Conclusion

> We never know a response to our word.
> *F.I. Tyutchev*

What makes us, the authors, look to further fruitful development of the scientific subject whose basic concepts we tried to present in the book? Replying to this question, we can mention several encouraging factors.

First of all, we are optimistic, because the created thermodynamic models have already been used to solve successfully a rather wide scope of theoretical and applied problems. They are: determination of maximum possible yields of the target products in fossil fuel conversion technologies; assessment of environmental characteristics of continuous and periodic combustion processes; analysis of harmful substance behavior in the atmosphere; and calculation of flow distribution in multiloop hydraulic systems.

An even greater number of unsolved problems including those manifested themselves in the analysis of the solved problems tell us that we have correctly chosen this specific area of studies. By Hilbert [69], "Any scientific sphere is viable, as long as there is an excess of new problems in it. The lack of new problems means dying off or termination of independent development." From the text of the book follow some problem statements for future studies. Some examples are creation of strictly formalized methods based on the idea of a thermodynamic tree, construction of the thermodynamic model of an atmospheric aerosol, and description of a sufficiently complete system of kinetic constraints in equilibrium models of combustion and atmospheric pollution processes.

In our opinion the book allows a deeper understanding of the logic of thermodynamics development, the link between the present-day models and the initial ideas of its founders. Whereas the principles of inertia, relativity, and equilibrium established by Galilei clarified the possibility to replace description of the uniform straight-line motion by the model of rest, the thermodynamic works by Boltzmann and Gibbs revealed the possibility of describing processes in systems consisting of a colossal number of elements and subject to statistical laws in equilibrium terms. Such systems in fact take in all the macroscopic systems interacting with the environment at fixed parameters in which the processes of substance and energy conversion take place. MEIS application enabled the use of potentialities of thermodynamics (that were understood yet by Boltzmann and Gibbs) to analyze any admissible states (complete and partial equilibria) of equilibrium systems and the search for thermodynamic attainability regions in these systems. Interrelations between models of motion (those including the time variable) and models of states, as well as areas of admissible and expedient application of these models to solve diverse physicochemical and technical problems are features that became more clear to us as researchers.

The noted circumstances make us hope that, in parallel with development of such acknowledged current scientific disciplines as synergetics and nonequilibrium thermodynamics, classical equilibrium thermodynamics will enter into a new stage of advancement.

There is also much doubt about such further favorable and desirable (for the authors) courses of events. This is not just because the "old" sciences are not fancy and attractive for young researchers; more to the point, if new models based on old theories are to become accessible to a wide circle of specialists and to find application in many research and design works, the appropriate software and commercial computing systems will have to be created. This requires great effort of entire teams because every new field of MEIS application calls for modification of the key algorithms, replenishment or creation of new data banks (primarily on the thermodynamic properties of substances), and design of special auxiliary software regarding the objectives of the study. The authors can only partially solve the problems that arise. In the immediate future we plan both to solve some theoretical and methodological problems (such as construction of the thermodynamic tree on partial graphs) and to create an effective heavy duty software for detailed analysis of particular applied problems, such as formation of harmful substances in torch and fixed-bed furnaces, description of processes on the surface of aerosols in the atmosphere, and air exchange in buildings and structures in normal and emergency (at fires) conditions.

Afterword

So far MEIS applications have been associated to a great extent with the regrettable consequences of human activity, adverse impacts on the environment we inhabit. We would prefer to be engaged in more pleasant calculations, for example, on the calculation of the extent to which nature eventually recovers from damage, a recovery owing to the skillful tending by human beings. Well, such a bright future could be imagined allowing that these calculations be necessary. "We never know... ."

Supplement

The Model of Extreme Intermediate States (MEIS) and Description of Nonequilibrium Irreversible Processes

> Die Energie der Welt ist Constant.
> Die Entropie der Welt strebt einem Maximum zu.
> *R. Clausius*

Introductory Remarks

During the four years after the publication of the Russian edition of this book, studies on attainability regions and partial equilibria took place in the areas considered in the book and in new areas of MEIS applications.

The new practical problems solved on the basis of MEIS included: modeling of heating surface slugging in boiler furnaces [153]; estimation of environmental characteristics of combustion chambers in gas turbines [87, 89]; calculation of low-grade fuel gasification processes [103]; analysis of condensation nuclei formation in the atmosphere [90]; and others.

The mathematical features of MEIS being analyzed include, among others: possibilities of solution degeneracy in the search for points x^{mat} and x_c^{ext}; cases of incompatible systems of constraints that determine $D_t(y)$; and dependence of total Gibbs energy of the atmospheric system on the radii of the aerosols formed in it. The problem of MEIS reducibility to the convex programming (CP) problems remains the main problem in the mathematical studies. We are now looking for convex approximations of the problems for the cases when: the sought variables include the radii of nuclei of the forming phases; the modeled system has Debey–Huckel solutions, and so on. The analysis of mathematical features, in turn, becomes the basis for correction and improvement of the computational algorithms.

Currently, the development of a commercial computational system is nearing completion. This system is intended for thermodynamic analysis of technological and natural processes [87] and may be applied to the problems of:

- estimating maximum energy and resource efficiency (efficiency, specific fuel consumption, specific yield of target products and by-products) of different industrial technologies;

- revealing the energy-saving potential in production of energy and chemicals, oil refining, metallurgy and other industries
- determining the assortment and maximum emissions of harmful substances by technological plants under normal and emergency operation conditions
- studying the transformations of anthropogenic emissions in the atmosphere, soil and water reservoirs.

The main direction of MEIS development is now formulation of MEIS-based thermodynamic descriptions (those eliminating the time variable) of chemical kinetics and transfer process. This work was encouraged, first of all, by the need to assess the practical feasibility of the calculated x^{ext} determined by reaction rates and transfer of mass, energy, impulse, and charges. The problems of equilibrium feasibility were considered briefly in Section 4.5. There we presented examples of the impact of chemical reaction rates on the feasibility of states x^{ext}.

Additionally, the equilibrium description of "motions," which is the subject of studies in nonequilibrium thermodynamics and synergetics, is important from the viewpoint of determining MEIS significance in modern scientific areas related to classical thermodynamics. It is quite clear that for this new scientific concept to become the handy tool for researchers and engineers, it is necessary not only to give it a strictly formalized description and theoretical and experimental grounds but to compare it with competing approaches in the area where it is applied.

Some results obtained from the analysis of MEIS containing description of motions and its efficiency are presented below.

On the Possibility to Describe "Motions" in Terms of Equilibrium Thermodynamics

The body of the book has already given the examples of "equilibrium" derivations of equations for nonequilibrium irreversible processes: diffusion, heat transfer, hydraulic shock, etc. In the Introduction (Section I.2) consideration was given to the applicability of the equilibrium principle to description of the systems that may have various effects (including self-oscillations and spatial ordering) during their relaxation towards equilibrium. Chapter 5 shows the MEIS applicability for the analysis of high-energy chemical processes (on the example of plasma coal gasification) and periodic solid fuel combustion processes. In the latter case the MEIS was applied along with kinetic models and full-scale experiments.

However, the potentialities of equilibrium thermodynamics in studying "motions" may most completely be revealed by analyzing the single model that contains both a description of a monotonically changing characteristic function of the system at issue and a description of the processes that limit the region of this change. Before discussing such a model let us make some remarks on the history of the equilibrium descriptions of motion. Unlike the excursus on the history that was made in Sections 1.1 and 1.2 here we will try to focus on the principles that will be directly used when developing new MEIS versions.

Originally, equilibrium models were developed within classical mechanics (Galilei, Euler, D'Alembert, Lagrange, Hamilton). Lagrange used the Galilei and D'Alembert equilibrium principles formalized as *mechanic system equilibrium equations* to describe the integral structure of the Newtonian mechanics [118]. His derivation of the equation for the optimal trajectory, in which he integrated this equation with respect to time, showed how he efficient the assumption of equilibrium is for studying trajectories. Similar to how film frames show static states of a body's motion, giving the idea of "continuous processes," the described mathematical aggregates of states of rest (equilibrium) give the idea of "characteristic trajectories." Lagrange's derivation made clear the applicability of the notion of *local potential* (the values of the potential and its derivative at each time instant are determined only by the state reached) and the description of motions by autonomous differential equations of the form $\dot{x} = f(x)$.

The founders of thermodynamics—Clausius, Maxwell, Gibbs, and Boltzmann—extended equilibrium principles to a description of various physicochemical systems. The notion of equilibrium was related to the ideas of reversible and irreversible processes and "the arrow of time." The second law of thermodynamics, which determines the irreversible motion of isolated systems to the maximum of entropy, was statistically proved by Boltzmann through two methods [21]: 1) using his kinetic equation (H-theorem); and 2) directly calculating probabilities of possible states of a system. The second method supposed that the values of macroscopic variables that characterized an admissible state were conditioned exclusively by the probabilities of a state's attainability and did not depend on the motion trajectory toward it. Therefore, the states that occur during relaxation of the system to final equilibrium and are normally interpreted as nonequilibrium can be considered *partial equilibria* (equilibrated not in all parameters). Thus, it becomes clear that the Boltzmann trajectories toward maximum entropy similar to the optimal trajectories of Euler–Lagrange–Hamilton are suitable to consider as passing through a continuous sequence of equilibria. At each point of both trajectories, there are potential functions and motion can be described by autonomous differential equations.

Sections I.6 and 1.3 gave examples that illustrate the efficiency of the Boltzmann and Gibbs' assumptions on equilibria in the analysis of irreversible processes. Here it should be additionally noted that one of the brightest examples is the book *On the Equilibrium of Heterogeneous Substances* itself [54], which presents the first systematic description of equilibrium macroscopic thermodynamics. It was written before the structure of statistical mechanics was completed by Boltzmann and Gibbs and was based on equilibrium principles borrowed from classical mechanics.

Development of nonequilibrium thermodynamics in the second half of the 20th century was also based on the assumption on equilibria in physical infinitesimal volumes of media for which the thermodynamic equation is true:

$$T\,dS = dU + P\,dV - \sum_j \mu_j\, dx_j$$

It should be noted that, in fact, one of the main theorems of nonequilibrium thermodynamics (Prigogine, 1947) [56, 143] on the minimum of entropy production in stationary states at given external conditions hindering achievement of the point x^{eq} had already been used in different formulations during the "equilibrium" period of the thermodynamics development. The Kirchhoff theorem (of 1848!) [108] on minimum heat production in an open, passive (without sources of electromotive forces) electric circuit can be considered a particular case of the Prigogine theorem. Planck and Einstein used maximization of entropy and, hence, minimization of its production, in their studies of stationary processes of irradiation, propagation, and absorption of radiant energy.

Owing to the universal principles of classical thermodynamics and, first of all, its second law, it is possible to determine the results of the processes in open nonequilibrium systems. For this purpose it is necessary to integrate the studied system with its environment and include the conditions of interaction with the latter in the description of the isolated system obtained. The conditions of maximum entropy in the integrated system will reveal the conditions of the equilibrium (stationary) state of the open subsystem. An example of transition from criterion $\max S$ in the isolated hydraulic system (model (3.33)–(3.36)) to the criterion of $\min Q$ in the passive hydraulic circuit (model (3.10)) is given in Section 3.3. The passive circuit described there can be considered a nonequilibrium system since presence of sinks and inflows in the circuit tells us about the difference of potentials (thermodynamic forces) and flows in the circuit.

The one-and-one-half-century history of equilibrium thermodynamics has revealed its enormous capabilities, yet unsolved remains the problem of a non-strictly formalized proof of the second law, related to Boltzmann's paradox (Section 1.2). To assess the current state of this problem let us refer to the papers by A.N. Gorban and I.V. Karlin [61, 63] that unfolded the idea of P. Ehrenfest and T. Ehrenfest [37] on tending of the isolated system towards the equilibrium Boltzmann trajectory due to "agitations."

Consider Fig. S.1 borrowed with some change from [63]. It shows graphically the processes in an isolated system. Closed curves stand for the entropy level. Dotted straight lines denote the states with constant values of macroscopic parameters. The contact points of curves with straight lines are equilibrium points that meet the equilibrium distributions. In these points entropy has maximum possible value on the corresponding tangent. The aggregate of these points forms equilibrium trajectory S^*, along which the system moves toward the point of global entropy maximum $S^{\max}$. Curved arrows stand for *isoentropy* (reversible) processes caused by reversible (elastic) interactions of particles. Straight arrows show the system "agitations" that are explained by the deviations of some of the interactions from reversibility and push the system to the equilibrium trajectory.

According to the presented interpretation, equilibrium processes differ principally from reversible isoentropy processes and represent at the limit (at tending to zero time intervals between agitations) a continuous sequence of local entropy maxima. The statement often given in manuals on macroscopic thermodynamics—that equilibrium and reversible processes are identical—can be brought into line

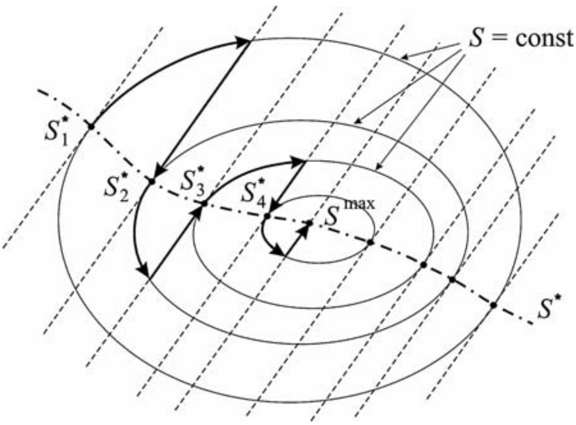

FIGURE S.1. Entropy-conserving dynamics with periodic coarse graining.

with the considered interpretation of these processes only under the assumption on the ultimate coincidence of nonequilibrium states, located on the trajectory $S = \text{const}$, and equilibrium states on the Boltzmann trajectory. In this case the whole set of possible states in Fig. S.1 is reduced to curve S^*.

The interpretation of reversible and equilibrium processes, though it probably does not solve completely the problem of Boltzmann's paradox, still provides us with additional arguments on the possibility of equilibrium descriptions of relaxation towards final equilibrium. At the same time it should be understood that description of motion in terms of equilibria often presents the approximation of real phenomena similar to the linear approximation of nonlinear relationships between physical values. It follows from the interpretations of the notion "far from equilibrium" that were considered in Section I.2 that this approximation becomes most complex when distributions of microscopic variables differ greatly from equilibrium ones.

The Method Being Developed to Analyze Irreversible Processes and MEIS Modifications that Provide Its Application

The above analysis of a possible equilibrium description of irreversible nonequilibrium processes can be used as the basis to formulate fundamental concepts of the thermodynamic method to study these processes, and, first of all, to solve applied large-dimensional problems.

The suggested method differs from the methods of nonequilibrium thermodynamics and the thermodynamic analysis of chemical kinetics equations (see Section 1.5). The method does not directly apply the equations of processes, but examines only equilibrium states attainable from the given initial point, assuming that any possible path to final equilibrium is a continuous sequence of equilibrium states.

These states do not depend on the prehistory of their attainment and the time variable can be excluded from their description. Correspondingly, the nonequilibrium states are interpreted as states of intermediate partial equilibria.

Along with the indicated physical assumptions, mathematical assumptions on convexity (concavity) of the characteristic thermodynamic function and convexity of the system of constraints—i.e., on reducibility of the problem solved to one of convex programming—are made. Reducibility can also be reached by approximation of the used mathematical expressions. When the constraints on kinetics and transfer processes are applied, in addition to the other constraints, these processes are presumed to satisfy autonomous differential equations of type $\dot{x} = f(x)$.

The time variable can be excluded from motion descriptions by two procedures. The first is dealt with in Section 1.5 and in [87, 89]. By this procedure, variables on the right-hand sides of autonomous equations are represented as functions of thermodynamic potentials and then the transformed right-hand sides are substituted into the expression for the overall characteristic thermodynamic function of the system. A condition of the monotonic change of the latter is included in MEIS, and its corresponding modification is described in [86, 87, 89].

MEIS construction on the basis of the first procedure involves essential difficulties. Indeed, one of the difficulties is that the main variants of the model of extreme intermediate states ((2.38)–(2.42), (2.43)–(2.50)) assume knowledge of a list of variables rather than the mechanism of the overall process. Since, in general, motion equations that limit the thermodynamic attainability region include only some of the sought variables, there is a need to formulate an expression for the characteristic function depending variously on different groups of arguments.

The second procedure, one which entails the exclusion of τ, is to directly apply either the right-hand sides of motion equations orthe integrals of these equations or linear approximations of them. This procedure is much simpler compared to the first one. Currently, MEIS with rate constraints are applied on the basis of the second procedure only.

For the physicochemical systems with the fixed T, P, and y a new modification has the following form:

Find

$$\max\left(F(x) = \sum_{j\in J^{\text{ext}}} c_j x_j\right) = F\left(x^{\text{ext}}\right) \tag{S.1}$$

subject to

$$Ax = b, \tag{S.2}$$

$$D_t(y) = \{x : x \le y\}, \tag{S.3}$$

$$\varphi(x) \le \Psi, \tag{S.4}$$

$$G(x) = \sum_j G_j(x)\, x_j, \tag{S.5}$$

$$x_j \ge 0, \tag{S.6}$$

where Ψ is a given limiting value of the expression for a process that decreases $D_t(y)$.

The presence of inequality (S.4) restricting the values of expressions for the limiting processes distinguishes the model (S.1)–(S.6) from model (2.38)–(2.42). In some respects the model (S.1)–(S.6) has some advantages over the models of nonequilibrium thermodynamics and over the thermodynamic transformations of the motion equations. Transition from the analysis of trajectories to the analysis of states substantially reduces the amount of necessary initial information. Thus, in a general case, it is unnecessary to know the whole mechanism of the studied process, i.e., its elementary or formally simple stages. There is a need only for the initial information on limiting motion equations. Besides, the applied mathematical technique is appreciably simplified. Differential equations are substituted by algebraic and transcendent ones. In this case it appears possible to describe by the finite values spatially inhomogeneous systems, ones in which the intensive parameters experience changes in some directions (see Section 2.3). Formulation of the problem in terms of mathematical programming allows the applied model to be supplemented with diverse equality and inequality constraints to take into account specific features of the considered phenomenon (see Section 2.2).

Examples of Equilibrium Description Application

The efficiency of MEIS-type model with descriptions of motion will be illustrated on examples of inclusion of constraints on chemical reaction rates and analysis of stationary and nonstationary flow distributions in hydraulic circuits.

At first we will deal with construction and application of MEIS modifications (S.1)–(S.6) on the simplest example of isomerization reaction for the system with three components, x_1, x_2 and x_3, that was described in Section 2.2. The process mechanism consists of the stages

$$x_1 \to x_2 \quad \text{and} \quad x_2 \to x_3$$

and the constraints on rate of the second of them, T, P, and the vector $y = (1, 0, 0)^T$ are given.

If the maximum attainable x_3 is determined, model (S.1)–(S.6) for this example takes the following form:

Find

$$\max x_3 \tag{S.7}$$

subject to

$$x_1 + x_2 + x_3 = 1, \tag{S.8}$$

$$D_t\,(y) = \{x : x \leq y\}, \tag{S.9}$$

$$k_2 x_2 \leq \Psi, \tag{S.10}$$

$$G\,(x) = \sum_j G_j\,(x)\,x_j, \tag{S.11}$$

$$x_j \geq 0. \tag{S.12}$$

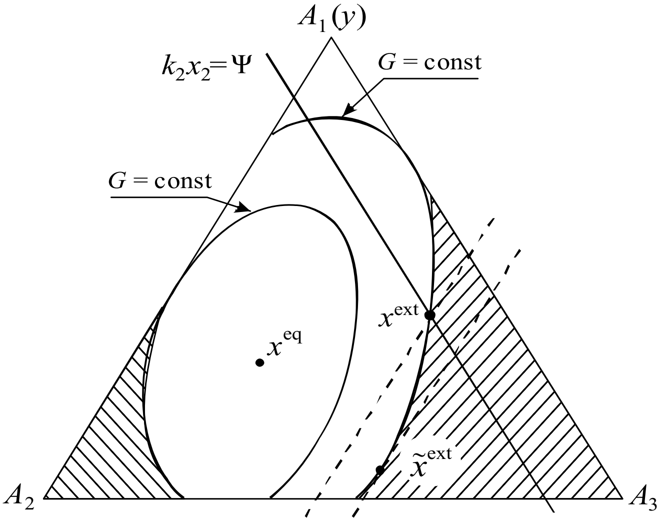

FIGURE S.2. Graphical interpretation of isomerization process.

Fig. S.2 presents graphically the effect of the constraint on the rate of the second stage (S.10). The thermodynamically unattainable zones from y subject to (S.9) are indicated by the hatched area of the triangle (the material balance polyhedron) and the following points are plotted: x^{eq}, the maximum x_3 without constraint (S.10), $\tilde{x}^{\text{ext}}$ and the largest attainable x_3 with a complete system of constraints (S.8)–(S.12), x^{ext}. The straight line $k_2x_2 \leq \Psi$ that is the kinetic constraint (S.10) divides $\tilde{D}_t(y)$ (the non-hatched part of the triangle) into two parts, the left of which turns out to be inaccessible. Owing to this constraint, solution to problem (S.7)–(S.12) shifts from $\tilde{x}^{\text{ext}}$ to the point x^{ext} (the intersection of the straight line $k_2x_2 = \Psi$ with the boundary of the inaccessibility zone near the vertex A_3). The point x^{ext} is located on the line of the constant x_3 that is more distant from the vertex A_3 (the point of maximum x_3 on the triangle $A_1A_2A_3$) than $\tilde{x}^{\text{ext}}$ is. Hence, $x^{\text{ext}} < \tilde{x}^{\text{ext}}$. Fig. S.2 also shows that with introduction of condition (S.10) the attainability region $D_t(y)$ from the vertex A_1 is considerably reduced (the part $\tilde{D}_t(y)$ of $D_t(y)$ that is situated to the right of the straight line $k_2x_2 = \Psi$ is much smaller than $\tilde{D}_t(y)$ as a whole).

The value of the constant Ψ in this case can be determined from the conditions

$$x_2 = \frac{k_1}{k_2 - k_1}\left(e^{-k_1\tau} - e^{-k_2\tau}\right) \quad \text{and} \quad \tau \leq \tau^b$$

(see Section 2.2).

In the second example, described in detail in [87, 88, 89] the maximum possible formation of thermal nitrogen oxide (formed from nitrogen and atmospheric oxygen) at burning of natural or synthetic gas is determined. To derive the inequality

(S.10) the following reactions are considered:

$$O + N_2 \rightarrow N + NO \tag{S.13}$$

$$N + O_2 \rightarrow O + NO \tag{S.14}$$

$$N + OH \rightarrow H + NO \tag{S.15}$$

Reaction (S.13) is limiting and the NO formation rate by this reaction is determined by the equation

$$\frac{dx_{NO}}{d\tau} = kx_O x_{N_2}. \tag{S.16}$$

Besides, the following two assumptions were made. By the Zeldovich mechanism [176] NO starts to form only after complete burning out of hydrocarbons and the relation of the initial state for reaction (S.13)–(S.15) y^z with the initial state of the general combustion process y can be described by the transformation

$$y = \left(y_{CH_4}, y_{O_2}, y_{N_2}\right)^T \rightarrow y^z = \left(y_{CO_2}, y_{H_2O}, y_{O_2}, y_{N_2}\right)^T.$$

For simplicity, among the hydrocarbons only methane is indicated in the vector y. The value of x_{N_2} is constant and equal to y_{N_2}. The maximum value of x_0 is determined by model (S.1)–(S.3), (S.5), (S.6), with the given objective function $F(x) = x_0$ and with given y^z.

With the assumptions made, condition (S.10) takes the form

$$x_{NO} \leq Kx_O^{ext}. \tag{S.17}$$

A linear form of the constraint on chemical kinetics that is obtained in this example (as well as in the previous one) does not influence the possibility of solving the problem by the convex programming (CP) method. When condition (S.10) cannot be written in a linear form, this possibility must be studied further.

Fig. S.3 illustrates the results obtained under the indicated assumptions. It presents a two-dimensional section of the polyhedron of material balance (S.2), (S.6) constructed by three fixed points y^z, x_{NO}^{mat} and x_O^{mat}. The lines of the constant Gibbs energy levels are drawn inside the section. Without (S.17) the thermodynamically attainable region is limited by the line $y^z aby^z$ (that is not hatched). The segment ab of this line represents an energy level whose point of contact is a with the section edge $y^z x_O^{mat}$. The tangent drawn to this line in parallel with the edge $y^z x_O^{mat}$ determines the value $\tilde{x}_{NO}^{z.ext}$—the maximum thermodynamically attainable content of NO in the system, if the Zeldovich mechanism is observed. This value, as is seen from the figure, considerably exceeds x_{NO}^{eq} at the minimum point $G(x)$ of the system. Neglecting the Zeldovich mechanism, the thermodynamic attainability region will be limited by the line $ycdy$ (the points corresponding to the vectors y^z and y coincide in the figure).

The condition $x_{NO} = Kx_O$ in Fig. S.3 is represented by the straight line $y^z e$. Passage of this line through the vertex y^z is caused by the equalities $x_{NO} = x_O = 0$. Inequality (S.17) results in an additional region of thermodynamic inattainability,

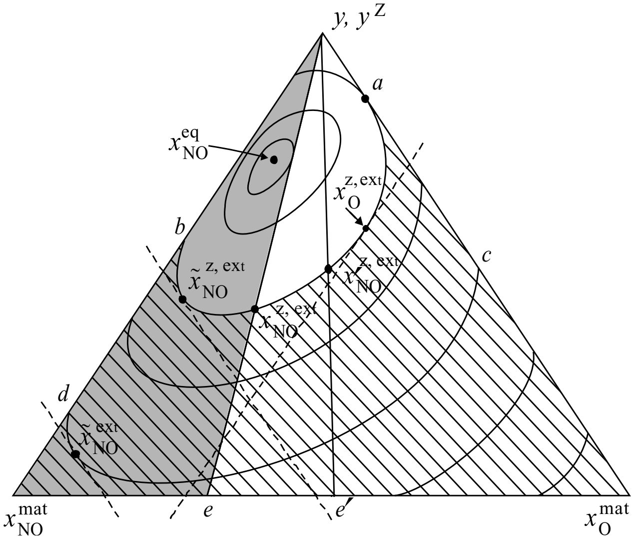

FIGURE S.3. Graphical interpretation of the nitrogen oxide formation.

which is depicted by shading. The extreme concentration of NO therewith, essentially falls, and the solution shifts to the point $x_{NO}^{z.ext}$. D_t (y^z) becomes substantially narrow and is limited by the line $y^z a x_{NO}^{z.ext} y^z$. If in the considered example the coefficient K is decreased (e.g., due to change in the residence time for the reacting mixture in the combustion chamber or change in the combustion temperature), the line limiting D_t (y^z) will shift to the right $(y^z e')$ and the maximum possible quantity of NO will go down $(x_{NO}^{\prime z.ext})$.

Thus, when we applied the MEIS variant (2.38)–(2.42) to the combustion analysis, the chemical kinetics were taken into account by the special kinetic model (see Section 5.2). Model (S.1)–(S.6), as is seen from the presented example, evaluates the reaction mechanism and factors affecting its rate based on the single thermodynamic description. Additionally, the choice of the objective function of MEIS in the presented examples (as in many other examples given in the body of the book) can be interpreted as a choice of the "subjective" *criterion of order* (self-organization) in the reacting system. As is known, formalization of such a criterion in the problems of non-equilibrium thermodynamics and synergetics often involves great difficulties. MEIS makes it possible to choose this criterion in accordance with the study's goals. In the two described examples, the *ordered system states* are naturally the states with the least amount of harmful (needless) products. Maximization of x_{NO} in the second example results in determination of the maximum possible degree of disorder.

In further examples, the flow distribution in multiloop hydraulic networks is taken as an object of modeling. In the example of hydrodynamics, the illustration of MEIS's capabilities for analyzing nonequilibrium systems is vivid. Here we will explain in terms of equilibria the irreversible processes of energy dissipation that are associated with viscosity and thermal conduction. In the examples we discuss, this problem is solved more easily owing to the assumption on the one-dimensional flows, as systems with such flows are potential systems (see Sections I.25 and 3.3).

First we will make some comments on the examples in Sections 3.3 and 3.4. We consider the derivation of the model of an open passive circuit with the Lagrange function

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

from the model of the closed active circuit (3.33)–(3.36). This derivation can be considered a special case of Prigogine's theorem for non-equilibrium processes, which was mentioned above.

The results of calculating the circuit diagram in Fig. 3.4 (see Table 3.2, variant 3) show the possibility of determining from the condition of isolated system equilibrium (max S) the order levels in open subsystems it comprises (the turbulent flow in branches 1–15 and the laminar flow in branch 16). In fact, the type of closing relations in this case was given in advance. However, optimization of these relations using the second law for circuits with lumped parameters involves only mathematical difficulties.

In Section 3.4 derivations of closing relations for nonideal multiphase and multicomponent liquids were illustrated by techniques of constructing one-dimensional potential models of irreversible flow of a viscous fluid. The sketch of equilibrium descriptions of fire spreading in systems of air exchange in buildings as presented in this section surely belong to modeling of irreversible processes.

Nonstationary flow distribution in a hydraulic network will be the last example [89, 93]. The Navier–Stokes equation determining the equilibrium of forces affecting liquid flow limits the region of attainable states in this example. For turbulent flow of an incompressible liquid this equation takes the following form, taking into account forces of pressure, friction, and inertia only:

$$-\frac{dP}{d\ell} = \lambda \frac{\rho w^2}{2d} + \rho \frac{dw}{d\tau}. \tag{S.18}$$

As a result of elementary transformations we pass from (S.18) to the expression

$$\frac{dx}{d\tau} = \frac{\pi d^2}{4\rho} P^{\mathrm{br}} - \frac{2\lambda}{\pi d^3} x^2 = \gamma^{\mathrm{br}} P^{\mathrm{br}} - \gamma^{\mathrm{fr}} x^2 \tag{S.19}$$

where x is the volumetric flow rate; P^{br} is the specific pressure loss in the branch; γ^{br} and γ^{fr} are coefficients.

Some comments are required before we present MEIS of non-stationary flow distribution by using equation (S.19). Time-independence of the right-hand side of equation (S.19) can be interpreted as follows. At any section of hydraulic network branch and at any time all flow characteristics, in particular, thermodynamic functions (enthalpy, entropy, and others) fully depend on the current state and do not depend explicitly on τ. If the flows are isothermal ($1/T$ is constant), study of the entropy behavior can be substituted by study of enthalpy behavior. Variation in the enthalpy of the network branches at $\rho = \text{const}$ and $w = \text{const}$ is reduced to variation in the potential energy (pressure).

Under the assumptions made and the made choice of extreme pressure at the given node of the scheme as the objective function MEIS for the closed network (without sources and sinks) takes the form:

Find

$$\text{ext}\left(P_r = eP_m + P_q^{\text{br}} - P_q^{\text{mov}}\right) \tag{S.20}$$

subject to

$$Ax^k = 0, \tag{S.21}$$

$$\sum_{i=1}^{n} \left|P_i^{\text{br.k}}\right| \left(\gamma_i^{\text{br}} P_i^{\text{br.k}} - \gamma_i^{\text{fr}} x_i^{k^2}\right) \geq 0, \tag{S.22}$$

$$\sum_{i=1}^{n} P_i^{\text{mov}} \left|x_i^k\right| - \sum_{i=1}^{n} \left|P_i^{\text{br.k}} x_i^k\right| \ell_i = 0, \tag{S.23}$$

$$P = eP_m - \bar{A}_q^{-1} \left(P_q^{\text{br}} - P_q^{\text{mov}}\right) \tag{S.24}$$

where P is the vector of pressure at the nodes; P_m is the fixed pressure at node $j = m$; P_i^{mov} is the effective head in the ith branch; P_q^{br} and P_q^{mov} are the vectors of pressure drop and the effective pressure in the branches of the "circuit tree" q that includes the paths from nodes $j = 1, \ldots, m - 1$ to node m (see Section 3.3, model (3.45)–(3.48)); A_q is the matrix of "paths" that corresponds to the circuit tree q; k is an index of iteration of the computational process; and r is an index of the node, at which the extreme pressure is sought.

Equation (S.21) represents the material balance of a closed network. Inequality (S.22) accounts for the condition of monotone nondecrease of entropy. Note that the expression in parentheses on the left-hand side of (S.22) is the right-hand side of the Navier–Stokes equation, i.e., it is the time–derivative of the flow. Equality (S.23) is the energy balance of the network for each equilibrium state considered in the iterative calculation. Equation (S.24) is applied to calculate nodal pressures that are also sought variables along with flows in the branches. The use of absolute values of variables in (S.22) and (S.23) is explained by the fact that energy dissipation does not depend on the direction of flows.

Physically, the accepted problem statement may (for example) consist of determining maximum pressure rise at fast flow closure in any branch or its maximum drop at pipe break. Of course, other statements on the problem of searching for partial equilibria in multiloop hydraulic systems—problems that involve analysis of normal or emergency nonstationary flow distribution—are also possible.

The form of model (S.20)–(S.24) shows that it is written for conditions where "fast" disturbances proceed so slowly that frictional forces have time to reveal themselves, i.e., the liquid does not become ideal. Basic difficulties emerge when describing "instantaneous" disturbances leading to wave processes and, in some cases, to hydraulic shocks. The authors have taken only the first steps in the analysis of the presented problem; however, these steps offer hope for its successful solution.

Derivation of the hydraulic shock equation from the Lagrange equilibrium equation as one of the steps to the solution is described in Section 1.3.

Conclusion

We reveal the capabilities of descriptions of equilibrium, not to oppose currently recognized scientific direction (such as nonequilibrium thermodynamics and synergetics [67, 143]), but to display the expediency of supplementing new approaches by old, "good" models of equilibria.

Nonequilibrium thermodynamics and synergetics involve undeniable progress in: the explanation of many of the phenomena in transfer processes; the development of the theories of self-organization; and the ordering in physical, chemical, biological, and social systems. Introduction of the methods of classical thermodynamics into these areas is advisable primarily for solving large-dimensional applied problems. Note that it was precisely the equilibrium thermodynamic models that were used in the first half of the 20th century to create numerous computational systems for computational studies in energy, metallurgy, astronautics, geology, ecology, and other spheres of science and technology. MEIS offers advantages over the traditional models of equilibrium thermodynamics in terms of its capabilities to account for constraints on kinetics and transfer processes, i.e., to estimate feasibility of equilibria sought.

Currently, we can construct computational MEIS-based algorithms for specific problems using the sufficiently detailed analysis of MEIS's mathematical properties and its reducibility to the convex programming problem. We have implemented the basic units of a commercial computational software, one that is available to users and that can easily be supplemented with the auxiliary units.

However, to make the equilibrium models of nonequilibrium systems accessible to a wide circle of researchers and engineers, we need to "detailize" the models to fit the basic processes of matter, energy, impulse, and charge transfer. For the time being, models of extreme intermediate states have been worked out in certain detail only in descriptions of chemical kinetics and one-dimensional hydrodynamics (for multiloop systems though). Strict thermodynamic description of different "motions," in turn, requires that mathematical interrelations between equilibrium models of mechanics and thermodynamics, and between the formalisms of equilibrium and nonequilibrium thermodynamics, be elucidated. The authors are currently investigating this problem.

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