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On the Interrelations Between Kinetics and Thermodynamics as the Theories of Trajectories and States

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1. Introduction

Existence of close and obligatory relations between kinetics and thermodynamics is the truth well known to experts. It is clear that propositions of the science based on the most general regularities of the macroscopic world (thermodynamics) should be used in the theories of macroscopic processes running over time (chemical and macroscopic kinetics). Application of general principles in solving specific kinetic problems in the majority of cases turns out to be related to specificity of their use. Observance of one or another principle or rule can require search for original both physicochemical statement of the problem, and mathematical model, and computational method. The art of thermodynamic analysis of kinetic equations was demonstrated in (Feinberg, 1972, 1999; Horn and Jackson, 1972; Gorban, 1984; Yablonsky et al., 1991) and works by other researchers. The character of relations between the theories of trajectories and theories of states changed qualitatively in the second half of the 20th century due to rapid development of computers and numerical methods of mathematical programming (MP). It became possible to considerably simplify formalized descriptions of problems owing to the transition from their analytical solutions to iterative, stepwise search processes. Analysis of possibilities to simplify the kinetic models and unfolding the methods to implement these possibilities on the basis of equilibrium thermodynamic principles constitute the aim of the chapter.

The main idea of the research being described is the refusal to use an equation of trajectory and construction of stepwise methods to analyse processes on the basis of the model of extreme intermediate states (MEIS) that was created by B.M.Kaganovich, S.P.Filippov and E.G.Antsiferov (Antsiferov et al., 1988; Kaganovich, 1991; Kaganovich et al., 1989). The features that make MEIS different from the traditional thermodynamic models are: 1) statement of the problem to be solved (instead of search for a sole point of final equilibrium x^{eq} the entire set of thermodynamic attainability $D_t(y)$ from the given initial state y is considered and the states x^{ext} with extreme values of modeled system characteristics of interest to a researcher are found); 2) dual interpretation of the equilibrium notion, i.e. both as a state of rest and as an instant of motion in which the equality of action and counteraction is observed; and 3) dual interpretation of dynamic quantities (work ℓ, heat q, rate w, flow of substance x, etc.) both

as functions of state and as functions of a trajectory. The last modifications of MEIS (Gorban et al., 2006; Kaganovich et al., 2007, 2010) include constraints on the rates of limiting stages of transformations, transfer and exchange of mass, energy and charges.

For these rates we set dependences on constants that have dimension of time (for example the total duration of chemical reaction or its certain stages). However, since it is possible to make an assumption about stationarity of motion when dividing the studied process into sufficiently small time periods the need for the use of time functions does not arise. Increasing the number of steps (segments) for choosing the solutions makes it possible to determine the trajectory of motion on the basis of these solutions with any required accuracy of calculations. The methods of affine scaling (Dikin, 1967, 2010; Dikin and Zorkaltsev, 1980) and dynamic programming (DP) (Bellman, 2003; Wentzel, 1964) are considered as numerical methods to be used to implement the MEIS capabilities.

The authors substantiated the validity of the entire methodological approach, mathematical models and computational methods on the basis of: 1) the historical analysis of developing interactions between the theories of trajectories and the theories of states; 2) the experience gained in the use of MEIS to study the processes of fuel combustion and processing, atmospheric pollution with anthropogenic emissions and motion of viscous liquids in multi-loop hydraulic systems; and 3) the establishment of mathematical relations between the applied dependences and thermodynamic principles.

Theoretical and applied efficiency of the equilibrium thermodynamic modeling in kinetic studies is illustrated by conditional and real examples: izomerization, formation of nitrogen oxides at fuel combustion, distribution of viscous liquid flows in multi-loop cirquits and optimization of schemes and parameters of these networks, analysis of mechanisms of physicochemical processes.

2. Remarks on the history of interactions between the theories of motion and the theories of rest

The authors believe that the joint development of statics and dynamics, theories of states and trajectories can be divided into five stages.

The first stage is related to the names of Galileo and Newton. Galileo was the first to consider the notions of equilibria as an obligatory component in the study of natural regularities. The principle of relativity that was discovered by Galileo revealed that the state of a body (a particle) subject to the action of forces that are in equilibrium can be described with the model of rest and the model of uniform rectilinear motion. The last formalized analysis made by D'Alamber showed that the dual interpretations can be extended to any instant of any nonuniform mechanical motion. The third law of Newton that should undoubtedly be observed in stationary and non-stationary, in reversible and irreversible processes helped greatly to better understand the relations between static and dynamic interpretations of equilibria. Newton used the equilibrium principles not only to establish the laws of nature but also to create a computational instrument intended to solve certain problems on the basis of these laws. The most important notion of infinitesimal calculus (the key Newton computational instrument) is the notion of differential – an infinitesimal linear increment in the function of state. But fixing the value of function is related to the assumption about equilibrium of the forces tending to change this value.

At the second stage of the considered historical process after Galileo and Newton a greater step in the development of equilibrium principles and their application to the analysis of trajectories and states was made by Lagrange. In (Lagrange, 1788) he gave the first systematic description of mechanics (which in the 18th century was equivalent to the description of physics) in terms of mathematics[1]. This book contains physical-mathematical explanation of the laws of nature and relations among them; the single theory of statics and dynamics, states and trajectories; choice of the methods to solve specific problems and substantiation of their physical (interpretational) and computational efficiencies; deductive derivation of partial regularities obtained by Newton in (Newton, 1999).

The initial equation chosen by Lagrange to build the structure of the Newton mechanics was the equation for equilibrium of a mechanical system

$$\sum_j c_j(x)dx_j + \sum_i \lambda_i(\varphi)d\varphi_i = 0 \,, \tag{1}$$

where c, x, λ and φ are a motive force, a coordinate, an uncertain multiplier (resistance force of bonds) and bond deformation, respectively; j – index of motive forces and respective coordinates; i – index of resistances and bonds. The first sum in the left-hand side of equation (1) represents a differential of work of motive forces tending to change the system state and the second sum – a differential of work of resistance forces that hinder any changes.

Formulation of equation (1) was based on two remarkable ideas. The first of them belongs to Newton who, according to Einstein, was the first to understand that physics can describe the laws of nature only in differential form. Integral relationships are often true only in certain ranges of values of variables and are less universal than differential ones used by Lagrange. The second idea implies division of potential forces applied to system into two groups: motive forces and resistances. Tendency of the difference between the works of these forces (taking into account the signs) to zero when nearing the point x^{eq} makes it possible to find the state of final equilibrium by solving the one-criterion extreme problem:

$$\text{find} \qquad \text{extr}\left(L = \sum_j c_j(x)x_j + \sum_i \lambda_i(\varphi)\varphi_i \right), \tag{2}$$

where L – the function that was later called the function of Lagrange.

The uniqueness of criterion (2) is explained by the uniqueness of division of forces into motive and "resisting" ones. Solving problem (2) as compared to solving the closed system of equations makes it also possible to easily vary statements of the problems by changing the set of variables, adding different equalities and inequalities to the system of constraints (bonds) or excluding them. Based on (1) we reveal physical and mathematical relations between the principles of equilibrium and principles of conservation. Since all the members in this equality have the dimension of work (energy) it can be interpreted as the principle of

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[1] Newton in (Newton, 1999) used mathematics exclusively as a calculation tool, i.e. as a means for solving certain problems. The laws were stated by him only in verbal formulations.

zero work, i.e. zero energy consumption (conservation) at an infinitesimal deviation of a system from equilibrium. This interpretation of (1) represents the principle of virtual work (PVW).

The identification of relations between statics and dynamics became a constituting part in the explanation of unity of the laws of mechanics in (Lagrange, 1788). Deriving the equations of trajectories from the equation of state (1) turned out to be possible owing to the assumptions made about observance of the relativity principle of Galileo and the third law of Newton and, hence, about representability of any trajectory in the form of a continuous sequence of equilibrium states. From the representability, in turn, follow the most important properties of the Lagrange motion curves: existence of the functions of states (independent of attainability path) at each point; possibility to describe the curves by autonomous differential equations that have the form $\dot{x} = f(x)$; dependence of the optimal configuration of any part of the curve upon its initial point only. These properties correspond to the extreme principles of the optimal control theory.

The single description of statics and dynamics made it also possible to extend the interpretations of the notions of state and trajectory functions. The work in an infinitesimal period of time in the vicinity of equilibrium point was interpreted by Lagrange as a function of state. Representation of the trajectory in the form of a continuous sequence of equilibrium states makes it possible to interpret the work as a virtual (possible) function of rest during the entire modeled process.

Based on the dual (dynamic and static) interpretations of equilibria and PVW (equations (1)) Lagrange formulated the integral extreme principle, i.e. the principle of the least action (PLA):

$$\delta J = \delta \int_{\tau_1}^{\tau_2} L d\tau = \delta \int_{\tau_1}^{\tau_2} (T - \Pi) d\tau = 0 \,, \tag{3}$$

where δ is variation of function; J – action; τ – time; T and Π – kinetic and potential energy of the system, respectively. The possibility to replace the Lagrange integrand L by the difference $(T - \Pi)$ is obvious, since the work of motive forces (the first sum in (1) and (2)) is performed by consuming kinetic energy and the work of resistance forces (the second sum) is a result of change in potential energy.

The equation of extreme trajectory that meets condition (3)

$$\frac{\partial L}{\partial x} - \frac{d}{d\tau}\left(\frac{\partial L}{\partial \dot{x}}\right) = 0 \tag{4}$$

was derived by Euler (for one point) and by Lagrange (for a system of points).

Along with many-sided and rigorous description of physical regularities the book by Lagrange (Lagrange, 1788) represents an invaluable contribution to the development of mathematical methods for analysis of states and trajectories. Specifically, the ideas of "The analytical mechanics" are related to the creation and application of the method of multipliers, mathematical programming and calculus of variations. The method of

multipliers which became the primary tool for Lagrange to derive and interpret the principles of statics and dynamics of mechanical systems also became a key tool for solving the problems of search for conditional extrema. Lagrange's analysis of the method of multipliers and conditions for equilibrium of mechanical systems laid foundation to construct in the second half of the 20th century the modern mathematical theory called mathematical programming (MP). The theory deals with search for extrema and equilibria. The work of motive forces started to play the role of objective function in the problems of mathematical programming and expressions for the work of bond deformation made up the system of constraints. The above physical interpretations of these works elucidated the possibility to divide the MP problems into direct (maximization) and dual (minimization), and clarified the term "dual estimates" which is used by mathematicians as applied to the Lagrange multiplier λ. Generally speaking, the unified physical-mathematical description of classical mechanics, that was made by Lagrange on the basis of equilibrium principles, i.e. his "Analytical mechanics" can be considered to be the first general theory of equilibrium states and equilibrium trajectories.

At the third stage the equilibrium thermodynamics was created by Clausius, Helmholtz, Boltzmann and Gibbs. Since that time the equilibrium principles started to develop as applied to macroscopic systems of any physical nature. The main, second law of thermodynamics was discovered by Clausius (Clausius, 2008). He found out the existence of the state function, entropy (S), that can change in the isolated systems exclusively towards increase. The inequality that shows such monotonicity of change

$$dS \geq 0 \qquad (5)$$

is one of the mathematical formulations of this law and determines irreversibility of natural processes, i.e. their compliance with "an arrow of time". They approach the point of global maximum of entropy, i.e. the state of final equilibrium x^{eq}. Thus, the second law is simultaneously the principle of both extremality and equilibrium. It can be applied to the analysis of trajectories ($dS \geq 0$) and states ($\max S$), reversible ($dS = 0$) and irreversible ($dS > 0$) processes. Motion towards point $\max S$ according to Clausius is an equilibrium motion since entropy was assumed by him as the function of state and its value can be fixed at any time instant only when respective forces are in equilibrium.

However, the practical application of the second law in the analysis of equilibrium irreversible trajectories faced great difficulties. Clausius and then Helmholtz, Boltzmann, J. Thomson, Planck and other researchers tried to harmonize the second law of thermodynamics with the principle of the least action and derive the equation that meets this principle similar to the equations (3) or (4) for dissipative macroscopic systems (in which the organized energy forms turn into a non-organized form, i.e. heat, due to friction). As is known their attempts were unsuccessful and resulted in understanding the necessity to statistically substantiate thermodynamics (Polak, 2010).

Such a substantiation was given by Boltzmann (Boltzmann, 1877), who chose the probability of attaining a state as its basic property that determines all other properties of thermodynamic system. Equilibrium transition from the least to the most probable states is at once irreversible since the reverse motion towards decrease in probabilities is immeasurably more difficult. Boltzmann's determination of a non-decreasing function (entropy) on the basis of equation

$$S = k \ln w \tag{6}$$

seems also natural, where k is the Boltzmann constant and w – thermodynamic probability (a statistical weight).

Similar to Lagrange, Boltzmann harmonized equilibrium theories of states and trajectories but in terms of probabilities. The transition from representation of entropy by a function of heat based on

$$dS = dq \,/\, T \tag{7}$$

(q is heat; T – absolute temperature) to the representation by a function of probability (6) interrelates deterministic and statistical descriptions. It also facilitates representability of heat as well as work as functions of state at infinitesimal time intervals. Indeed, according to Boltzmann the probability of a state does not depend on the path of its destination and, correspondingly, is a function of solely that state. Therefore, the entropy and heat, that are single-valued functions of probability, are logically to be considered as functions of state. Therefore, any trajectory related to both reversible and irreversible dynamics can be described by a continuous sequence of equilibrium states. In this case if variable w is used the modeled processes are interpreted as random ones, and if variable q – as deterministic ones. The mathematical macroscopic explanation of the applicability of differential equations to thermodynamic problems was given by Caratheodory (Caratheodory, 1909) and Born (Born, 1921).

The Boltzmann integro-differential kinetic equation written in terms of statistical physics became the foundation for construction of the structure of physical kinetics that included derivation of equations for transfer of matter, energy and charges, and determination of kinetic coefficients that entered into them, i.e. the coefficients of viscosity, heat conductivity, diffusion, electric conductivity, etc. Though the interpretations of physical kinetics as description of non-equilibrium processes of relaxation towards the state of equilibrium are widespread, the Boltzmann interpretations of the probability and entropy notions as functions of state allow us to consider physical kinetics as a theory of equilibrium trajectories. These trajectories as well as the trajectories of Euler–Lagrange have the properties of extremality (any infinitesimal part of a trajectory has this property) and representability in the form of a continuous sequence of states of rest. These trajectories can be used to describe the behavior of (a) isolated systems that spontaneously proceed to final equilibrium; (b) the systems for which the differences of potentials with the environment are fixed; (c) and non-homogeneous systems in which different parts have different values of the same intensive parameters.

Despite the creation of physical kinetics at the third stage of the history of interactions between statics and dynamics substantiated admissibility of equilibrium modeling of macroscopic processes of any physical nature at the forth stage the relations between macroscopic theories of motion and rest have sharply weakened. According to some scientists this was greatly due to the known discussion about the Boltzmann paradox (a seeming contradiction between the assumptions about a reversible character of interaction among separate particles and an irreversible result of these interactions aggregate). With development of the theory of dynamic systems (Arnold, 1989, Katok and Hasselblat, 2005),

non-equilibrium thermodynamics' emerged from the classical thermodynamics (Prigogine, 1967; Glansdorf and Prigogine, 1971; Jou et.al., 2001), and synergetics (Haken, 1983, 2006) the equilibrium approach relating the models of states and trajectories became widely deemed to be principally unsuitable in modeling of irreversible processes, degradation and self-organization. The experience gained in equilibrium analysis of various non-equilibria and irreversibilities (for example, emission of heat by electric current, diffusion, radiation, superfluidity and superconductivity, formation of stars, phase transitions of the second kind) by the classics of physics: Kirchhoff, Maxwell, Plank, Einstein, Landau, et al. discussed in (Gorban et al., 2006; Kaganovich, 2011; Kaganovich et al., 2007, 2010) was mostly ignored.

Such an attitude to equilibrium thermodynamics – the science which revealed irreversibility of the evolution of isolated systems and asymmetry of natural processes with respect to time – is related to some circumstances that require a thorough analysis. Here we will emphasize only one of them which is the most important for understanding further text. It lies in the fact that the most important notion of thermodynamics, i.e. equilibrium, became interpreted exclusively as the state of rest (absence of any forces and flows in the thermodynamic system) and equilibrium processes – as those identical to reversible ones. These one-sided interpretations ignored the Galileo principle of relativity, the third law of Newton and the Boltzmann probabilistic interpretations of entropy that allow dynamic interpretations of equilibria and irreversible interpretations of equilibrium processes.

An incomplete one-sided definition of the main notions resulted in an erroneous assessment of equilibrium thermodynamics capabilities and some misunderstandings with respect to applicability of equilibrium modeling in different areas. A vivid misconception was the opinion that self-organization can occur only in non-equilibrium systems. The opinion was undoubtedly caused by great success of non-equilibrium thermodynamics (Glansdorff and Prigogine, 1971; Jou et al., 2001) and synergetics (Haken, 1983) in explanation of the ordering processes. These disciplines helped to reveal the mechanisms of laser radiation, the Benard phenomenon and formation of turbulent vortexes in fluid, self-organizing chemical reactions and many other phenomena. We can say that the single theory of self-organization in the inanimate nature started to take shape. However, the abovementioned results, that were obtained on the basis of the propositions of equilibrium thermodynamics and were required for integrity and versatile applicability of this theory turned out to be in no demand.

The relations between the theories of trajectories and states, kinetics and thermodynamics that were lost started to recover at the fifth stage (the last third of the 20th century) owing to the works by M.Feinberg (Feinberg, 1972, 1999; Feinberg and Hildebrant, 1997; Feinberg and Horn, 1974); F.Horn (Horn, 1964; Horn and Jackson, 1972); A.N.Gorban (Gorban, 1984, Gorban et al., 2001, 2006, 2007); G.S.Yablonsky (Yablonsky et al., 1991) and other experts in thermodynamic analysis of chemical kinetics equations that were used to assess thermodynamically attainable results of chemical processes that correspond to attainable partial or complete (final x^{eq}) equilibria.

Two remarkable ideas put forward by A.N.Gorban should be emphasized in the studies related to thermodynamic analysis of kinetics. The first of them is the idea of a thermodynamic tree (Gorban, 1984) – a one-dimension graph, whose branches are related by one-to-one correspondence to the components of arcwise connectivity (regions on the

material balance polyhedron of a thermodynamic system, in which two any points can be connected by thermodynamically admissible paths), and a point of the branch reflects a set of equilibrium states on the respective component, in which the characteristic thermodynamic function has the same value. "The Gorban tree" can also be defined as a mapping of the entire thermodynamically admissible set of kinetic trajectories of the modeled system in the one-dimensional space. The presented definitions suggest high efficiency of applying the notion of a tree in geometrical explanations of relations between kinetics and thermodynamics.

The second and, apparently, the more general idea is the idea of formation of a new scientific discipline – "Model Engineering" (Gorban and Karlin, 2005; Gorban et al., 2007). The subject of the discipline is the choice of an outset statement of the solved problem which is the most suitable (optimal) both for conceptual analysis and for computations. The transfer of kinetic description into the space of thermodynamic variables became a main method for this discipline. In the method the solved problem can be represented as one-criterion problem of search for extremum of the function that has the properties of the Lyapunov functions (monotonously moving to fixed points).

3. Models of extreme intermediate states and construction of trajectories

The idea of MEIS creation first arose in analysis of synthetic liquid fuels production out of coal. The first modifications of this model were intended for estimation of the maximum yields of products in the chemical reactions (for example the maximum attainable concentration of light hydrocarbons in the process of hydrogenation of solid organic substances). The study on physical-mathematical features of MEIS that accompanied its application led to better understanding of the model capabilities and directions in its improvement. The capabilities were revealed largely owing to the specification of properties of a set of thermodynamically attainable states $D_t(y)$ from a given initial state y. Today we consider four specific features of this set to be the most important: 1) on the whole it belongs to the class of invariant manifolds in which any trajectory passing through any point of the considered manifold belongs entirely to it; 2) all the points of partial (intermediate) equilibria that belong to the manifold can be interpreted both as a state of rest (which is related to a supposition on the possibility of complete deceleration of all processes running through it) and as an instant of motion along one of the admissible trajectories; 3) dynamic variables: work, heat, flow, velocity, kinetic coefficients (including those the Onsager ones) that are applied to the description of a modeled system have the properties of the functions of states making up the set; 4) computational procedures related to the consequent monotonous change of the system's characteristic function on the set of values show one of the admissible trajectories in the space of chosen variables. The fourth feature is the sequence of the first one.

In accord with the described features the MEIS modifications gradually improved. Whereas in their first variants the admissible values of objective functions were limited only by the conditions of material and energy balances, monotonicity of entropy and thermodynamic potentials, yet in the first years of their application they started to include the constraints on possible values and limiting change of certain intensive parameters, quantities of reaction mix components and energy. The capabilities of MEIS increased sharply after the modules

of macroscopic kinetics had been added to them. The modules allow one to take account of the impact the rates of the limiting stages of a modeled process have on the attainable results. The variants of formalization of constraints on macrokinetics were discussed in detail in (Gorban et al., 2006; Kaganovich, 2011; Kaganovich et al., 2007, 2010). Now a new direction in development of the models of extreme intermediate states is taking shape. It is related to their application not only in thermodynamic analysis of possible results of the processes but also in determination of the trajectories along which these results can be attained.

Setting about developing the latter direction, the authors relied on the historical experience that was briefly presented in the previous section (the experience in joint equilibrium modeling of states and trajectories), capabilities of modern computers and computational mathematics, and on their own experience acquired in the course of MEIS development and analysis of various physicochemical and technical-economic problems on its basis. The main idea in solution of the stated problem was refusal to use the equation of the sought extreme trajectory and its determination in the stepwise decision making process. During the stepwise process the assumptions about the observance of the above characteristics of $D_t(y)$ turn out to be admissible on each negligibly small section (of space or time).

To explain the suggested approach to construction of trajectories a brief description of the MEISs underlying it is necessary. Unlike the descriptions presented in (Kaganovich et al., 1993, 1995, 2007, 2010) here a new classification attribute (a form of extremality criterion which can be objective and subjective) will be added to the MEIS classification. The objective criterion is the one the system itself tends to observe under the set conditions of its change. The subjective criterion corresponds to the interest expressed by a researcher during the study[2]. An example of the objective criterion is the minimum Gibbs energy ($\min G$) of a system in which temperature T and pressure P are held constant. The examples of subjective criterion can be the maximum yield of methanol ($\max x_{CH_4O}$) at its synthesis from the mixture of CO and H_2, or the minimum formation of nitrogen oxide ($\min x_{NO}$) at coal combustion. According to the old classification features here we will consider three types of MEIS: MEIS with variable parameters, MEIS of the mechanisms of physicochemical processes and MEIS of hydraulic circuits.

At fixed T, P and initial composition of components y of the physicochemical system the MEIS with variable parameters and subjective extremality criterion (the maximum concentration of a set of useful or harmful products of the process) has the form:

find

$$\max\left(F(x) = \sum_{j \in J^{ext}} c_j x_j \right) = F\left(x^{ext} \right) \tag{8}$$

subject to

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[2] The idea of such a classification was suggested to authors by the works by Yu.L.Klimontovish who used the notions of objective and subjective criteria of order (Klimontovich, 1995)

$$Ax = b,\tag{9}$$

$$D_t(y) = \left\{ x : \left| \begin{array}{l} x \le y, \\ \varphi_r(x_r) \le \psi_r, r \in R^{\text{lim}}, \end{array} \right. \right.\qquad\begin{array}{l}(10)\\[1.2em](11)\end{array}$$

$$G(x) = \sum_j G_j(x)x_j,\tag{12}$$

$$x_j \ge 0,\tag{13}$$

where $x = (x_1, ..., x_n)^T$ is vector of composition; $y \subset x$ – vector of initial composition; c_j – coefficient ranking the property of the j-th component x of interest to a researcher; x^{ext} – vector of composition in the desired extreme state; J^{ext} – set of indices of components with the extreme concentration of their mix to be determined; $A - (m \times n)$ – matrix of contents of the elements in the system components; b – vector of mole quantities of components of dimension m; φ_r – limiting kinetic function of the r-th component x, Ψ_r – its limiting value which depends on admissible values of variables that enter into the equation of limiting stage of the modeled process and on constants that determine its duration; R^{lim} – a set of indices of constraints on macroscopic kinetics; G and G_j – Gibbs energies of the system and its j-th component. The sign "$\le$" in expression (10) is understood in thermodynamic sense: $x \le y$, if it is possible to pass from y to x along a continuous trajectory along which $G(x)$ monotonously does not increase.

The equalities (9) and (13) represent a material balance. Expressions (10) and (11) determine the region of thermodynamic attainability from the point y. Equation (11) is used to specify constraints on macroscopic kinetics. The choice of equations for calculation of certain terms under the sign of sum in the right-hand side of equality (12) depends on the properties of the considered system.

The MEIS of a system described by the model (8)-(13) when choosing the objective extremality criterion has the form:

find

$$\min\left[G(x) = \sum_j G_j(x)x_j \right] = G\left(x^{\text{eq}}\right)$$

subject to

$$\left. \begin{array}{c} Ax = b, \\ \varphi_r(x_r) \le \Psi_r, \quad r \in R^{\text{lim}}, \\ x_j \ge 0. \end{array} \right\}\tag{14}$$

Analysis of the model (14) shows that fulfillment of the condition of the minimum Gibbs energy (extremality criterion) is in line with the Lagrange PVW if to assume that the fundamental equation written for the state of equilibrium (Gibbs, 1876, 1878)

$$dG = -SdT + VdP + \sum_{j=1}^{n} \mu_j dx_j = 0 \qquad (15)$$

(V is volume; μ – chemical potential) is an extension of equation (1) to thermodynamic systems with independent T, P and x. Following the formalism of Lagrange it can be conditionally considered that dG equals differential of the work of motive forces, whereas the terms in the right-hand side of the first equality (15) – differentials of the work of resistance forces, which in this case may have different signs.

Taking account of stationary process on the negligibly small trajectory section we can make sure that the product $G \cdot \tau$ (τ – time) is minimum, i.e. the principle of the least action is observed. Relations between the principles of conservative and dissipative systems were considered by the authors in (Kaganovich, 2011; Kaganovich et al., 2007, 2010). Below they will be additionally discussed in brief on the example of the models of hydraulic circuits.

By the analogy with parametric models it is also possible to represent the MEIS of mechanisms of physicochemical processes that are mapped on a conditional graph (Kaganovich, 2011; Kaganovich et al., 1993, 1995, 2007, 2010; Gorban et al., 2006) as those meeting the subjective and objective criteria. Each i-th branch of the conditional graph corresponds to the flows of matter, energy, charges that take part in the i-th stage of the overall process. The MEIS of the mechanism of chemical system with fixed T, P and y and subjective extremality criterion, similar to (8), is written in the form:

find

$$\max\left[F(x(\xi)) = \sum_{j \in J^{\text{ext}}} c_j x_j(\xi) \right] = F(x(\xi^{\text{ext}})) \qquad (16)$$

subject to

$$x_j = y_j + \sum_j \nu_{ij}\xi_i, \quad j = 1,...,n, \quad i = 1,...,m, \qquad (17)$$

$$D_{\text{t}}(y) = \left\{ \xi : \left| \begin{array}{l} x(\xi) \le y, \\ \varphi_r(x(\xi)) \le \Psi_r, \quad r \in R^{\text{lim}}, \end{array} \right. \right\} \qquad \begin{array}{l} (18) \\ (19) \end{array}$$

$$G(x(\xi)) = \sum_j G_j(x(\xi))x_j, \qquad (20)$$

$$x_j \ge 0, \quad 0 \le \xi_i \le 1, \qquad (21)$$

where $\xi = (\xi_1, ..., \xi_m)^T$; ξ_i is degree of completeness (coordinate) of the i-th reaction; ν_{ij} are stoichiometric coefficients. Equation (17) describes material balance of the j-th system component transformations. Inequalities (18) and (19) are similar to (10) and (11).

By the analogy with transition from model (8)-(13) to (14) it is possible to proceed from (16)-(20) to MEIS with the objective extremality criterion:

find

$$\min\left[G(x(\xi)) = \sum_j G_j(x(\xi)x_j) \right] = G(x^{\text{eq}}(\xi^{\text{eq}}))$$

subject to

$$x_j = y_j + \sum_i v_{ij}\xi_i, \ j = 1, ..., n, \ j = 1, ..., m,$$

$$\varphi_r(x_r(\xi)) \le \Psi_r, \ r \in R^{\text{lim}},$$

$$x_j \ge 0, \ 0 \le \xi_i \le 1.$$

(22)

Analysis of relations between the principles of extremality of characteristic thermodynamic functions and other physical principles of extremality on the basis of models of mechanisms methodologically coincides completely with the analysis of these relations with the help of MEIS of type (8)-(13) and (14).

Possibilities to use the above presented MEIS modifications to determine both attainable results of macroscopic processes and admissible trajectories of motion towards these results are illustrated with two examples that were already used in (Kaganovich et al, 2007, 2010) to find the states x^{ext}, i.e. those meeting the subjective criteria of extremality.

The first example is a system of three isomers with constant T, P and $y = (1,0,0)$. Idealizing the problem statement, let us assume that isomers are ideal gases with standard Gibbs energies $G_1^0 = -421.034$, $G_2^0 = -424.620$ and $G_3^0 = -420.255$ kJ/mole, the mechanism of the process that occurs in the system includes two stages: $x_1 \to x_2$ and $x_2 \to x_3$. Also we assume that the first stage lasts for an instant and the constant of the rate of the second k_2 equals 0.2 s⁻¹; the total duration of the chemical reactions τ_b =1.6 s. Unlike the earlier proposed MEIS (Kaganovich et al., 2007, 2010) the model with subjective criterion $\max x_3$ is replaced by the model:

find

$$\min\left[G(x) = \sum_1^3 G_j(x)x_j \right] = G(x^{\text{eq}})$$

(23)

subject to

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

(24)

$$x_3^l \le x_3^{l-1} + k_2 x_2^{l-1}\tau^l,$$

(25)

$$x_j \ge 0,$$

(26)

where index l is the number of the next calculation step that corresponds to one of the stages into which τ_b is split.

When determining the attainable state of the system on the basis of model (23-26) we did not divide τ_b into separate time segments and inequality (25) was represented as

$$x_3 \leq k_2 x_2^0 \tau_b \, ,$$

where x_2^0 is an instantaneously emerging (before formation of isomer x_3) concentration x_2. The process of transition from the state $y = (1,0,0)$ to the state $\varepsilon = (x_1^0, x_2^0)$ is shown on the triangle of material balance $A_1 A_2 A_3$ (Fig. 1, a) through the motion along the edge $A_1 A_2$ from vertex A_1 $(x = y)$ towards point ε. Point ε is the equilibrium point, i.e. the point of $\min G(x)$. At this point the edge $A_1 A_2$ touches the curve $G = G(\varepsilon)$.

For construction of the trajectory the process duration τ_b was initially divided into 5 segments. For the considered elementary example the composition of reaction mix and Gibbs energy at the final point of the process coincided with the same characteristics of x^{eq}, that were obtained from a one-stage calculation with an accuracy to the fraction of percent. Increase in the number of calculation periods did not change anyhow the calculation results.
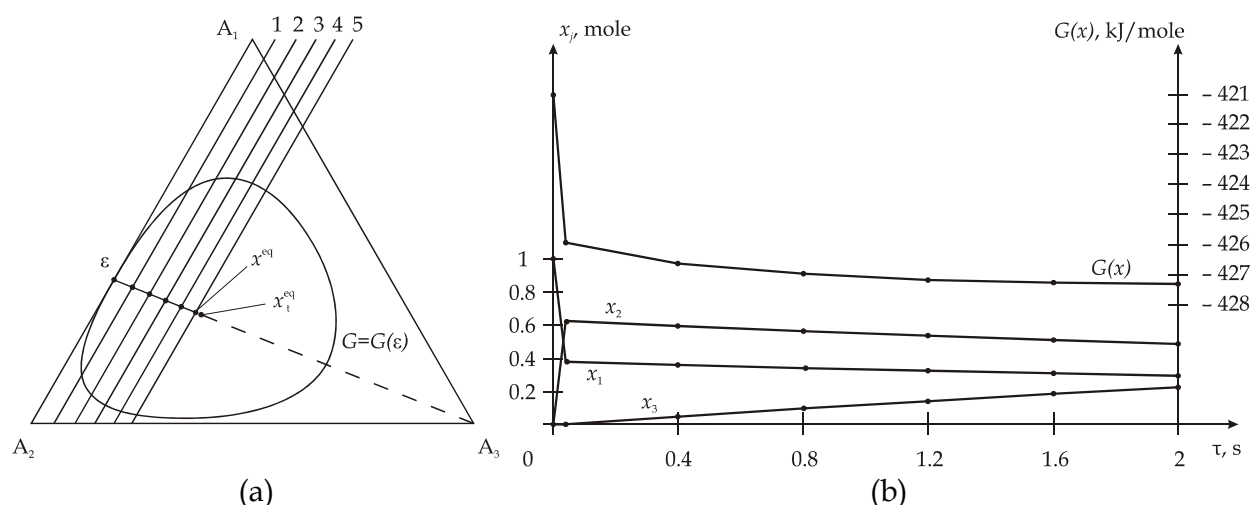
Fig. 1. Representation of the isomerization process results and trajectory on the triangle of material balance (a) and in the spaces (x, τ) and (G, τ) (b).

Lines 1–5 in Fig.1,a, that are parallel to the edge $A_1 A_2$ are the lines of constant concentrations x_3, that are attained by the end of the first, second, third, fourth and fifth calculation periods, respectively. Intersection points of these lines with the trajectory leading from ε to point x^{eq}, for the chosen problem statement, turned out to be located on one straight line, i.e. the trajectory of motion towards equilibrium in the space of compositions (x) turned out to be rectilinear. A conditional extension of this line from x^{eq} to the purely thermodynamic (without regard to constraint (25)) equilibrium x_t^{eq} and further to the thermodynamically forbidden region of Gibbs energy rise (Fig.1 a, shown by a dashed line) leads to vertex A_3 (the point of the value x_3, equal to unity, maximum possible under the condition of material balance). The revealed linearity of the trajectory is suggested by the linearity of equality (24) and inequality (25). Physicochemical explanation of the obtained result, at least partially was already given in (Kaganovich et al, 2007, 2010). Point A_3 is a solution to the system of differential equations of chemical kinetics that was made up without regard to thermodynamic constraints for the assumed mechanism of the process

with an infinitely large time interval. The revealed, though for the partial and simplest case, coincidence on the section $\varepsilon\text{-}x^{\text{eq}}$ of the lines of "the shortest kinetic and thermodynamic distances" (the fastest change in kinetic (x_3) and thermodynamic (G) functions on set time intervals) emphasizes the unity of kinetics and thermodynamics and the unity of descriptions of natural phenomena on the basis of their principles.

The analysis of the second example – formation of nitrogen oxides at coal combustion in torch furnace at constant T and P was made on the basis of MEIS with subjective criterion of extremality:

find

$$\max x_{\text{NO}} \tag{27}$$

subject to

$$Ax = b , \tag{28}$$

$$D_t(y) = \left\{ x : \left| \begin{array}{c} x \le y, \\ x_r \le \Psi_r, \ r \in R^{\lim}, \end{array} \right. \right\} \tag{29} \tag{30}$$

$$G = \sum_j G_j x_j , \tag{31}$$

$$x_j \ge 0 . \tag{32}$$

The condition for observance of macrokinetics requirements (30) was written as a system of inequalities (Kaganovich et al., 2007, 2010):

$$x_{\text{NO}} \le 2\left[\bar{x}_{\text{N}} \left(k_1 x_{OH} + k_2 y_{O_2} \right) \tau_f + k_3 x_0 y_{N_2} \left(\tau_b - \tau_f \right) \right] , \tag{33}$$

$$x_{\text{N}} \le k_{\text{N}}^{\text{daf}} K_f \text{N}_{(\text{coal})} + \left(k_3 x_0 y_{N_2} + k_4 x_{\text{CH}} y_{N_2} \right) \tau_D , \tag{34}$$

$$x_{OH} \le (K_1 y_{H_2O})^{0.5}, \ x_O \le (K_2 y_{O_2})^{0.5} , \tag{35}$$

$$x_{\text{CH}} \le k_{\text{CH}}^{\text{daf}} K_f \text{H}_{(\text{coal})} , \tag{36}$$

where τ_b, τ_f and τ_D are times of passing the reaction mixture through the furnace volume, combustion of volatiles, and diffusion of pyrolysis components from the surface of coal particle into turbulent reaction region; k_1, k_2, k_3 and k_4 – constants of reaction rates: N+OH→NO+H, N+O$_2$→NO+O, O+N$_2$→NO+N, CH+N$_2$→HCN+N; K_f is coefficient determining the share of volatile substances that pass from a coal particle to the gas phase during τ_D; K_1 and K_2 are equilibrium constants for reactions $H + OH \leftrightarrows H_2O$ and $O + O \leftrightarrows O_2$; N$_{(\text{coal})}$ and H$_{(\text{coal})}$ – amounts of nitrogen and hydrogen in coal; $k_{\text{CH}}^{\text{daf}}$ and $k_{\text{N}}^{\text{daf}}$ – coefficients depending on the composition of volatiles.

For comparison of efficiencies of thermodynamic and purely kinetic descriptions of coal combustion it should be noted that for kinetic description the whole mechanism of each stage forming the overall process (pyrolysis, combustion of volatiles and coke) and the values of kinetic coefficients of elementary stages should be known. Pyrolysis can be described based on the information about diffusion coefficients on the surface of coal particle and inside the surface layer. Measurement or theoretical description of these coefficients is very complex and unreliable because of inhomogeneity of coal particle surface and its change during combustion. A formalized representation of elementary kinetics of volatile combustion turns out unfeasible due to unavailability of exact knowledge about the composition of reaction mixture components and parameters of evaporation processes from particle surface and diffusion. The theoretical kinetic analysis of coke burning that supposes to apply the equations for molecule adsorption on the surface, surface reactions, desorption of reaction products, diffusion through pores and on particle surface is associated with insurmountable difficulties. Major portion of these processes for coke is poorly investigated. Inclusion of conditions (30), i.e. the system of inequalities (33)–(36), in MEIS requires only thermodynamic description of limiting stages. In this case the thermodynamic quantities can be determined with a sufficiently high degree of accuracy, which was shown in (Kaganovich et al., 2007, 2010).

The thermodynamic analysis of NO formation during fuel combustion is additionally improved by inclusion of trajectory construction problem in it, which is illustrated in Fig. 2,a and b. The Fig. 2 presents the calculation results for the Kansk-Achinsky coal pulverized combustion. Residence time τ_b for the reacting agent in combustion zone is taken equal to a second. Fig. 2,a shows solutions to the problem of determining attainable states: the state with maximum possible concentration of nitrogen oxide x_{NO}^{ext} and the state of final equilibrium x_t^{eq}. The latter was calculated not at the complete system of conditions (29), (30) that determine the region $D_t(y)$, but with an account of the condition for monotony (29) only. Application of the notion of equilibrium that is not related to kinetics in this case
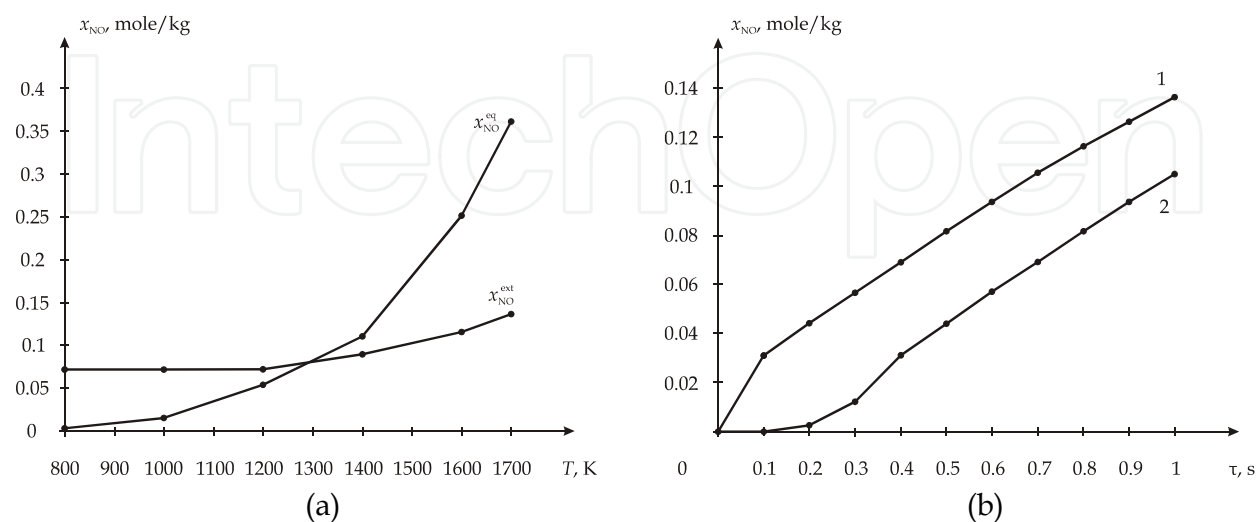

Fig. 2. Attainable equilibrium and extreme concentrations of NO as a function of temperature (a) and trajectory of attainment of x_{NO}^{ext} (b).

proved to be interesting, since $x_{\mathrm{NO}}^{\mathrm{ext}}$ at not very high temperatures (below 1200 K) were much higher than concentrations $x_{\mathrm{NO}}^{\mathrm{eq}}$ even at such equilibria. The value $x_{\mathrm{NO}}^{\mathrm{ext}}$, with which we compared the value $x_{\mathrm{NO}}^{\mathrm{eq}}$ determined by the stepwise computation of trajectory, was certainly found subject to the entire system of model constraints (27)-(32).

When constructing the trajectories the total process duration τ_b was divided at first into ten stages each equal to 0.1 s. As in the first example, increase in the number of stages was not needed to enhance calculation accuracy. Fig. 2,b presents two of the constructed trajectories. One of them (line 1) is determined on the basis of assumptions about ideal mixing of reagents and constant temperature (1700 K) in the whole furnace volume. The value of x_{NO} at the final point of this trajectory turned out equal to the value of the ordinate of line $x_{\mathrm{NO}}^{\mathrm{ext}}$ in Fig. 2,a at point T=1700 K. The other (line 2) was constructed considering poor mixing of the initial air-fuel mixture and combustion products at the initial stages of process and temperature equality: at the first time stage – 600 K, at the second – 1200 K and at the remaining eight stages – 1700 K. The final point of this trajectory was naturally situated on the ordinate much lower than those of the first trajectory. The multistage calculation of motion in time for the second considered case illustrates the most important advantage of the stepwise process of decision making. It implies the possibility to take into account individual properties of separate time stages forming a modeled process. In the considered analysis of NO formation, for example, when passing from one step of calculations to another account can be taken of change in both the temperature and the initial composition of components that was determined at the previous step. Such a change may be caused by recirculation of flue gases, secondary blast or steam injection into the gas flow. Many other factors can also be taken into consideration. Versatile study on the change in process course in time should obviously contribute to development of justified recommendations on the process control.

Relations between the theories of states and trajectories and capabilities of equilibrium thermodynamic analysis to study reversible and irreversible kinetics can be more fully revealed by considering another type of models of extreme intermediate states, namely MEIS of hydraulic circuits (Gorban et al., 2001, 2006; Kaganovich et al., 1997, 2007, 2010). Convenience and clearness of using these models to describe the considered problems are determined by the fact that they are intended to study an essentially irreversible process, i.e. motion of a viscous fluid. Besides, they can be treated as models of the mechanism of fluid transportation from the specified source nodes of a hydraulic system to the specified consumption nodes. The major variable of the hydraulic circuit theory (Khasilev, 1957, 1964; Merenkov and Khasilev, 1985), i.e. continuous medium flow, has an obvious kinetic sense.

As opposed to the described MEIS with variable parameters and the mechanisms of physicochemical processes in this case we will try to determine the objective function of applied model for a dissipative system based on the equilibrium principle of conservative systems, i.e. the Lagrange principle of virtual works. Derivation will be given on the example of the closed (not exchanging the fluid flows with the environment) active (with sources of motive pressures) circuit. The simplest scheme of such a circuit is presented in Fig. 3,a. A common character of the chosen example is explained by the easiness of passing to other possible schemes. For example, if at the modeled network nodes there are external
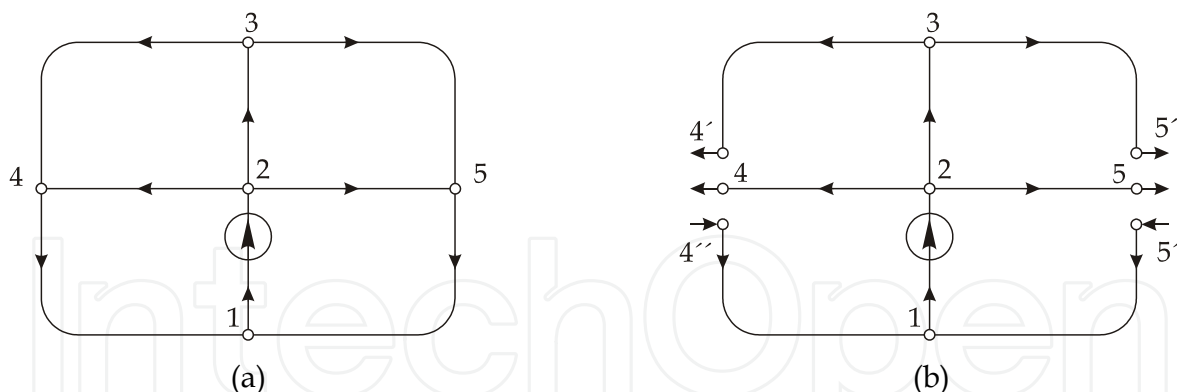
Fig. 3. Closed active circuit (a) and its transformation into a tree (b). 1–4(4´, 4´´), 5(5´, 5´´) – numbers of nodes; arrow in the circle – source of the motive pressure; arrows – specified directions of flows in branches.

sources and sinks, i.e. the circuit is open, it can be transformed to a closed scheme by adding conditional branches that connect nodes of the external sources (sinks) with the node representing environment. The motive pressures equal to the difference of pressures between the source node and environment are specified for the branches, along which the external flows move to the initial circuit. Transition to the analysis of open passive circuits (that do not contain motive pressures) is performed by removal from the initial scheme of branches with such pressures and addition of corresponding sources (sinks) to the nodes adjacent to removed branches.

Let us determine the principle of virtual works for the hydraulic circuit as follows: for every branch in any infinitesimal period of time an equilibrium of all forces (pressure, friction, gravity, etc.) acting on the fluid is observed and the work expended for infinitesimal deviation of flow on the branch from its equilibrium value is equal to zero. If only three forces are available on the i-th branch: the force caused by the difference in pressures between the initial and final cross-sections ΔP_i, the force of motive pressure (created by pump) P_i^{mov} and the force of friction, the following equation corresponds to the Lagrange principle

$$\Delta P_i dx_i + P_i^{\mathrm{mov}} dx_i - \gamma_i x_i^\beta dx_i = 0 , \tag{37}$$

where x_i is volumetric flow in a branch; γ_i and β are constant coefficient and exponent in the formula relating the pressure loss because of friction to the flow

$$P_i^{\mathrm{br}} = \gamma_i x_i^\beta . \tag{38}$$

For the whole circuit the Lagrange equation (1) will have the form

$$dL = \sum_i P_i^{\mathrm{mov}} dx_i - \sum_i \gamma_i x_i^\beta dx_i = 0, \ i = 1, \ ..., \ n , \tag{39}$$

where L is the Lagrange function. The term containing summands $\Delta P_i dx_i$ is not included in equation (39), since the sum ΔP_i for each closed loop and for the entire circuit is equal to

zero according to the second Kirchhoff law. Products $\gamma_i x_i^\beta = P_i^{\mathrm{br}}$, i.e. resistance forces of bonds, act as multipliers λ_i in (39). According to equation (39) changes of coordinates under motive forces and resistance (friction) forces are of the same sense (increase or decrease of the volumetric flow x_i) and value.

Equation (39) makes it possible to determine the objective function of MEIS and correspondingly the objective extremality criterion for stationary isothermal flow distribution of incompressible fluid in a closed active circuit. Account will be taken of the fact that because of equilibrium point stationarity the integrals corresponding to both sums in (39) take equal extreme values. For further analysis it is more convenient to make use of the latter and MEIS can be written in the form:

find

$$\mathrm{extr}(1/T)\sum_{i=1}^{n}\gamma_i x_i^{\beta+1} \tag{40}$$

subject to

$$Ax = 0, \tag{41}$$

$$\sum_{i=1}^{n}P_i^{\mathrm{mov}}x_i - \sum_{i=1}^{n}\gamma_i x_i^{\beta+1} = 0, \tag{42}$$

$$\sum_{i=1}^{n}\gamma_i x_i^{\beta+1} - k(T - T_{\mathrm{env}}) = 0, \tag{43}$$

where T and T_{env} are temperatures of fluid and environment; $A = [a_{ij}]$ is $(m-1)\times n$ - matrix of independent nodes and branches incidence; m – number of nodes; k – coefficient in formula $q = k(T - T_{\mathrm{env}})$. Equalities (41) and (42) describe material and energy balances of the circuit and equality (43) – balance of heat exchange between the circuit and environment. It is clear that multiplication of the sum in formula (40) for the objective function by multiplier $(1/T)$ that provides the function dimension and value of entropy, does not shift the extreme point along axis x at constant temperature.

The Lagrange function for problem (40)–(43) has the form:

$$L = (1/T)\sum_{i=1}^{n}\gamma_i x_i^{\beta+1} - \sum_{j=1}^{m-1}\lambda_j\sum_{i\in I_j}a_{ij}x_j + \lambda_m\left(\sum_{i=1}^{n}\gamma_i x_i^{\beta+1} - \sum_{i=1}^{n}P_i^{\mathrm{mov}}x_i\right) + \lambda_{m+1}\left(k(T - T_{\mathrm{env}}) - \sum_{i=1}^{n}\gamma_i x_i^{\beta+1}\right), \tag{44}$$

where I_j is subset of branches incident to node j.

It can be shown that the second partial derivatives are

$$\partial^2 L / \partial x_i^2 \le 0 \quad \text{and} \quad \partial^2 L / \partial T^2 \ge 0, \tag{45}$$

i.e. at point x^{eq} that corresponds to the steady stationary flow distribution in the circuit, the objective function has the maximum with respect to coordinates x_i and the minimum with

respect to T. Hence, the second law of thermodynamics holds true in the isolated system (circuit plus environment). In this case it is derived from the principle of virtual works assumed by Lagrange as initial in the analysis of conservative systems. The minimum of T that results from (45) does not contradict the second law, since when approaching the global equilibrium point the energy dissipation (entropy production) and the difference of thermal potentials (in the considered case ($T - T_{\mathrm{env}}$)) that directly provokes it, decrease. Therefore, in a way the second law may be called "an economy law". Energy dissipation that is not needed for complete degradation of the isolated system does not take place.

In the circuit the stationary action principle is observed. (Note that for the stationary processes the work can be multiplied by any given time without change of optimization result and for negligibly small time periods applied in our analysis the processes are always stationary). At the imposed constraints the maximum work of motive forces is done most economically. Since the fluid temperature takes a minimal value, the heat that is not caused by the work performed does not appear and the extra energy is not dissipated as well as in the case of isolated system degradation.

In the analysis of behavior of passive circuits they can be considered as "fragments" of active ones. Thus, the passive scheme that includes independent loops 2342, 2352 and 24152 can be obtained by removing from the scheme of Fig. 3,a the branch 1–2 with motive pressure and setting the source at node 2 and the sink at node 1, each being equal to the flow in the removed branch. The flow distribution for such a scheme will be determined from the model:

find

subject to
$$\left.\begin{array}{l} \mathrm{extr}(1/T)\sum_{i=1}^{n}\gamma_i x_i^{\beta+1} \\ Ax = Q, \quad i = 1, \, ..., \, n. \end{array}\right\} \tag{46}$$

where Q is vector of independent external sources and sinks. Condition similar to (43) is excluded from model (46) upon the assumption that the temperature can be determined in calculation of the active circuit that includes a modeled one. The second derivatives of the Lagrange function

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

of the model (46) have the form

$$\partial^2 L / \partial x_i^2 = \beta(\beta+1)\gamma_i x_i^{\beta-1} \geq 0,$$

i.e. the extremum of L is the point of minimum. Hence, it is clear that for passive circuits the least action principle and the Onsager-Prigogine theorem hold true. This is easy to explain physically, since in the passive circuits there are no work performers and exchange of flows with the environment should be fulfilled most economically.

The technique to reveal relations between different principles of extremality and equilibrium for infinitesimal time spans that is developed on the basis of thermodynamic circuit theory will be undoubtedly useful for devising methods for construction of trajectories representing continuous sequences of such spans.

4. Solution of computational problems in the analysis of trajectories

There is an appreciable groundwork for development of methods for construction and analysis of trajectories on the MEIS base. It resulted from extensive studies on the search for results of processes possible in the region of thermodynamic attainability $D_t(y)$. A key component of these studies is an extension of the experience gained in the convex analysis of ideal systems (Van der Waals and Konstamm, 1936; Zeldovich, 1938; Gorban, 1984) to modeling of real ones (Antsiferov, 1991; Kaganovich et al., 1989, 1993, 1995, 2007, 2010). They may include: an ideal (or real) gas phase, plasma, condensed substances, solutions and other components. The components of this analysis are determination of particularities of the objective function and study on the properties of set $D_t(y)$. For MEIS with variable parameters solution of the first mentioned problem proves to be non-trivial, when the sum $\sum_j c_j x_j$ in expression (8) with the constant value of y is replaced by the fractional expression $\sum_j c_j x_j / \sum_j g_j y_j$ (g is coefficient ranking worth of the j-th initial system component). The second problem contains studies on the impact of characteristic thermodynamic functions and formulations of kinetic constraints on the properties of $D_t(y)$.

The performed analysis of problems solved by using MEIS has shown the possibilities for their reduction to convex programming (CP) problems in many important cases. Such reduction is often associated with approximation of dependences among variables. There are cases of multivalued solutions to the formulated CP problems, when the linear objective function is parallel to one of the linear part of set $D_t(y)$. Naturally the problems with non-convex objective functions or non-convex attainability sets became irreducible to CP. Non-convexity of the latter can occur at setting kinetic constraints by a system of linear inequalities, part of which is specified not for the whole region $D_t(y)$, but its individual zones.

Studies on the specific features of MEIS made it possible to work out some modifications of mathematical programming methods that ensure effective application of the considered models. However, great difficulties are met even in the case when a problem solved can be reduced to a CP problem. For example, when applying MEIS of type (8)–(13) they are: 1) implicit setting of the constraints on monotony of characteristic functions (inequality (10)) and 2) large (up to 10–12 orders of magnitude) scatter in the values of sought variables, which happens in the analysis of environmental problems.

Both difficulties were successfully overcome with the help of the affine scaling method suggested by I.I. Dikin (Dikin, 1967, 2010; Dikin and Zorcaltsev, 1980). It became a key method for using models (8)–(13) and (14). The method is convenient, as it employs only interior points of the polyhedron of material balance, at which the objective function

gradient can be calculated, and the motion to the extreme point always proceeds at an acute angle to this gradient taken with a reversed sign. This fact contributes to method convergence at unfavorable (with zones of minor steepness) shape of the surface, on which the extreme point is sought for. Direction of motion to this point from the point obtained in the k-th iteration is determined on the ellipsoid

$$\sum_{j=1}^{n} \frac{z_j^2}{(x_j^k)^2} \leq 1 \,, \tag{47}$$

where $z_j = x_j^{k+1} - x_j^k$. Using the figurative comparison we can say that the affine scaling method used when descending the mountain allows determination of motion direction not by touch, as it is done, for example, in the steepest descent method, but by choosing the lowest point in the observable neighborhood. This neighborhood is represented by ellipsoid (47), whose axes are distances from x^k to the boundaries of positive orthant that determine a "visibility zone" inside the polyhedron of material balance. After the lowest point is reached in the k-th neighborhood the route of search is adjusted by means of constructing the ($k+1$)-th ellipsoid. The affine scaling method has proved high computational efficiency in the analysis of various physicochemical problems.

The mentioned difficulties were overcome in the following way. The first of them was eliminated by the two-stage technique for searching the extreme state x^{ext} that was suggested by E.G. Antsiferov (Antsiferov, 1991; Kaganovich et al., 1993, 1995, 2006). According to his idea the surface of thermodynamic function equation with point x^{ext} on it is determined at the first stage and the sought point coordinates are found on this surface at the second stage. At the first stage an auxiliary problem of linear programming is solved. As a result the maximum value (x^{mat}) of objective function (8) is determined on polyhedron (9), (13), i.e. without considering thermodynamic (10) and kinetic (11) constraints. Then the vertex of polyhedron x^{mat} is connected with the point of initial composition y, and the minimum point of characteristic function $G(x)$ is found on segment $y - x^{\text{mat}}$. At the second stage the affine scaling method is used to find x^{ext} on surface $G(x) = \text{const}$ containing this point. The chosen two-stage method is certainly approximate. However, its results have been compared with the results of the exact method of thermodynamic tree (Gorban, 1984; Gorban et al., 2006) on the examples of small dimensional systems. The latter is not implemented so far for large dimensional systems. The comparison has shown that the errors in calculations do not exceed 2-3%.

The problem of large scatter in the values of sought variables due to sharp deceleration in convergence of the computation process was solved by I.A. Shirkalin (Shirkalin, 1997) on the basis of factual transition from the affine scaling method to the general Newton method (the method of tangents) when approaching the extreme point.

Despite the long-term successful application of the affine scaling method to the MEIS-based thermodynamic analysis, extension of this analysis and primarily its extension to the studies on kinetics call for the use of dynamic programming (DP) (Bellman, 2003; Wentzel, 1964). In this context it implies not only the method of stepwise decision making, but a part of mathematical programming as the mathematical theory of equilibrium extreme states. For

rigorous explanation of relations between MEIS and DP this model should be evidently treated as the basis for devising concrete methods and as part of equilibrium thermodynamics, i.e. the physical theory of equilibria and extrema. A common nature of contents of the mentioned parts is that they relate the theories of states with the theories of trajectories: DP is mathematical programming with calculus of variations and theory of optimal control; MEIS is equilibrium thermodynamics with kinetics, irreversible thermodynamics, theory of dynamic systems. For application of both MEIS and DP it is unnecessary to know (to determine) a trajectory equation and to use a time variable. The process course is clarified as a result of the stepwise (in space or time) decision making.

The relations between MEIS and DP can be better elucidated by determining connections between the ideas applied at their creation with the idea of the mentioned thermodynamic tree of A.N.Gorban. The set of thermodynamic attainability $D_t(y)$ and correspondingly all admissible macrokinetic trajectories are projected on this tree being a one-dimensional graph. Therefore, it is reasonable to apply the tree for the analysis of correctness of the results obtained on the basis of MEIS and DP. Difficulty in this application is that possible construction of a tree in (Gorban, 1984) is substantiated only for the case of convexity of set $D_t(y)$ and convexity of the characteristic thermodynamic function. But it is believed that new computational approaches will eliminate this difficulty.

The known computational advantages of the DP method are:
- possibility for comprehensive consideration of the solved problem specificity, its many aspects and multiple scale nature, particularities of decision making at individual stages;
- applicability to searching for a global extremum of non-convex, unsmoothed functions with the break points (including functions of discrete variables);
- admissibility of using complex algorithms with application of logical expressions and tables in the computation process;
- automatic determination of several optimal variants, which is very convenient for versatile analysis of the obtained solutions in terms of physicochemical, technical, economic and ecological requirements.

Neither the affine scaling method nor the other MP methods possess the majority of the noted DP advantages.

Unfortunately, until now the MEIS-based dynamic programming method has found application only in the analysis of problems of technical and economic optimization (optimal synthesis) of circuits. This particular application, however, allowed a valuable experience to be accumulated in solving the most important DP problem, namely the search for extremum of the non-additive function. We will exemplify complexities and effectiveness of applying dynamic programming by the scheme in Fig. 3,a that was already used in the MEIS-based analysis of hydraulic circuits.

Suppose it is necessary to determine the most economical variant of fluid transportation from the pumping station on branch 1–2 to consumption nodes 3, 4 and 5, i.e. find the minimum of function $F(x,d)$, where $x = (x_1,...,x_n)^T$ and $d = (d_1,...,d_n)^T$ are vectors of volumetric flow and parameters (e.g. pipe diameters on network branches); x_i and d_i – their components. MEIS of optimal flow distribution and the method of multiloop

optimization that were applied for solving the stated problem were discussed in (Sumarokov, 1976; Kaganovich, 2011; Kaganovich et al., 1995, 2007, 2010; Gorban et al., 2001, 2006). The common algorithm of applying these model and method assumes division of the optimization process into five stages.

1. Setting the closed (without external sources and sinks) redundant scheme including all possible directions in locating individual branches (pipelaying).

2. Fixing parameters for each branch (e.g. maximum admissible diameters of pipes at preliminarily planned flows).

3. Determination of flow distribution on the basis of model (40)–(43) for the given scheme and parameters. As a result of this stage the interaction between flows in the scheme branches that cause non-additivity of function $F(x,d)$ is fixed, since the flow distribution is the result of this interaction. So far as the scheme is closed, there is no interaction involving constant pressures or flows at nodes of external sources or sinks. Thermal interaction of the circuit described by equation (43) as a whole with the environment remains, but does not influences additivity of the minimized function.

4. Transformation with the fixed interaction (distribution of flows among the branches) of the closed scheme (Fig. 3,a) to the tree (Fig. 3,b), specifying conditional external sources and sinks at break nodes (4, 4′, 4′′, 5, 5′, 5′′). They make it possible to preserve material balances in the network that were determined at the previous stage.

5. Choice of the optimal (corresponding to the minimum of additive function $F(x,d)$) parameters of the tree branches by the DP method. The process of stepwise search for solutions on the basis of this method is described by the functional equations

$$\left.\begin{array}{l} F_j = \min(F_{j+1} + F_{j,j+1}), \\ F_{j-1} = \min(F_j + F_{j-1,j}), \end{array}\right\} \tag{48}$$

where numbers $j+1$, j, $j-1$, etc. decrease from the end nodes (5, 5′, 5′′) to the node 1 of fluid flow arrival to pumping station. It is clear that at the node, where flows are joining the minimum values of function F are summed up. Thus,

$$F_2 = \min(F_3 + F_{2,3}) + \min(F_4 + F_{2,4}) + \min(F_5 + F_{2,5}).$$

Summation is made for each of the zones, into which the admissible range of change in variables is divided and the objective function depends on these variables. (The range, for example, can be related to admissible pressures at the corresponding node that in turn depend on the chosen diameters d_i).

Procedures 3–5 are repeated iteratively. The branches with negligibly small flows are excluded from the considered scheme. (For the scheme to remain close, in the iterations of flow distribution calculation removal can be simulated by setting negligible values of d_i). The calculation process terminates, when the difference in values for $F(x,d)$ becomes lower than the given negligible value at transition from one iteration to another.

Convergence of the multiloop optimization method that is based on iterative application of dynamic programming has a strict physical explanation. The stationary flow distribution

that is determined at the third stage corresponds to equilibrium optimal interaction between the flows in branches (the scheme closeness, as was noted above, stipulates the uniqueness of this interaction inside the network) and to the extreme network interaction with the environment (see Section 3). In this case in the isolated system (network plus environment) the maximum value of entropy is achieved and in the circuit the maximum work of motive pressure source is done at minimum possible fluid temperature, i.e. at minimum heat release and transfer to the environment and the minimum energy dissipation (entropy production). Optimization of network parameters by the DP method is related with sequential transition from the equilibrium extreme state of an ideal (with non-interacting components) additive system at node $j+1$ to the same state at node j. Optimization of network parameters by the DP method results in minimum dissipation of "economic energy" – money and minimum production of "economic entropy". Monotony of change in entropy production during iterative calculations of interaction between the system components for the given scheme and parameters at the fixed interaction ensures convergence of the computation process.

The results obtained in the thermodynamic analysis of circuits on the basis of dynamic programming give grounds to hope that the experience gained during this analysis will be extensively used in modeling the mechanisms of physicochemical processes on the graphs. Indeed, calculation of current or flow distribution in the circuit can be considered as determination of the mechanism of transporting charges or a substance from nodes – "suppliers" to nodes – "consumers". Unfortunately, up to now experience in thermodynamic modeling of circuits in the analysis of mechanisms was extended only to the studies of chemical reactions represented by open schemes of the form:
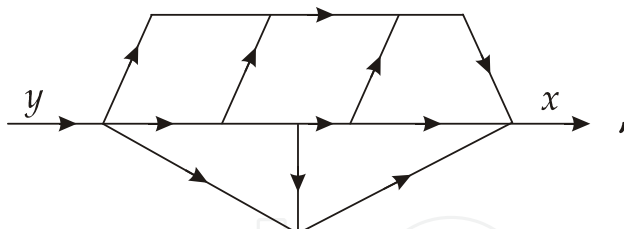
in which y and x denote vectors of the composition of initial reagents and reaction products, respectively (Kaganovich et al., 1993, 1995, 2007, 2010; Gorban et al., 2006). Transition from open schemes to closed ones that allow the iterative determination of interactions between the modeled system components and its representation as an ideal one can cause severe difficulties for complex mechanisms with processes of diverse types (transformation, exchange and transfer of substance, energy and charges). Thus, if the open electric or hydraulic circuit is transformed to the closed one by a rather easy procedure of connecting the nodes of external sources and sinks by conditional branches with the conditional node representing environment and by placement of sources of single-type motive forces on the branches connecting sources with the environment, the scheme of mechanism with stages of different physical nature will be transformed by means of including conditional branches with different (by nature) motive forces in the closed scheme. In general it is not by far a trivial problem.

Certainly, solving this problem deserves further studies. If they are successful, the dynamic programming method can prove to be an important tool for the analysis of mechanisms. DP application seems to be most effective to search for a mechanism satisfying some subjective criterion of extremality. Such application can be exemplified by the considered algorithm of optimal circuit synthesis that can be treated as a procedure of simultaneous determination of economic and physical components of the whole mechanism of pipeline system construction. In the context of physicochemical problems the optimality criteria may be the maximum yield of useful products of the modeled process or its minimum harmful impact on the environment.

MEIS with variable parameters and subjective extremality criteria of type (8)–(13) may turn out even more convenient objects for DP applications than MEIS represented by schemes in the form of graphs. This is due to the fact that the stepwise optimization on the basis of these models (e.g. determination of concentrations for the specified set of substances) can be performed without dividing the model into interacting parts. This fact ensures additivity of the objective function. Certainly it does not mean that construction of DP algorithms for MEIS (8)–(13) is an easy process. Dividing the computation process into individual steps and taking an account of specific features of these steps are still rather difficult due to a lack of formalized techniques to perform those processes.

Construction of trajectories by the DP method proves to be even more complex, when the models of type (14) with objective criteria of extremality are applied. In this case the objective function is a characteristic thermodynamic function of the system and for non-ideal systems its representation as a non-additive function of components becomes inevitable. Experience accumulated in circuit modeling is undoubtedly highly useful to solve the arising problem. Its use, however, will necessitate the search for new original methodological procedures. The search for trajectories in the case of successful intra step optimization is much easier, because it does not require inadditivity to be accounted for.

The idea of DP and relations similar to (48) have actually been used in analysis of trajectory construction examples as applied to the processes of isomerization an nitrogen oxides formation, which are considered in the section 3. Though, the possibility to simultaneously search for several "optimal" variants and to choose the best one among them subject to peculiarities of the problem solved. Development of algorithms for such a search is to be the aim of further studies.

5. Conclusion

Estimation of the results achieved until now in joint analysis of kinetics and thermodynamics, trajectories and states makes it possible to assert that the directions of further studies are laid down to a certain extent and some ideas of solving basic problems of these studies are suggested.

However, the made groundwork in studying physical-mathematical properties of the models of extreme intermediate states and in their application enables one to highly estimate the forthcoming achievements in solution of discussed problems and to prove the necessity for continuation and expansion of the scope of kinetic-thermodynamic studies.

This is so, because MEISs form the basis for analysis of states and trajectories in macroscopic systems, and they are intended for determination of (a) the results (useful or harmful) attainable on admissible motion trajectories of modeled systems and (b) control technique for their obtaining (preventing).

Rapid progress in computer technology that contributes to enhancement of competitiveness for simple algorithms that require multiple increase in computations and at the same time immeasurably decrease the labor input in creation of software and preparation of initial information gives a weighty support in the required proofs. The algorithms constructed on the basis of simple and universal prerequisites of equilibrium thermodynamics are obviously simple. They are used for stepwise description of trajectories that does not require derivation of "underivable" equations. The preparation process of initial experimental and theoretical data needed for their application becomes sharply easier. In this case the characteristics of rest states, whose sequences are applied to describe steps in decision making, are measured and calculated rather easier than characteristics of motion.

Development of the kinetic-thermodynamic direction in the analysis of macroscopic systems must essentially enrich both the applied and fundamental components of this analysis.

Improvement of the applied component is achieved first of all by increasing the versatility of studies of the most diverse technical and natural systems, which will allow the quality solution of numerous problems: updating of production processes, saving of resources, environmental protection.

Contribution to the fundamental science will influence development of macrscopic kinetics, classical equilibrium thermodynamics, and joint application of these disciplines to study the macroworld. The capabilities of kinetic analysis will be surely expanded considerably, if traditional kinetic methods that are reduced to the analysis of trajectory equations are supplemented by novel numerical methods. The latter are to be based on consideration of continuous sequences of stationary processes in infinitesimal time intervals. The problems of searching for the trajectories, being included into the subject of equilibrium thermodynamics, would make deserved the definition of this discipline as a closed theory that allows the study of any macroscopic systems and processes on the basis of equilibrium principles. Like the equilibrium analytical mechanics of Lagrange the thermodynamics may be called the unified theory of statics and dynamics. Joint application of kinetic and thermodynamic models further increases the noted potential advantages of the discussed directions of studies.

Certainly, the expected progress in development of kinetic-thermodynamic analysis cannot render worthless the current theories of evolution, the trajectories of development: the theory of dynamic systems, irreversible thermodynamics, synergy due to their great contribution to explanation of self-organization and degradation phenomena in animate and inanimate nature. When solving complex problems the researcher must have a set of models and methods and know how to choose among this set the elements, which correspond in the best way to specific properties of the considered problem. In the analysis of chemical kinetics problems the equilibrium thermodynamic models should obligatorily be included

in the research instruments, because these models make it possible to study the entire region of thermodynamic attainability and to search for admissible trajectories of the modeled system motion in it.

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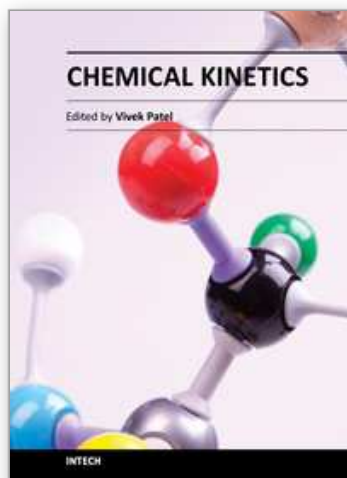
Chemical Kinetics

Edited by Dr Vivek Patel

Chemical Kinetics relates to the rates of chemical reactions and factors such as concentration and temperature, which affects the rates of chemical reactions. Such studies are important in providing essential evidence as to the mechanisms of chemical processes. The book is designed to help the reader, particularly students and researchers of physical science, understand the chemical kinetics mechanics and chemical reactions. The selection of topics addressed and the examples, tables and graphs used to illustrate them are governed, to a large extent, by the fact that this book is aimed primarily at physical science (mainly chemistry) technologists. Undoubtedly, this book contains "must read" materials for students, engineers, and researchers working in the chemistry and chemical kinetics area. This book provides valuable insight into the mechanisms and chemical reactions. It is written in concise, self-explanatory and informative manner by a world class scientists in the field.

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