

# Thermodynamic Models of Extreme Intermediate States and Their Applications in Power Engineering

B. M. Kaganovich<sup>a</sup>, S. P. Filippov<sup>b</sup>, A. V. Keiko<sup>a</sup>, and V. A. Shamanskii<sup>a</sup>

<sup>a</sup>*Melentev Energy System Institute, Siberian Branch, Russian Academy of Sciences, ul. Lermontova 130, Irkutsk, 664033 Russia*

<sup>b</sup>*Energy Research Institute, Russian Academy of Sciences, ul. Nagornaya 31/2, Moscow, 113186 Russia*

**Abstract**—Thermodynamic models of extreme intermediate states intended primarily for solving scientific and technical problems of power engineering are described. Examples illustrating the potential possibilities of using these models in developments and investigations of power engineering technologies are given.

**DOI:** 10.1134/S0040601511020054

The birth and development of thermodynamics is inseparably linked with the development of power engineering. Starting with Carnot, evaluation of thermodynamic efficiency became the initial point in carrying out a theoretical analysis of each new type of power installations. Thanks to the works of Clausius, Helmholtz, Thompson, Boltzmann, and Gibbs, thermodynamics evolved into a general macroscopic science about conversion of matter and energy. A great variety of processes that take place in nature and technical installations, in particular, chemical conversions, became subjects of its study. Owing to achievements of the modern computer engineering and applied mathematics, dedicated computation tools have become available, the use of which made it possible to extend the range of problems solved by the methods of thermodynamics [1–3].

However, great experience gained from thermodynamic studies has shown that the methods of classic thermodynamics based on the traditional formulations of the problem of searching for the final equilibrium state by determining the extrema of appropriate functions or solving the equations of the mass action law have a limited field of application. This relates primarily to studies of chemical conversions, the target products in which are generated not at the point of final equilibrium but in intermediate states of the process, through which a reacting system relaxes from its initial to its final state. The spectrum of studied technologies is fairly wide; it includes, in particular, such processes important from a practical point of view as hydrogenation and pyrolysis of coal and synthesis of methanol and other alcohols and hydrocarbons from synthesis gas. These are all grounds to believe that the number of such technologies will grow, including those used in power engineering. This growth is facilitated by progress in the field of catalysis (the use of

structured nanocatalysts, etc.) and extension of physical effect methods (radiation, microwave, laser, etc.) for chemical processes. A similar situation in which high concentrations of harmful substances are generated at partial equilibrium points is often encountered in studying the behavior of emissions (wastes) from power engineering facilities into the environment. Therefore, a pressing need has ripened for making a transition from models of final equilibria to models describing thermodynamic attainability regions, which include the entire multitude of partial equilibria that may occur on the path from the initial state of a system to its final (overall) equilibrium.

Theoretical studies of partial equilibria, in which relevant concepts were introduced using different terms, were already contained in the classic thermodynamic works of Gibbs, Planck, Einstein, Sommerfeld, and Landau. In the 1980s, A.N. Gorban', V.I. Bykov, and G.S. Yablonsky used an analysis of thermodynamic attainability regions [4, 5] for studying the specific features pertinent to the equations of chemical kinetics. A detailed description of the problem can be found in [4], where possible effects were revealed on the path along which systems reached their final equilibrium, in particular, the formation of superequilibrium concentrations of substances. Some works in this line were also carried out abroad Russia, for example, [6–9].

Unlike these approaches, B.M. Kaganovich, S.P. Filippov, and E. G. Antsiferov stated another problem, more important from a practical point of view: finding points having an extreme content of the products of a chemical process lying in the thermodynamically accessible zone of a reacting system that are of interest for a researcher [10–12]. Mathematical programming, i.e., the modern theory for solving extremum problems, was selected as simulation techniques in those studies. As a result, a new class of ther-

modynamic models called models of extreme intermediate states (MEIS) was developed and implemented on computers. A detailed description and analysis of these models are given in [10–14]. The use of new models widened considerably the possibilities and application field of thermodynamic analysis. This relates primarily to studies technological forecasting in power engineering [15, 16].

Using thermodynamics, a researcher can abstract his or her mind from the real process. As a result, it becomes possible to determine its limiting characteristics. This is unique information that can hardly be obtained using another method. The value of this information for forecasting studies is obvious. Using such data, one can take into account the potential for improvement of technologies in comparing them. The knowledge of limiting characteristics is of interest for those who are directly involved in development of prospective technologies and serves as substantiation for searching new means for achieving better efficiency, higher yield of target products, and smaller generation of harmful substances if, of course, there are such possibilities, which is possible to determine using MEIS. By varying the level to which a process is idealized by introducing additional (e.g., kinetic) constraints into a thermodynamic model, it is possible to simulate modern values of the indices characterizing processes under study. With such an approach, it is possible to study the influence of various factors on the possibility of achieving the limiting indices and prepare more substantiated recommendations for improving existing technologies and developing new ones [14].

### MODELS OF EXTREME INTERMEDIATE STATES

In contrast to traditional thermodynamic models intended for finding a single point of final equilibrium  $x^{eq}$ , the use of MEIS makes it possible to study the entire attainability region from the specified initial state of a system and find a point in this region at which the property of interest for a researcher reaches its extreme value (e.g., the extreme yield of target or harmful products from the chemical process running in the system). Unlike models intended for carrying out a thermodynamic analysis of process trajectories, the use of MEIS does not involve the need to determine the actual sequence in which a system passes its states along the path to the sought extreme point (kinetics equations), due to which the construction of a model becomes several times simpler. In recent years, new versions of MEIS containing constraints for irreversible macroscopic kinetics written in thermodynamic form (without using the time variable) have been constructed [14].

One of the most general formulations of an EISM containing kinetic constraints for a physicochemical system with the fixed temperature  $T$  and pressure  $p$  has the following form.

Find

$$\max F(\mathbf{x}, \mathbf{y}) = \sum_{j \in \mathbf{J}^{ext}} c_j x_j / \sum_{j \in \mathbf{J}^0} g_j y_j = F(x^{ext}, y^{ext}) \quad (1)$$

subject to

$$\sum_1^l \mu_j y_j = 1; \quad (2)$$

$$\mathbf{Ax} = \mathbf{b}(\mathbf{y}); \quad (3)$$

$$\mathbf{Ay} = \mathbf{b}(\mathbf{y}); \quad (4)$$

$$\alpha_k \sum_{j \in \mathbf{J}_k} y_j \leq y_k \leq \beta_k \sum_{j \in \mathbf{J}_k} y_j, \quad k \in \mathbf{K}; \quad (5)$$

$$\mathbf{D}_r(\mathbf{y}) = \left\{ \mathbf{x}: \begin{array}{l} \mathbf{x} \leq \mathbf{y}, \\ \varphi_r(\mathbf{x}) \leq \psi_r, \quad r \in \mathbf{R}^{lim}; \end{array} \right\} \quad (6)$$

$$G(\mathbf{x}) = \sum_j G_j(\mathbf{x}) x_j; \quad (8)$$

$$x_j \geq 0; \quad y_j \geq 0, \quad (9)$$

where  $\mathbf{x} = (x_1, \dots, x_n)^T$  is the vector characterizing the amount of components in a reaction mixture;  $\mathbf{y} = (y_1, \dots, y_l)^T$  is the vector characterizing the amount of substance in the initial reagents;  $\mathbf{T}$  is the transpose symbol;  $\mathbf{y} \subset \mathbf{x}$ ;  $c_j$  and  $g_j$  are the coefficients ranking the value of the  $j$ th component of the vectors  $\mathbf{x}$  and  $\mathbf{y}$ , respectively;  $x^{ext}$  and  $y^{ext}$  are the sought extreme values of the vectors  $\mathbf{x}$  and  $\mathbf{y}$ ;  $\mathbf{A}$  is the matrix of size  $m \times n$  characterizing the content of elements in the system components;  $\mu$  is molar mass;  $\mathbf{b}$  is the vector of the quantity of elements;  $\alpha$  and  $\beta$  are coefficients;  $\mathbf{D}_r(\mathbf{y})$  is the region (set) of thermodynamic attainability from the initial state;  $\varphi_r$  and  $\psi_r$  are the limited kinetic function of the  $r$ th component of  $\mathbf{x}$  and its limiting value;  $G$  is the Gibbs energy; and  $\mathbf{J}^{ext}$ ,  $\mathbf{J}^0$ ,  $\mathbf{K}$ , and  $\mathbf{R}^{lim}$  are sets of symbols denoting, respectively, the components the extreme concentration of whose mixture has to be determined, initial reagents the efficiency of using which is of interest for a researcher, initial reagents with limited concentrations, and constraints for macroscopic kinetics.

The kind of objective function (1) is stemming from the fact that efficient use of individual components rather than the initial mixture of reagents as a whole may often be of interest in searching for the optimal composition of the vector  $\mathbf{y}$ . For example, in studying the coal hydrogenation process it is more important to estimate the possibility of efficient use of expensive hydrogen than the same for inexpensive coal. If the



tion by introducing various constraints in it in the form of equalities or inequalities. Another important advantage of using MP is the possibility of specifying the basic input information in simulating chemical processes in the form of lists of reagents (substances) rather than lists of reactions, which is often necessary when these processes are simulated on the basis of the mass action law. In the majority of cases, it is considerably easier to prepare the first list than to draw up the second one.

The comparative advantages of MEIS become immensely greater when constraints of form (7) for macroscopic kinetics are included in them. First of all, greater possibilities for carrying out a thermodynamic analysis of intrinsically irreversible processes such as diffusion and heat- and mass transfer become available. In this case, the thermodynamic attainability region  $D_r(y)$  becomes much smaller, and better accuracy of thermodynamic simulation is achieved.

The advantages of MEIS as compared with the models of nonequilibrium thermodynamics and kinetics, and other models of motion and trajectories are determined by the simple and universal nature of the initial assumptions of equilibrium thermodynamics. These advantages show themselves also in the comparative computational efficiency of MEIS, in the possibility of carrying out a comprehensive analysis of different physicochemical processes without using approximations that make the simulation results less accurate, and in a smaller effort required to prepare the initial data. The latter is true for both preliminary theoretical calculations and for experimental determination of various dependences used in the mathematical model. Indeed, it is considerably easier to determine the characteristics of steady state than the characteristics of motion.

For extending the field of using the above-mentioned advantages, several model versions were developed for systems represented on graphs along with the versions of MEIS with variable parameters similar to (1)–(9):

(i) models corresponding to actually existing schemes representing the motion of substance or charges [13, 14, 17] and

(ii) models representing conditional schemes of mechanisms governing physicochemical processes [13, 14, 18].

The former were intended for analyzing the distribution of flows (currents) in hydraulic and electrical circuits and for optimally synthesizing them (technical-and-economic optimization), and the latter were mainly intended for finding the optimal mechanisms used to implement technological processes.

## USE OF MEIS IN THEORETICAL AND APPLIED STUDIES

At present, MEIS with variable parameters (so-called parametric MEIS) have been developed best and are most widely used. Such models were successfully applied many times for solving the following problems:

(i) in carrying out energy and environmental analyses of fuel combustion and treatment processes [12, 19, 20];

(ii) in comparing different methods for removing sulfur and nitrogen compounds from flue gases discharged from technological installations [12, 14]; and

(iii) in estimating the contribution of energy-related and other man-made emissions in pollution of the atmosphere [12, 21].

A fruitful effect from using equilibrium simulation of chemical processes occurring in the atmosphere was revealed in the course of such investigations. For a long period of time, many specialists had been considering this field of investigations forbidden for the applications of classic thermodynamics. The use of MEIS makes it possible to remove the prohibition both for this field and for thermodynamic description of fuel processing technologies, in particular, hydrogenation and pyrolysis of coal.

Three methods for formalizing constraints on process kinetics have found use and are being developed in constructing parametric MEIS containing kinetic blocks of form (7).

1. Using the integrals of kinetic equations limiting individual stages of the mechanism governing a simulated process.

2. Limitation of these stages by specifying additional thermodynamic relations for them.

3. Direct derivation of kinetic equations and kinetic coefficients from the equilibrium conditions of a thermodynamic formulation.

The first two methods are presently used in solving applied problems. At the same time, it is exactly the third method that makes it possible to obtain the most consistent thermodynamic formulation of an EISM and illustrates most prominently the range of applications and depth to which thermodynamics are analyzed [13, 14].

The application field of the studies of circuits (electrical, hydraulic, and others) carried out using MEIS has hitherto been limited to an analysis of pipeline systems for transporting energy carriers. This analysis has revealed the possibilities of equilibrium simulation of the motion of viscous liquid in pipelines both in the cases of laminar and turbulent flow modes, which is an irreversible process in its nature, and technical-and-economic optimization (maximizing the extent of

ordering) of heat supply systems [17] using the principles of equilibrium thermodynamics. In so doing, the growth of entropy was related to irreversible dissipation of so-called “economic” energy in the form of capital and money. An important theoretical result obtained from thermodynamic simulation of hydraulic systems is that mathematical correlations between the second law of thermodynamics, the principles of steady and least action, and Onsager–Prigogin’s theorem have been revealed as applied to these systems [17]. This, of course, gives a deeper insight into links between equilibrium and nonequilibrium thermodynamics and possibilities of using them.

Versions of MEIS containing a “graphic” description of mechanisms governing physicochemical processes [13, 14] are still at an early stage of their development; nonetheless, they have already found use, e.g., in solving the problem of selecting catalysts [17].

### THE PROCEDURE OF APPLYING MEIS

In the general case, studies carried out using MEIS include the following stages.

1. Formulating the problem and constructing a model with specifying the lists of substances (the vectors  $\mathbf{x}$  and  $\mathbf{y}$ ), composition of target products, system of constraints, calculation conditions, etc.

2. Calculating the final equilibrium state  $x^{eq}$ . Analyzing the effect on  $x^{eq}$  of the thermodynamic parameters ( $p$  and  $T$ ), composition of initial substances  $\mathbf{y}$ , etc. The obtained information makes it possible to construct the motion trajectories of  $x^{eq}$  in the space of compositions  $\mathbf{D}_i(\mathbf{y})$ , including the trajectories of its motion when changes occur in the geometrical characteristics of the space of compositions.

3. Finding the extreme concentrations  $x^{ext}$  of reaction products that are of interest for the researcher when there are only thermodynamic constraints, i.e., conditions (6). It should be emphasized that the estimates of  $x^{ext}$  are unique information that, apparently, can be obtained in a comparatively simple way only using MEIS. Such information is of indubitable value for making forecasts. The difference between extreme concentrations and those observed in practical applications enables one to make a judgment about the potential for improving the technologies being considered (or about the potential risk of producing undesirable substances).

4. Studying the effect on  $x^{ext}$  of the parameters  $p$  and  $T$ , composition of initial substances  $\mathbf{y}$ , and other factors. The results obtained from these studies make it possible to construct the  $x^{ext}$  motion trajectories in the space of compositions  $\mathbf{D}_i(\mathbf{y})$  and find the region of parameters and conditions having a favorable effect on increasing  $x^{ext}$ .

5. Analyzing the energy balance of a system, the results of which determine whether constraints for supplying energy from outside in form (10) need to be introduced in the model.

6. Sequentially applying macrokinetic constraints (7) on a thermodynamic system in some approximation and estimating their effect on the extreme yield of target products  $x^{ext}$ . Introduction of additional constraints, even in the simplest form (e.g., for the concentrations of individual components of the vector  $\mathbf{x}$ ), opens possibilities for using MEIS to carry out detailed studies of any states in the zone of thermodynamic attainability. Obviously, this is a unique advantage of MEIS. The process under study can be simulated by varying the degree to which the initial substances (and in the necessary cases, also the intermediate products of reactions) are converted. It is important to point out that in principle, introduction of macrokinetic constraints makes it possible to approach as close as one wishes to the description of states observed in practice. By studying and comparing macrokinetic constraints one can judge the efficiency of control inputs on technological processes.

7. Analyzing the study results accumulated in carrying out the preceding stages to find the conditions under which the found extreme state can be obtained. The arsenal of means by which the process under study can be adjusted is quite considerable: it includes the use of catalysts, freezing of reactions (by quickly changing the external parameters), removal of intermediate components (using physical or chemical methods), use of a multistage scheme for carrying out the process, etc. Owing to such a wide arsenal of means for adjusting the process, there is no need to discuss the problem of estimating the probability of implementing the state  $x^{ext}$  (the probability of a process to pass through this state) in solving the majority of applied problems. There is an opinion that all states permitted by thermodynamics can be implemented under certain conditions [22]. Many biochemical processes can serve as confirmation of this statement.

The problem of estimating the feasibility of found extreme states may turn to be extremely difficult and generate the need to carry out additional investigations, e.g., extending the component composition of a system (the vector  $\mathbf{x}$ ) in searching for a catalyst with inclusion into this composition of components determining the properties of a catalyst (active surface sites etc.). Extension of the vector  $\mathbf{x}$  means that new coordinates (and accessible zones) will appear in the space of compositions and, hence, that new ways will open for bypassing the final equilibrium, and new possible trajectories with a new set of reactions and other rates of their course will become available (which is just the essence of catalysis). In many cases, a combined application of MEIS and other dedicated tools (e.g., mod-

Extent to which initial carbon transfers into methane ( $T = 800$  K), %

| Molar ratio<br>$O_2 : C$ | Extent to which C transfers into $CH_4$ , % |                |
|--------------------------|---|----------------|
|                          | $H_2O : C = 2$                              | $H_2O : C = 3$ |
| 0                        | 46  | 45             |
| 0.1                      | 42  | 40             |
| 0.2                      | 37  | 35             |
| 0.3                      | 32  | 30             |
| 0.4                      | 27  | 25             |
| 0.5                      | 22  | 20             |

els of chemical kinetics), as well as field experiments, may be useful in solving the problem of attaining  $x^{ext}$ .

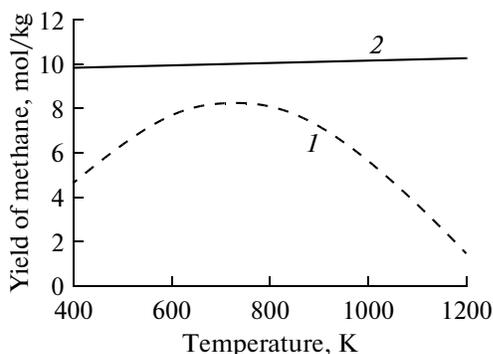
### EXAMPLES OF THERMODYNAMIC SIMULATION

The effectiveness of equilibrium thermodynamic simulation is disclosed below by examples of using MEIS for analyzing steam conversion of coal and generation of nitrogen oxides during coal combustion. The first example illustrates the potential possibilities of MEIS in solving problems relating to development of new technologies, and the second one shows their possibilities in studying well-known processes.

**Steam conversion of coal.** The generalized equation of this process looks as follows:



This process was found to be very sensitive for variations of temperature and ratio between the reagents in the initial mixture. These variations entail a change in the topology of Gibbs energy, in the configuration and sizes of the thermodynamic accessibility region, and in the positions of the final equilibrium point ( $x^{eq}$ ) and the extreme point ( $x_{CH_4}^{ext}$ ). Thermodynamic con-



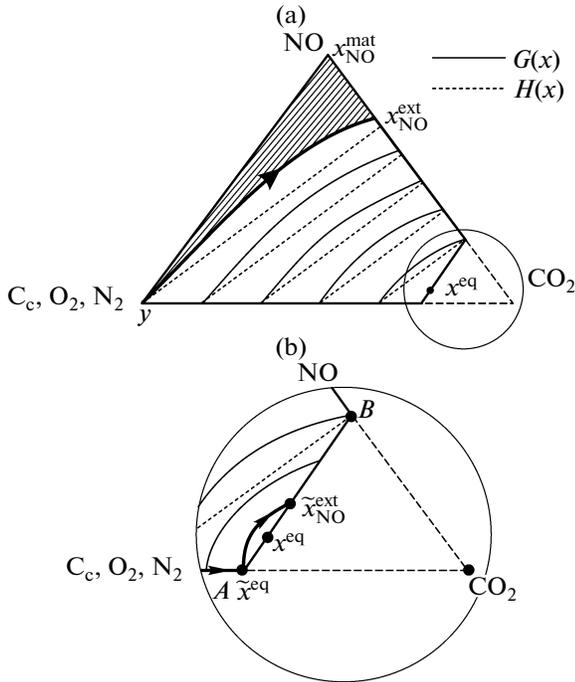
**Fig. 2.** Effect of temperature on the equilibrium and extreme yields of methane (the concentration of methane in a mixture). (1) Final equilibrium and (2) extreme states.

straints are essential: the point  $x_{CH_4}^{ext}$  lies on the initial surface of Gibbs energy. The condition  $x_{CH_4}^{ext} < x_{CH_4}^{mat}$ , where  $x_{CH_4}^{mat}$  is the theoretically possible equilibrium according to the conditions of material balance, is satisfied in the entire studied range of external parameters (the temperature is in the range from 400 to 1200 K and the molar ratios  $O_2 : C = 0-0.5$  and  $H_2O : C = 2-3$ ). In this case, the extreme yield of methane is no more than 52% of  $x_{CH_4}^{mat}$ . This value determines the degree to which the initial carbon transfers into methane (see the table). The yield of methane decreases as the molar ratios  $O_2 : C$  and  $H_2O : C$  increase. At  $O_2 : C = 0$  and the process temperature equal to 800°C, it can be expected that the degree to which the initial carbon of fuel is converted into methane will not be more than 45–46% of the theoretically possible value. Under these conditions, the process is essentially endothermic in nature.

The effect the temperature of the process has on the yield of methane (for the extreme state and final equilibrium) is shown in Fig. 2. High extreme concentrations of methane in the reaction mixture are observed in the entire range of studied temperatures (400–1200 K) and their values increase monotonically from 9.8 to 10.2 mol/kg of mixture. This means that searching for catalysts for running the process under milder conditions, i.e., in the low-temperature region, has good prospects, which will make the relevant technology more energy-efficient and make it possible to achieve a smaller requirement in supply of energy from outside.

The equilibrium yields of methane change essentially as the temperature increases and reach a maximum at a temperature of around 700 K. At this point, the equilibrium yield of methane reaches 83% of its extreme value. It can be concluded from the data of thermodynamic studies shown in Fig. 2 that the rational temperature at which steam conversion of coal with high equilibrium yields of methane can be implemented in the absence of new low-temperature catalysts lies in the range 700–800 K. These conditions are quite acceptable for using the heat of high-temperature gas-cooled reactors to cover the large requirements of the considered process in energy.

**Generation of nitrogen oxides in firing coal.** If there are no macrokinetic and energy constraints, the laws of thermodynamics allow generation of NO during the combustion of carbon in very large quantities that are two to three orders of magnitude higher than the equilibrium values in which NO is generated in the range of temperatures typical for the furnace chambers of coal-fired boilers. In this case, however, a large amount of energy must be supplied to the system from

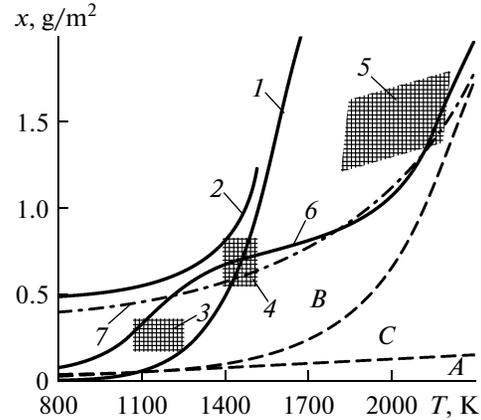


**Fig. 3.** For the thermodynamic analysis of NO generation during the combustion of carbon.  $C_c$  is the condensed carbon, and  $x_{NO}^{mat}$  is the state with the maximum possible quantity of NO in the system according to the conditions of material balance (the other important notation is explained in the text).

outside (around 300 kJ/kg of reaction mixture). For these conditions, the states  $x^{ext}$  with the maximal concentrations of NO lie on the initial surface of Gibbs energy (Fig. 3a).

The thermodynamic attainability region for nitrogen oxide generation processes becomes essentially smaller if macrokinetic constraints are introduced into the model (Fig. 3b). The maximal values of NO emissions  $\tilde{x}^{ext}$  (Fig. 4, curve 2) become essentially closer to their actual values (curve 6) even if the simplest mechanism governing the generation of thermal NO (according to Zel'dovich) is taken into account. According to the Zel'dovich mechanism, thermal NO begin to appear upon completion of the oxidation of the fuel's organic substance (i.e., after the system reaches the state  $\tilde{x}^{eq}$ , see Fig. 3b) due to different rates of the corresponding reactions. In this case, the thermodynamic attainability region for the NO generation process is bounded by the edge  $AB$  and the curve connecting the points  $\tilde{x}^{eq}$  and  $\tilde{x}_{NO}^{ext}$ .

With an extended NO generation mechanism included in the model, it becomes possible to come close to the actual emissions of nitrogen oxide in a wide range of temperatures (Fig. 4, curve 7). The



**Fig. 4.** Calculated and actual yields of NO during coal combustion. Calculated yields of NO: (1) equilibrium, (2) maximal for the Zel'dovich mechanism, and (7) maximal for the extended mechanism. Actual yields of NO with different combustion technologies: Region (3)—firing of coal in fluidized bed, field region (4)—low-temperature combustion of brown coals, and region (5)—high-temperature combustion of brown coals. Actual averaged yields for coal-fired boilers (curve 6), with the regions  $A$ ,  $B$ , and  $C$  corresponding to fast, fuel, and thermal NO, respectively.

extended mechanism was represented as a system of equations reflecting the limiting stages of the main three mechanisms through which nitrogen oxides are produced: fuel, thermal, and fast ones. The final system of inequalities replacing (7) took the form

$$x_{NO} \leq 2[x_N(k_1x_{OH} + k_2y_{O_2})\tau_f + k_3x_Oy_{N_2}(\tau_b - \tau_f)]; \quad (11)$$

$$x_N \leq N_{(carbon)}k_N^{daf}K_f + (k_3x_Oy_{N_2} + k_4x_{CH}y_{N_2})\tau_D; \quad (12)$$

$$x_{OH} \leq (K_1y_{H_2O})^{0.5}; \quad x_O \leq (K_2y_{O_2})^{0.5}; \quad (13)$$

$$x_{CH} \leq H_{(carbon)}k_{CH}^{daf}K_f, \quad (14)$$

where  $\tau_b$ ,  $\tau_f$ , and  $\tau_D$  are the times taken for the reaction mixture to pass through the furnace space, for the volatiles to burn, and for the components of pyrolysis to diffuse from the surface of a coal particle to the turbulent reaction region;  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are the  $N + OH \rightarrow NO + H$ ,  $N + O_2 \rightarrow NO + O$ ,  $O + N_2 \rightarrow NO + N$ , and  $CH + N_2 \rightarrow HCN + N$  reactions rate constants;  $K_f$  is the coefficient determining the fraction of volatile substances that transfer from a coal particle into the gas phase for the time  $\tau_D$ ;  $K_1$  and  $K_2$  are the equilibrium constants of the reactions  $H + OH \rightleftharpoons H_2O$  and  $O + O \rightleftharpoons O_2$ ;  $N_{(carbon)}$  and  $H_{(carbon)}$  are the quantities of nitrogen and hydrogen in coal; and  $k_N^{daf}$  and  $k_{CH}^{daf}$  are the coefficients depending on the composition of volatiles.

System (11)–(14) is linear in the variables  $x_j$ . This system was constructed simultaneously taking into

account different mechanisms governing generation of nitrogen oxides, different stages of combustion (pyrolysis, burning of volatiles, and burning of coke), rates of chemical reactions and transfer processes (diffusion), and specific features relating to changes of fast and slow variables. For analyzing different types of variables on the basis of Eqs. (11)–(14), two of the above-mentioned methods for formalizing kinetic constraints were in fact combined: using the integrals of kinetic equations and specifying additional limiting thermodynamic correlations for fast variables. In the discussed example,  $x_{\text{OH}}$  and  $x_{\text{O}}$  were related to the category of fast variables.

That the calculated yields of NO (Fig. 4, curve 7) exceed their actual values (curve 6) in the low-temperature region (below 1100 K) is in all likelihood due to the fact that model (11)–(14) does not take into account the reactions of NO with the nitrogen of reduced forms, such as NH, NH<sub>2</sub>, and NH<sub>3</sub>, e.g.,  $\text{NO} + \text{NH}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$  or  $\text{NO} + \text{NH} \rightarrow \text{N}_2 + \text{OH}$ , which are typical for comparatively low temperatures [23].

A change in the temperature has a relatively weak effect on the maximal yields of NO (curve 7), but it has an extremely strong effect on its equilibrium yields (curve 1). As the temperature increases, the point  $x^{\text{eq}}$  shifts toward the vertex of NO more rapidly than do the points  $\tilde{x}^{\text{ext}}$  (Fig. 3). This explains the fact that the equilibrium concentrations (Fig. 4, curve 1) exceed their extreme values (Fig. 4, curve 7), as well as their actual values (Fig. 4, curve 6) at  $T > 1500$  K that was revealed from the calculations.

#### THE EFFECTIVENESS OF THE THERMODYNAMIC SIMULATION METHOD

The presented example of analyzing the NO generation processes during coal combustion demonstrates the potential possibilities of thermodynamic studies carried out using MEIS. Owing to the fact that it is possible to do without special kinetic models and field experiments, the studies being performed have become much less laborious. The use of a unified approach for simulating different mechanisms through which nitrogen oxides are generated made it possible to avoid situations in which superposition of separate solutions may turn out to be ambiguous.

In carrying out a kinetic simulation, each of the three main stages making up the overall coal combustion process, i.e., pyrolysis of coal, combustion of volatiles, and combustion of coke must be described in detail and united by means of their material and energy balances. In the case of using MEIS, it is sufficient to estimate only the rates of limiting stages. For example, for taking pyrolysis into account, it is neces-

sary to know only the release rate of volatiles, for which semiempirical and empirical correlations are suitable and were used in the given case. For drawing up a kinetic description of pyrolysis, it is necessary to have information not only about the chemical mechanism of the process, but also about the diffusion coefficients at the surface of a coal particle and in the surface layer. Only a hypothesis can be made about the values of these coefficients, because it is extremely difficult to measure them and describe them theoretically; in addition, the results of measurements and theoretical description are unreliable because the surface of a coal particle is not uniform and varies during the combustion process. Thus, pyrolysis is kinetically described only by rough empirical and in the best case semiempirical correlations, which are valid only in a narrow interval of conditions and cannot be extrapolated for other cases.

For the considered example, it was not required to describe the combustion of volatiles in the MEIS. The vector  $\mathbf{x}$  contained 68 components and the number of these components was limited only by the effort required to prepare the initial data and the attainability in principle of the desired accuracy of calculations. In the case of a kinetic model, a lack of certainty in the composition of volatile substances makes the description of their combustion based on elementary kinetics impossible, which must also take into account evaporation from the particle surface and diffusion. The parameters of these processes are, as a rule, also unknown.

Attempts to make a strict theoretical description of the kinetics of heterogeneous coke combustion still encounter insurmountable difficulties. This description includes mathematical expressions for adsorption of molecules on surface, surface reactions, desorption of reaction products, and diffusion through pores and on the surface of a particle. The majority of these processes for coke have been studied to a relatively poor extent. The main feature in which surface reactions differ from gas-phase ones consists in the need to involve the concepts of active surface sites and adsorbed particles for describing them. Different natures of active sites (energy of dislocations) result in the need to construct kinetic models in which similar particles adsorbed at these sites are considered as dissimilar ones due to different surface rate constants. In MEIS, different phase states are assigned to such particles, which results only in an increase in the dimension of the vectors  $\mathbf{x}$  and  $\mathbf{y}$ , which is not critical for MEIS implemented at a modern computer. Unlike surface reaction rate constants, theoretical calculation of which is a difficult problem and measurements a poorly reproducible, thermodynamic parameters can be determined, as was already noted, with sufficiently high accuracy.

Since it is impossible to construct a strict theoretical kinetic model describing the burning of coal particles that would combine all three stages of combustion, empirical models based on separation and experimental studies of limiting stages are finding wide use. However, it is difficult to make any generalizing conclusions on the basis of such models. At the same time, by using the model of extreme intermediate states it is possible to study conversions of any component in the entire simulated system depending on various kinetic constraints written in fairly simple form even for such intricate processes as coal combustion.

The advantages of using MEIS for simulating the considered nitrogen oxide generation processes as compared with using models of nonequilibrium thermodynamics are still more clear and significant than the advantages with respect to kinetic analysis. It is sufficient to mention just a few circumstances. If the complete mechanism of a process is not known, it is not possible to construct its analytical description as required by nonequilibrium thermodynamics. It seems very difficult to formalize constraints for the time during which individual stages proceed and for the concentrations of individual components. There are a lot of transfer processes for which it is very difficult to find formulae for Onsager coefficients, e.g., for diffusion in a multicomponent heterogeneous medium.

Thus, the modern equilibrium thermodynamic models and technologies of using them make it possible to study intricate phenomena, including irreversible ones. By using models of extreme intermediate states it is possible to quantitatively determine zones of thermodynamic attainability in the considered systems and find extreme states with the target properties within their boundaries subject to linear and nonlinear constraints of different nature. As a result, new formulations of problems and approaches for solving them have become possible. Estimates of the limiting indices characterizing the efficiency of physicochemical processes form a practical basis for shaping research and experimental development works aimed at creating fundamentally new and improving existing technologies used in power engineering and other industries.

At the same time, while disclosing the possibilities of equilibrium thermodynamic simulation, the authors of this paper of course do not assert that thermodynamics can replace and make unnecessary the models of motion that determine the rate and duration of processes running in physicochemical and engineering systems. Kinetics remains an important element in designing various technical facilities and in studying nature, but the application fields of equilibrium thermodynamics will surely be broadened, and development of the technology of thermodynamic

simulation should become one of the important subjects of scientific investigations.

## ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (grant no. 09-08-00245-a).

## REFERENCES

1. I. K. Karpov, A. I. Kiselev, and F. A. Letnikov, *Simulating Natural Formation of Minerals on a Computer* (Nedra, Moscow, 1976) [in Russian].
2. G. B. Sinerev, I. A. Vatolin, B. G. Trusov, and G. K. Moiseev, *Use of Computers for Carrying Out Thermodynamic Calculations of Metallurgic Processes* (Nauka, Moscow, 1982) [in Russian].
3. *Thermodynamic Investigations of Coal Treatment and Combustion Processes: Proceedings of the Krzhizhzhonovskii Energy Research Institute* (ENIN, Moscow, 1984) [in Russian].
4. A. N. Gorban', *Bypassing Equilibrium: Equations of Chemical Kinetics and Their Thermodynamic Analysis* (Nauka, Novosibirsk, 1984) [in Russian].
5. A. N. Gorban', V. I. Bykov, and G. S. Yablonskii, *Outlines on Chemical Relaxation* (Nauka, Novosibirsk, 1986) [in Russian].
6. R. Shinnar and C. A. Feng, "Structure of Complex Catalytic Reactions," *Industr. Eng. Chem. Fundam.* **24** (2), 153–169 (1985).
7. R. Shinnar, "Thermodynamic Analysis in Chemical Processes and Reactor Design," *Chem. Eng. Sci.* **43** (8), 2303–2318 (1988).
8. M. Feinberg, "On Chemical Kinetics of a Certain Class," *Arch. Rat. Mech. Anal.* **46** (1), 1–41 (1972).
9. D. Hildebrant and D. Glasser, "Predicting Phase and Chemical Equilibrium Using the Convex Hull of the Gibbs Energy," *Chem. Eng. J. (Lausanne)* **54** (3), 187–197 (1994).
10. B. M. Kaganovich, S. P. Filippov, and E. G. Antsiferov, *Effectiveness of Energy Technologies: Thermodynamics, Economics, and Forecasts* (Nauka, Novosibirsk, 1989) [in Russian].
11. B. M. Kaganovich, S. P. Filippov, and E. G. Antsiferov, *Simulation of Thermodynamic Processes* (Nauka, Novosibirsk, 1993) [in Russian].
12. B. M. Kaganovich and S. P. Filippov, *Equilibrium Thermodynamics and Mathematical Programming* (Nauka, Novosibirsk, 1995) [in Russian].
13. A. N. Gorban', B. M. Kaganovich, and S. P. Filippov, *Thermodynamic Equilibria and Extrema: Analysis of Attainability Regions and Partial Equilibria in Physicochemical and Engineering Systems* (Nauka, Novosibirsk, 2001) [in Russian].
14. A. N. Gorban, B. M. Kaganovich, S. P. Filippov, et al., *Thermodynamic Equilibria and Extrema Analysis of Attainability Regions and Partial Equilibria* (Springer, 2006).
15. B. M. Kaganovich and S. P. Filippov, "Analysis of Power Engineering's Technical and Economic Problems Using the Methods of Equilibrium Thermodynamics,"

- Izv. Ross. Akad. Nauk, Energetika, No. 6, 13–21 (2000).
16. B. M. Kaganovich, S. P. Filippov, V. A. Shamanskii, and I. A. Shirkalin, "On Attainability of Equilibria in Substance and Energy Conversion Processes," *Izv. Ross. Akad. Nauk, Energetika*, No. 5, 122–130 (2004).
  17. B. M. Kaganovich, A. V. Keiko, and V. A. Shamanskii, *Equilibrium Thermodynamic Simulation of Dissipative Macroscopic Systems* (ISEM, Sib. Otd., Ross. Akad. Nauk, Irkutsk, 2007) [in Russian].
  18. B. M. Kaganovich, A. P. Merenkov, and O. A. Balyshev, *Elements of the Theory of Heterogeneous Hydraulic Circuits* (Nauka, Novosibirsk, 1977) [in Russian].
  19. B. M. Kaganovich, S. P. Filippov, and E. G. Antsiferov, "Studies of the Environmental Pollution Using Thermodynamics," *Int. J. Energy, Envir., Econ.* **2** (1), 7–13 (1992).
  20. S. P. Filippov, B. M. Kaganovich, and P. P. Pavlov, "Thermodynamic Modeling of Nitrogen Oxides Formation during Coal Combustion," *Int. J. Energy, Envir., Econ.* **6** (1), 47–65 (1997).
  21. A. V. Keiko, S. P. Filippov, and B. M. Kaganovich, "Thermodynamic Analysis of the Secondary Pollution of the Atmosphere," *Int. J. Energy, Envir., Econ.* **4** (4), 247–260 (1997).
  22. G. K. Boreskov, *Catalysis: Questions of Theory and Practice: Selected Works*, Ed. by K. I. Zamaraev and G. I. Panov (Nauka, Novosibirsk, 1987) [in Russian].
  23. Yu. Varnats, U. Maas, and R. Dibble, *Combustion. Physical and Chemical Aspects, Simulation, Experiments, and Formation of Polluting Substances* (Fizmatgiz, Moscow, 2003) [in Russian].