{p(106)} y_{\text{O}_2})^{0.5} \\ x_{\text{CH}} &\leq x_{\text{CH}(\text{carbon})} \end{aligned} \right\}. \quad (108)$$

Here τ_f —the time of complete burning of volatile components of coal (Ots, 1977):

$$\tau_f = k_f^{-1} \exp\left(\frac{E_f}{RT}\right) \ln\left(\frac{\alpha}{\alpha + 0.01V^{\text{daf}}}\right), \quad (109)$$

where α —a coefficient of excess air; V^{daf} —content of volatiles in coal; k_f and E_f —variables depending on the statistic characteristics of coal particle sizes. At the values of $T = 1500$ K, $\alpha = 1.2$ and $V^{\text{daf}} = 47\%$ the time interval τ_f accounts for approximately 0.02 s. The parameter τ_D characterizes the time of diffusion of pyrolysis components from the coal particle surface into the turbulent reaction region and along with the chemical kinetics reflects the possibility of accounting for limiting processes of transfer in MEIS like it is done in (Ots, 1977). For the assumed initial parameters of the model $\tau_D \sim 3 \cdot 10^{-4}$ s the “thermal” summand in (104) will be small because of diffusion-limited supply of oxygen atoms to the surface layer and mainly because of high concentration of such active reducing radicals in this layer as H, CH, CH₂, etc. These radicals have no activation barrier, when they interact with oxygen, and will reduce the probability of course for reaction (85) practically to zero. Therefore, this summand can be neglected in calculations.

The quantities $x_{\text{N}(\text{carbon})}$ and $x_{\text{CH}(\text{carbon})}$ can be determined from the following relations:

$$x_{\text{N}(\text{carbon})} \leq N_{(\text{carbon})} k_{\text{N}}^{\text{daf}} K_f \quad (110)$$

$$x_{\text{CH}(\text{carbon})} \leq H_{(\text{carbon})} k_{\text{CH}}^{\text{daf}} K_f \quad (111)$$

where $N_{(\text{carbon})}$ and $H_{(\text{carbon})}$ —the number of these elements in coal; $k_{\text{CH}}^{\text{daf}}$ and $k_{\text{N}}^{\text{daf}}$ —coefficients for the composition of volatiles; K_f —a coefficient that determines the share of volatile substances moving from the coal particle to the gas phase for the time interval τ_D . The quantity K_f can be calculated from the relation (Ots, 1977):

$$K_f \alpha / 0.01V^{\text{daf}} [1 - \exp(-k_f \tau_D \exp(-E_f/RT))]. \quad (112)$$

Conceivably, in the limit all nitrogen of coal organic matter in the burning zone of volatiles turns into the active state, i.e., $k_{\text{N}}^{\text{daf}} = 1$. The

quantity $k_{\text{CH}}^{\text{daf}}$ can be determined using an auxiliary MEIS which determines $\max x_{\text{CH}}$ and the composition of volatiles as an initial vector y . Then $k_{\text{CH}}^{\text{daf}} = x_{\text{CH}}^{\text{ext}}/H_{(\text{carbon})}$. Use of the auxiliary model as the use of Equations (102), (103), and (107) supplements the kinetic deduction (94) with a thermodynamic one.

System (108) determines constraints on nitrogen oxide formation on the basis of the three indicated mechanisms. Formation of thermal NO, however, continues after the burning of volatile components of coal up to some decrease in the reaction medium temperature⁵. Therefore, the right-hand side of the first inequality of system (108) should be supplemented with the quantity $x_{\text{NO}}^{\text{term}}$ —the amount of thermal NO formed in the whole high temperature region of the torch:

$$x_{\text{NO}}^{\text{term}} = 2k_{(85)}x_{\text{O}}y_{\text{N}_2}|_{\tau_f}^{\tau_b}, \quad (113)$$

where τ_b —the mean time of reaction mixture passage through the combustion chamber. Thus, the key kinetic constraints of the model that simultaneously describe three basic mechanisms of NO formation are determined. Finally, based on the aforesaid the system of constraints (94) is transformed in the following way:

$$\left. \begin{aligned} x_{\text{NO}} &\leq 2[\bar{x}_{\text{N}}(k_{(82)}x_{\text{OH}} + k_{(83)}y_{\text{O}_2})\tau_f + k_{(85)}x_{\text{O}}y_{\text{N}_2}(\tau_b - \tau_f)], \\ \bar{x}_{\text{N}} &\leq N_{(\text{carbon})}k_{\text{N}}^{\text{daf}}K_f + (k_{(85)}x_{\text{O}}y_{\text{N}_2} + k_{(86)}x_{\text{CH}}y_{\text{N}_2})\tau_D, \\ x_{\text{OH}} &\leq (K_{p(101)}y_{\text{H}_2\text{O}})^{0.5}; x_{\text{O}} \leq (K_{p(106)}y_{\text{O}_2})^{0.5}, \\ x_{\text{CH}} &\leq H_{(\text{carbon})}k_{\text{CH}}^{\text{daf}}K_f. \end{aligned} \right\} \quad (114)$$

It is easily seen that this system is linear with respect to the variables x_j .

The studies on NO formation by the traditional MEIS have been performed at Melentiev Energy Systems Institute for a long time. In parallel with MEIS the use was made of kinetic models and full-scale experiments that assisted in turn to gain information for variant calculations on MEIS. The results of these calculations allowed the conditions for nitrogen oxides formation by different mechanisms to be determined and the ways for improvement of coal combustion technology to increase environmental safety of boiler units to be outlined.

Figure 12 presents the results of calculations on model (90)–(95) (curve 7) in comparison with those performed earlier (Gorban et al., 2001, 2006) and experimental data. As is seen from the figure the calculations on the new model were in good agreement with the earlier results and proved to be even closer to experimental volumes of NO emissions by pulverized-coal boilers.

⁵ The quantity of thermal oxides sharply falls at T below ~ 1400 K.

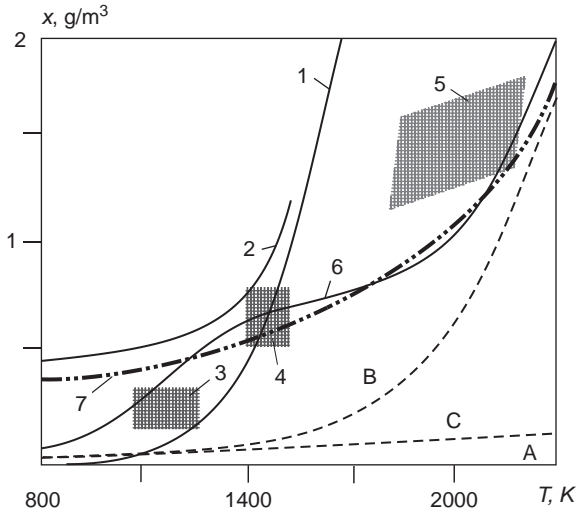


Figure 12 Theoretical and experimental NO emissions at coal combustion that were calculated by model (90)–(95) (curve 7) and presented in the work by Gorban (2001, 2006): equilibrium (1), maximum (2); actual (3–6): fluidized bed combustion (3), low-temperature combustion of brown coals (4), high-temperature combustion of hard coals (5), averaged for coal-fired boilers (6); A—“prompt” NO, B—“fuel” NO, C—“thermal” NO.

Somewhat overestimated calculation results in comparison with the in-situ measurements in a low-temperature region are explained probably by the fact that the model does not take into account NO reactions with nitrogen of reduced forms such as NH , NH_2 , NH_3 , etc., for example, $\text{NO} + \text{NH}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ or $\text{NO} + \text{NH} \rightarrow \text{N}_2 + \text{HO}$ that are typical of comparatively low temperatures (Warnatz et al., 2001).

At the same time calculations on the modified MEIS are possible without additional kinetic models and do not require extra experimental data for calculations, which makes it possible to use less initial information and obviously reduces the time and labor spent for computing experiment. Furthermore, there arise principally new possibilities for the analysis of methods to mitigate emissions from pulverized-coal boilers, since at separate modeling of different mechanisms of NO formation the measures taken can result in different consequences for each in terms of efficiency. Consideration of kinetic constraints in MEIS will substantially expand the sphere of their application to study other methods of coal combustion (fluidized bed, fixed bed, etc.) and to model processes of forming other pollutants such as polyaromatic hydrocarbons, CO, soot, etc.

The advantage of thermodynamic models of such complex processes as coal combustion over kinetic ones can be clearly understood, if we briefly deal with the current problems of kinetic description of this process

(Warnatz et al., 2001) and compare it with the described thermodynamic approach.

Coal burning is associated with three basic interrelated processes: coal pyrolysis, burning of volatiles and burning of coke. The kinetic model must include all these processes combined by the material and energy balances. In the thermodynamic model dealing with states it is sufficient to estimate limiting stages. To take into account, for example, pyrolysis it is enough to know only the rate of volatiles yield that can be calculated, as was shown, from the semi-empirical or even empirical relations. Kinetic description of pyrolysis requires that the chemical mechanism of the process and the diffusion coefficients on the coal particle surface and in the surface layer be known. Since the molecular chemical composition of coal used is not known exactly, even the listing of chemical reactions is a very complex scientific problem up to now. One can only guess the diffusion coefficient values, in so far as their measurement or theoretic description is extremely sophisticated and unreliable because of inhomogeneity and variation of coal particle surface during combustion. Note that this change should also be taken into consideration in the kinetic model. Hence even the first stage of coal combustion—pyrolysis—can be described only by the rough empirical (in the best case—semi-empirical) kinetic models that are true only in a narrow range of conditions typical of specific cases.

In MEIS there is no need to describe the process of volatiles burning. Their preset composition is limited by the dimension of vector x , and can be increased to several hundreds of components, which virtually does not affect model complexity but somewhat increases the time of calculations. The results obtained allow the estimation and withdrawal from the vector x of the components of low impact on the calculation results. In the calculations we used 68 chemical components. In the kinetic model uncertainty in the composition of volatile substances makes it impossible to describe in detail their combustion based on the elementary kinetics. The description in this case should also include processes of evaporation from the particle surface and diffusion. As a rule the parameters of these processes are unknown as well.

And finally, the coke burning is a heterogeneous process. Its modeling includes description of the processes of molecule adsorption on the surface, surface reactions, desorption of reaction products, diffusion through the pores and diffusion to the particle surface. At present the majority of these processes for coke are relatively poorly known. The key distinction of surface reactions from reactions at the gas phase consists in the necessity to attract for description of their rates such notions as surface active centers and adsorbed particles. And in the kinetic models a different nature of active centers (different energy of dislocations) necessitates consideration of the same particles adsorbed on them as different compounds because of

different constants of the surface rates. In MEIS different phase states are assigned to such particles, which leads only to the increasing dimension of component composition. In contrast to the constants of surface reaction rates, whose theoretical calculation is a rather complex problem and practical measurements have a low reproducibility, the thermodynamic parameters can be determined with a sufficiently high degree of accuracy from the spectral data and statistical calculations (Adamson and Gast, 1997).

From the above said, it may be concluded that a detailed kinetic model of coal combustion process that combines all three basic processes can not virtually be constructed, as it is impossible to do for each process separately. Therefore, the empirical models based on separation and experimental study of the limiting stages are extensively used. Such models separately do not reveal general regularities and do not allow the generalized conclusions to be drawn. The thermodynamic model makes it possible to study the whole attainability region and hence to consider states of the considered system as a whole and to keep track of the variation in the amounts of any component as a function of some or other kinetic constraints. The latter are written, as was shown above, easily enough even for such complex processes as coal combustion.

Advantages of the MEIS-based modeling of such complex chemical processes as nitrogen oxides formation at coal burning in comparison with the models of nonequilibrium thermodynamics prove to be even more clear and significant than its advantages compared with kinetic analysis. It is sufficient to mention only several facts. If the process mechanism is unknown, its analytic description required by the nonequilibrium thermodynamics is impossible. Formalization of constraints on duration of individual stages and concentrations of individual components seems to be highly difficult. For some transfer processes it is very hard to determine formulas for the Onsager coefficients such as for diffusion in the multi-component medium. The assumption on linearity of motion equations will certainly adversely affect the accuracy of calculations.

5.4 Stationary flow distribution in hydraulic circuits

The analysis of stationary and nonstationary flow distributions in multi-loop hydraulic systems with lumped, regulated, and distributed parameters and in heterogeneous systems was given in (Gorban et al., 2001, 2006; Kaganovich et al., 1997). In the concluding section of Section 5 the abundant capabilities of the flow MEIS are illustrated by the simplest example of stationary isothermal flow distribution of incompressible fluid in the three-loop circuit. It is shown how the degrees of order (laminar or turbulent modes) on the branches of this circuit are determined from calculation of the final equilibrium.

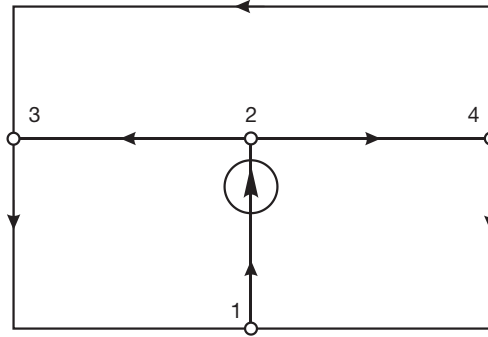


Figure 13 A scheme of the hydraulic circuit. 1–4—the numbers of nodes; the arrow in the circle—a source of effective pressure; the arrows specified directions of flows in the branches.

The design diagram of the hydraulic system is presented in [Figure 13](#). The pressure generated by the pump P^{mov} (2 MPa) and characteristics of branches (pipe lengths and diameters, coefficients of resistances γ_i) are given.

The model of final equilibrium (13)–(17) for the assumed conditions has the form: find

$$\max \left(\Delta S = T^{-1} \sum_i P_i^{\text{br}} x_i \right) \quad (115)$$

subject to

$$Ax = 0, \quad (116)$$

$$P^{\text{mov}} x_i - \sum_{i=1}^6 P_i^{\text{br}} x_i = 0, \quad (117)$$

$$P_j^{\text{br}} = \gamma_i x_i^\beta, \quad i = 1, \dots, 6, \quad (118)$$

where the exponent β in (118) is taken equal to unity for the laminar mode and to 2 for the turbulent mode. The sum in the parenthesis of the objective function equation (115) is the total kinetic energy of fluid flows that is converted into heat and then transferred to the environment. The results of flow distribution calculations are presented in [Table 1](#).

[Table 1](#) shows that with the equilibrium stationary flow distribution that corresponds to the maximum entropy of an isolated system

Table 1 Results of flow distribution calculation

Branch	γ_i	ΔP_i , MPa	x_i , m ³ /s	β
1–2	1.00×10^{-2}	1	10	2
2–3	1.56×10^{-3}	0.1	8	2
2–4	2.50×10^{-2}	0.05	2	1
1–3	1.25×10^{-2}	0.9	8.5	2
3–4	1.00×10^{-1}	0.05	0.5	1
1–4	4.22×10^{-1}	0.95	1.5	2

Note. The dimension of γ is not indicated because of its dependence on the value β .

(a combination of the circuit and the environment) and the minimum energy dissipation in a circuit (see Section 2.3) we have a quadratic closing relation (the turbulent flow mode) on four branches and a linear relation on two branches (the laminar mode). Thus, this example reveals the possibility of assessing the levels of order (self-organization) in individual elements (subsystems) of complex systems by means of the models of thermodynamic equilibria. As is known, in the nonequilibrium thermodynamics and synergetics the turbulent mode is believed to be more organized than the laminar one.

It should also be noted that the Prigogine theorem on the minimum entropy production is applicable to the circuit as a whole and for its individual branches (open subsystems). Actually, the maximum amount of entropy is formed in the environment owing to heat transfer to it from the hydraulic circuit. In the circuit itself the energy imparted to the fluid is entirely spent on its motion along the branches, i.e., on performance of effective work, and the entropy production at given conditions of interaction with the environment takes its minimal value equal to zero. The minimality of ΔS_i was shown in (Gorban et al., 2001, 2006).

6. CONCLUSION: WHAT WE HAVE AND WHAT WILL BE?

In the first years of the current century a new direction was formed in development of the model of extreme intermediate states (Kaganovich, 2002; Kaganovich et al., 2004a, 2004b, 2005a, 2006a, 2006b, 2006c) that is defined in this paperchapter as equilibrium macroscopic modeling of nonconservative systems. The described attempts to generalize and develop the studies presented in (Kaganovich, 2002; Kaganovich et al., 2004a, 2004b, 2005a, 2006a, 2006b, 2006c) allow the progress achieved on this path to be assessed.

The following problems were solved as a first approximation. The capabilities of equilibrium macroscopic modeling of irreversible processes in chemical transformations and mass and energy transfer, reduction of motion models to rest models (states) were revealed.

The possibility to address kinetic constraints within a thermodynamic model (MEIS) unfolds the ideas first suggested in thermodynamic analysis of kinetic equations (Feinberg, 1972, 1999; Feinberg and Hildebrandt, 1997; Feinberg and Horn, 1974; Gorban, 1984; Horn, 1964; Horn and Jackson, 1972). MEIS modifications with variable parameters and variable flows and also of spatially inhomogeneous systems were created. They include constraints represented in the thermodynamic form (without time variable) on the irreversible macroscopic kinetics. Computational problems of devising methods on the basis of these modifications that reduce to CP were somewhat solved, which made it possible to construct some relevant computing algorithms.

The efficiency of MEIS modifications was tested on the examples of modeling and analysis of fuel combustion and processing and flow distribution in multiloop hydraulic systems.

The capabilities of MEIS and the models of kinetics and nonequilibrium thermodynamics were compared based on the theoretical analysis and concrete examples. The main MEIS advantage was shown to consist in simplicity of initial assumptions on the equilibrium of modeled processes, their possible description by using the autonomous differential equations and the monotonicity of characteristic thermodynamic functions. Simplicity of the assumptions and universality of the applied principles of equilibrium and extremality lead to: the lack of need in special formalized descriptions that automatically satisfy the Gibbs phase rule, the Prigogine theorem, the Curie principle, and some other factors; comparative simplicity of the applied mathematical apparatus (differential equations are replaced by algebraic and transcendent ones) and easiness of initial information preparation; possibility of sufficiently complete consideration of specific features of the modeled phenomena.

At the same time the indicated valuable results may be treated only as a groundwork for further more versatile studies in comparison with the performed ones. The increasing versatility is due to more detailed comparison of MEIS with each of the basic macroscopic disciplines dealing with studies on the motion trajectories: chemical kinetics (Feinberg, 1972, 1999; Feinberg and Hildebrandt, 1997; Gorban, 1984), theory of dynamic systems (Arnold, 1989; Katok and Hasselblatt, 1997), synergetics (Haken, 1983, 1988), nonequilibrium thermodynamics (Glansdorff et al., 1971; Kondepudi et al., 2000; Prigogine, 1967; Zubarev, 1998); finite time thermodynamics (Rozonoer L et al., 1973; Tsirlin, 2006) and with physico-mathematical description and analysis of the main transfer processes; heat and mass exchange, electric current, radiation, including such phenomena

as thermal diffusion, Dufour effect, electrokinetic and thermoelectric processes; and with computational problems arising because of nonlinearity and nonautonomy of equations that describe constraints on the macroscopic kinetics; and with the solution of a large number of specific theoretical and applied problems.

Special attention should be paid to determination of the role of the discussed scientific direction in the recently formulated more general direction—"Model Engineering" (Gorban, 2007; Gorban and Karlin, 2005; Gorban et al., 2007). The technology developed there makes it possible to choose an initial formalized problem statement that would be optimal from the standpoints of calculations and analysis. The best formulations are searched for based on the reduction of the known equations of statistical physics, physical kinetics, or some macroscopic theories. Analysis of equilibrium thermodynamic modeling within the "technology" in general requires that the possibilities of such modeling as the ultimate method of reduction—transformation of the models of motion to the models of rest be estimated.

The list of the most important problems to be solved during further studies is presented in the following pages. Let us briefly comment upon this list, paying attention to the facts that are not described or almost not described in this chapter. The first group of problems (1–4) deals with the determination of fundamental capabilities of macroscopic models of equilibria in the study of irreversible processes. Whereas in the performed studies of MEIS the formalism of the motion and rest (equilibrium) theories was compared exclusively at the macroscopic level, in the future it is intended to obligatorily reveal MEIS relationships with statistical physics and physical kinetics. Analysis of admissibility of equilibrium approximations should become important in the statistical microscopic substantiation of state models for devising macroscopic equations from the initial probabilistic descriptions. Mathematical substantiation is based on the consideration of a wide scope of problems: from application of differential calculus as a whole (note that the infinitesimal changes of heat and work are not in general differentials) to the possibility of using autonomous differential equations and MP. Special analysis of correctness of equilibrium descriptions of explosions, hydraulic shocks, and other similar apparently irreversible processes seems to be needed, at least to be sure of the admissibility of equilibrium interpretations of "less nonequilibrium" phenomena.

The second group of problems (5–8) is associated directly with MEIS construction. Here the main goal for the future is to expand directions of analysis of the formalized descriptions of transfer processes, whose necessity was underlined above. Of particular interest are the studies on interrelations between thermal, electric, and chemical phenomena (the cross effects). Greater attention to transfer processes should be paid in

geometrical interpretations of MEIS. The idea of using a thermodynamic tree in the analysis of both chemical and macroscopic kinetics as a whole is also attractive.

The computational problems of the third group (9–16) inevitably stem from the conditions of solving the problems of the first and second groups. Analysis of situations, when a high irreversibility level complicates application of the notion of function differential and especially the CP methods (items 10 and 13), is considered as the greatest extent of novelty here.

Certainly, the list of specific problems of the fourth group may be extended unrestrictedly. The authors favored the problems concerning the energy research area they are engaged in. The problem of MEIS creation for an economic system (item 21) that was dwelt on in Section 4.2 is undoubtedly of interest from the viewpoint of assessing the capabilities of equilibrium thermodynamic modeling and revealing the identity in description of physical and socio-economic regularities.

All 29 enumerated problems can be solved on the basis of long-standing studies of many experts. However, we hope that even partial performance of the stated tasks will make the models and methods of the present-day equilibrium thermodynamics the property of a wide circle of researchers and engineers and they would find extensive application in the basic and applied science.

7. PROBLEMS OF EQUILIBRIUM THERMODYNAMIC DESCRIPTIONS OF MACROSCOPIC NONCONSERVATIVE SYSTEMS

7.1 Substantiation of the capabilities of equilibrium descriptions and reduction of the models of irreversible motion to the models of rest

1. Comparison of MEIS capabilities (equilibrium descriptions) with capabilities of kinetics, theory of dynamic systems, nonequilibrium thermodynamics, synergetics, thermodynamic finite time, and thermodynamic analysis of motion equations.
2. Statistical substantiation of MEIS. MEIS relations with equilibrium and nonequilibrium statistical thermodynamics and physical kinetics.
3. Choice of the mathematical apparatus of macroscopic equilibrium descriptions. Problems in modeling the nonholonomic, nonscleronomous, and nonconservative systems. Possibilities for using differential equations (autonomous and nonautonomous) and MP.

4. Reduction of the motion models to the rest models and determination of their role in the general model engineering. Transformation of the equations of irreversible macroscopic kinetics. Equilibrium description of explosions, hydraulic shock, short circuit, and other “supernonequilibrium” processes.

7.2 Analysis and development of MEISs

1. Comparison of MEISs with traditional methods of equilibrium thermodynamics. Initial physico-mathematical assumptions. Physico-mathematical characteristics. Admissible and efficient spheres of application: physics, chemistry, engineering systems, biology, and socio-economic systems.
2. Classification of MEISs. Models with variable parameters: with variable flows and spatially inhomogeneous systems; with constraints on the macroscopic kinetics and without them. Specific features of modifications and their comparative capabilities.
3. MEISs and macroscopic kinetics. Formalization of constraints on chemical kinetics and transfer processes. Reduction of initial equations determining the limiting rates of processes. Development of the formalization methods of kinetic constraints: direct application of kinetics equations, transition from the kinetic to the thermodynamic space, and direct setting of thermodynamic constraints on individual stages of the studied process. Specific features of description of constraints on motion of the ideal and nonideal fluids, heat and mass exchange, transfer of electric charges, radiation, and cross effects. Physicochemical and computational analysis of MEISs with kinetic constraints and the spheres of their effective application.
4. Geometrical interpretations of MEISs. Kinetic and thermodynamic surfaces. Representation of kinetics in the space of thermodynamic variables. Thermodynamic tree. Graphs of chemical reactions, hydraulic flows, and electric currents.

7.3 Analysis of computational problems in MEIS application and MEIS-based devising of methods, algorithms, and computing system

1. Computational problems of setting kinetic constraints. Development of methods for transformation and approximation of the motion equations applied.

2. Convex analysis of MEIS and determination of the areas of admissible and effective application of the CP methods.
3. Development of methods of searching for the optimal level of a characteristic thermodynamic function of the system $G(x^{\text{ext}})$. Interpretation of the proposed methods on the basis of a thermodynamic tree.
4. Development of optimization methods for systems with a variable composition of reagents ($y = \text{var}$).
5. Development of optimization methods for MEIS with variable flows of a substance participating in chemical reactions and transfer processes of heat, mass, and electric charges.
6. Development of optimization methods for MEIS of flow or current distribution in circuits.
7. Devising the methods for analysis of spatially inhomogeneous systems, applied first of all to nonisothermal natural systems and installations for fuel combustion and processing.
8. Creation of the computing system to perform laborious multivariant computing experiments with the maximum automation of man-machine interface.

7.4 Solution of specific theoretical and applied problems on MEIS

1. Modeling the processes of energy transfer by electromagnetic field.
2. Modeling the transfer processes with available phase transitions, sorption, dissolution, etc.
3. Description of nonstationary kinetics and transfer in spatially inhomogeneous systems.
4. Construction of models of electrochemical processes.
5. Construction of MEIS for an economic system.
6. Modeling the macroscopic kinetics of forming harmful substances in the processes of fuel combustion and processing.
7. Modeling the processes of pollution of air, soil, and water bodies.
8. Construction of models of equipment corrosion.
9. Modeling the slag and scale formation in energy installations.
10. Construction of thermodynamic models of stationary and nonstationary operating mode of pipeline systems for energy carrier transportation.
11. Construction of thermodynamic models of stationary and nonstationary operating mode of electric power systems.
12. Modeling the air conditioning systems including release and transformation of harmful substances.
13. Modeling the fires in buildings and installations.

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