

Introduction

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown (for the special attention of those who are skeptics on principle).

A. Einstein

I.1. Subject of Research

The authors analyze possible results of processes in physicochemical and technical systems that can consist of hundreds of components and in general be nonideal, open, and multiphase. The processes themselves include multistage chemical transformations, phase transitions, and phenomena of mass and energy transfer; they are characterized to some degree or another by their irreversibility (nonequilibrium). Examples of such complex processes are coal combustion in boiler furnaces at power and boiler plants; production of chemicals in industrial reactors; pollution of the atmosphere, soil, and water by anthropogenic discharges, and so on.

In studying similar real objects the main difficulty is certainly to create their ideal models we need to choose initial premises that make it possible to obtain results that expand our knowledge about the subject of research when accessible initial information is severely restricted and sophisticated computational experiments are required. Therefore, possible models of physicochemical systems and processes, problems in application of these models, and interpretation of the results of modeling become the direct subject of discussion in the book. We consider two types of models: kinetic (in brief) and thermodynamic (in detail). The latter are the main object of our attention.

Kinetics enables one to study system motion in time and to gain the most comprehensive view of its peculiarities. Thermodynamics alone provides a way to determine states attainable from an initial state. However, universality of thermodynamics concepts and the comparative simplicity of the models based on them

make the sphere of thermodynamic analysis applications practically unlimited, provided the errors caused by ignoring irreversibilities inherent in real processes are reduced to admissible sizes. Correct transfer of kinetic problems to thermodynamic ones simplifies descriptions of the objects under study, on the one hand, and makes these descriptions more versatile, on the other. *Joint application of the coordinated models of motion (kinetics) and states (thermodynamics) provides a deeper insight into the studied processes than if analysis is based on just one of the mentioned models.*

The issues of coordinating the kinetic and thermodynamic descriptions of chemical systems that are addressed in detail in *Equilibrium Encircling*, by A.N. Gorban [58] are treated in Sections 1.4, 1.5 and 3.2 of this book in a concise way.

We give the bulk of attention to equations of the chemical kinetics for a closed homogeneous system under constant and equilibrium external conditions. They are derived on the basis of a process mechanism that is understood in terms of a list of elementary reactions specified by their stoichiometric equations. We employ the *Lyapunov functions technique* to determine conditions for kinetics and thermodynamics coordination. We do so because a thermodynamic quantity that possesses properties of Lyapunov functions decreases over time according to the second principle of thermodynamics for a chemical system under fixed conditions of a process. Uniqueness of the thermodynamic equilibrium point for the given balance relations is proved when we establish convexity of the Lyapunov functions. The ergodic Markov chain is the key model of microdescription for analyzing the problem of coordinating macro- and micro kinetics.

We give consideration to knowing what a chemical system's dynamics are, provided its thermodynamic functions are known. Constraints imposed on the dynamics by different components of initial data are analyzed in this case. (These components usually differ in reliability; e.g., list of substances, thermodynamic functions, process mechanism, kinetic law, rate constants). We know the possibility of describing the constraints on the system motion's trajectory without direct application of kinetic equations. The regions of thermodynamic attainability are studied on the balance polyhedron (in the simplest case, the material balance polyhedron).

An aggregate of paths on the balance polyhedron along which the thermodynamic Lyapunov function changes monotonically; the regions of inaccessibility, and sets of compositions attainable from the given initial system are represented in a clear and simple way as a graph called a "thermodynamic tree". This tree is constructed by the relations of thermodynamic equivalence: $x_1 \sim x_2$ if there exists a continuous line passing from the composition x_1 to the composition x_2 , along which the thermodynamic Lyapunov function is constant. Identification of thermodynamically equivalent compositions with respect to each other leads to transition of the balance polyhedron to one-dimensional space, i.e., the thermodynamic tree, which facilitates appreciably analysis of the behavior of chemical systems.

We consider the possibilities for applying the simplest models of ideal closed systems to the study of real open systems with the equilibrium and nonequilibrium environment, homogeneous and heterogeneous systems. The cases in which these

models should be modified are revealed. Conditions of radical inapplicability of the classical thermodynamics are determined.

Our application of the principles formulated in *Equilibrium Encircling* [58] to the analysis of natural and chemical-technological processes is based on the use of thermodynamic models. And whereas in the theoretical analysis presented in the cited book, the kinetic (dynamic) characteristics of a system showing how and where it moves are examined in the book *Equilibrium Thermodynamics*, by B.M. Kaganovich, S.P. Filippov, and E.G. Antziverov [81] in this book we deal with the problem of searching for states (where the system could stop). The presumably accessible initial information on process kinetics and conditions of energy and mass transfer is employed to describe problem constraints.

Chapter 2 presents a model of *extreme intermediate states* (MEIS) of physicochemical systems. The model is applied to determine points having extreme concentrations of substances, such substances being of interest to the researcher in the region of thermodynamic attainability from the given initial state. Model modifications are described for different heterogeneous systems (i.e., ones that contain ideal and real gaseous phases, pure condensed substances and solutions, electrically charged particles, surface gas and other components) and for different conditions of interaction between these systems and the environment.

In chapter 3 we discuss thermodynamic models in which constraints are described based on the ideas of graphs rather than balance polyhedrons. Two types of graphs are dealt with: 1) the aforementioned thermodynamic trees; 2) hydraulic circuits, in which flows along the branches obey hydrodynamic laws. The use of circuits supplements to some extent, a fundamental idea of the thermodynamic tree as applied to determining a complete list of the advantages to the use of one-dimensional spaces over polyhedron. In particular, circuit models enable the mathematical substantiation of transformation of the Pfaffian forms to total differentials (for one-dimensional flows the Pfaffian forms are always holonomic) and application of functions with the properties of potentials to describe irreversible processes.

Chapter 4 is devoted to the problem of constructing computational algorithms on the basis of the suggested models.

Chapter 5 exemplifies the MEIS application to the study real processes and shows capabilities and fruitfulness of the thermodynamic analysis, on the one hand, and the “art of the possible”—the nontriviality of constructing ideal models and quantitatively estimating the system parameters in every concrete study—on the other. Interesting problems of estimating air pollution by anthropogenic emissions and determining environmental characteristics of fuel combustion and processing are presented as an illustration.

The essence of the problems to be discussed is stated below, although not in order of their consideration in the book, but in a sequence that facilitates the entire perception of these problems in terms of both radical complexity and inexhaustible capabilities of using thermodynamic modeling.

We begin the book with an extensive introduction in order to help readers comprehend critically its contents, apply the results of the studies (our own and those of

others), and let readers to know all the “reefs” that may be encountered. Toward this goal, we give methodological features of thermodynamic analysis (among them, choice of the key notions, applied functions, premises) along with problems.

I.2. To the Use of Equilibrium Principle

Applicability of the equilibrium principle is undoubtedly a central issue in constructing the models of chemical systems. The fact is that thermodynamics itself may be defined as the *science about equilibria*: The use of its concepts becomes correct only in cases where assumptions on the equilibrium of studied processes and states prove to be admissible. The basic law of kinetics of ideal systems—the *law of mass action* (LMA)—is also associated with the equilibrium principle.

Estimation of the correctness of assumptions on observance of this principle, in turn, is normally nontrivial. Indeed, thermodynamics deals with mutual conversions of heat and work associated with energy dissipation, i.e., irreversibility and nonequilibrium. Therefore, description of such conversions in terms of equilibria is by no means obvious and calls for special analysis in each specific case.

In the analysis it is useful for us to compare thermodynamic systems to mechanical ones, as the latter are simpler and in some cases can serve as standards. Mechanics may also be interpreted as the science of equilibria. It is precisely the equilibrium equation applied by Lagrange that allowed its complete and strict formalized description. Correctness of the equilibrium models in mechanics is ensured by the fact that the mechanic models study conservative systems only, i.e., ones in which no energy is dissipated, whose considered functions possess properties of potentials, and whose infinitesimal changes are total differentials. As to the thermodynamics, infinitesimal changes in heat and work depend on the transition path from one state to another and are not differentials. Hence, description of the thermodynamic system by differential equations stems from a choice of the variable space that allows us to observe the system’s conservative nature.

In order to analyze applicability of the thermodynamics concepts to nonequilibrium processes, one should explain in detail the meaning of the phrase “far from equilibrium.” In different contexts it has at least three meanings. First, it refers to systems for which distribution of some microscopic variables (such as energy of translational motion of particles) differs essentially from the equilibrium distribution. Hence, the evolution of ordinary macroscopic variables of the chemical kinetics (x , the composition, U , the internal energy, V , the volume) cannot be described by first-order differential equations (by autonomous ones, if the environment is stationary). Second, a system that is closed (in particular, isolated) from the equilibrium environment is supposed to be far from equilibrium if its relaxation from the given state into a small neighborhood of equilibrium continues for a long time, during which time diverse nonlinear effects can take place: auto-oscillations, spatial ordering, etc. Third, “far from equilibrium” relates to “open systems”, which exchange substance and energy with an environment that is not in the thermodynamic equilibrium state.

Inapplicability of the classical thermodynamics be due to system remoteness from equilibrium in the first meaning. With remoteness in the second and third meanings and appropriate choice of space for variables, the thermodynamics generally can be used, though an additional analysis is needed in each particular case.

When discussing the problems of transition from kinetic to the thermodynamic description, we also examine conditions for applicability of the detailed equilibrium principle. The use of LMA supposes that the relation of rate constants of direct and reverse elementary reactions is equal to the equilibrium constant calculated by thermodynamics rules. This equality apparently follows from the thermodynamics when only two elementary reactions (direct and reverse) proceed in the system or when all stages are linearly independent. It is also obvious that generally, in a complex chemical reaction, the equality cannot be justified by thermodynamics and it can be substantiated based on the microscopic arguments only, such as the principle of microscopic reversibility [58]. Among all the methods for coordinating thermodynamics and kinetics examined in the book *Equilibrium Encircling*, the authors select two for discussion in this chapter: (1) stage-by-stage coordination that leads to the detailed equilibrium principle; and (2) the balance condition. The former can be derived from microreversibility, and the latter is interpreted as a consequence of applicability of the Markov description of microkinetics, i.e., admissibility of the assumption on equilibrium character of microscopic processes. In the absence of microreversibility, the balance condition replaces the detailed equilibrium principle and the Onsager relations.

The chapters devoted to the MEIS application present macroscopic explanations for validity of the thermodynamic approach, along with microscopic (statistical) grounds for using equilibrium macroscopic models. This discussion relies on graph-based models. In view of the one-dimensionality of space and correspondingly the holonomy of the Pfaffian forms, it becomes possible for one to validly apply differentiable thermodynamic functions for model construction.

In the analysis of real processes we sometimes can only deal with a fragmentary experimental check of the admissible application of thermodynamic models. Thus, Chapter 5 presents an example of the MEIS application for calculating *plasma-chemical processes*, i.e., processes of high-energy chemistry, for which the notion “far from equilibrium” has the first mentioned meaning (distribution of some microscopic variables differs essentially from the equilibrium distribution in the systems of these processes). The high intensity of these processes, however, contributes to rapid transition from the nonequilibrium to the equilibrium trajectory and attainability of points of final or partial equilibrium. This is confirmed through comparison of the results of computational studies with the full-scale experiments on pilot plants for plasma gasification of coal.

I.3. Modeling of Open and Closed Systems

This book covers the applications of thermodynamic analysis only to open systems, which is easily explained. Virtually all natural systems and the vast majority

of chemical-technological systems are open. Only some periodic processes, for example, processes in autoclaves, go forward in closed systems.

However, in many cases, real open systems can be studied by the models of closed systems. Thus, the type of the thermodynamic Lyapunov functions we uses does not change in principle if, instead of the closed system, we model an open one—one which exchanges the substance with the equilibrium environment. This theoretically simplest case refers to the study on the most important stationary processes: conversion of substances in different chemical reactors, fuel combustion in energy plants and vehicle engines, transformation of harmful anthropogenic emissions in the atmosphere, and so on.

Dynamics can differ qualitatively if the studied system exchanges substance or energy with the nonequilibrium environment. In this case it is naturally supposed that the environment represents a rather large system whose state does not practically change over the time period of interest to us. Otherwise, if we combined the studied system with the environment we would have an isolated system tending toward its equilibrium.

The theoretical analysis of thermodynamic system models that is presented in Chapters 2 and 3 is much broader than the sphere of applications of these models in Chapter 5. This is, however, characteristic of the relation between the theoretical and applied parts of the book as a whole; such an approach can be justified by the fact that sufficiently deep insight into specific features of individual processes and their models is achieved only when we have the full picture to which these “fragments” belong.

In analyzing the results of thermodynamic modeling it is advisable to apply the approach developed in Chapter 6 of *Equilibrium Encircling* for localization of stationary states by the Lyapunov functions technique. This chapter presents estimations of the regions of possible stationary states and nonstationary limiting points of the system with a given reaction mechanism. The following result was obtained on the model given by a continuous stir flow reactor. Let us compare an open and a closed system and choose in the latter an initial composition that agrees with the incoming composition of an open system. By virtue of the thermodynamic constraints the set of possible limiting points w (stationary states, points of limiting cycles, etc.) of the open system coincides with the set of compositions attainable from the given initial one in the closed system on the path to equilibrium.

In the theoretical analysis of open systems it is supposed that the state of a nonequilibrium environment is constant, and that kinetics is coordinated with thermodynamics by stages. An interesting example for applications is described; in it, a part of the substances was entered into the system and not removed from it. Estimation of the possibility for multiple stationary states to occur is apparently the main objective in [58] for employing MEIS to study specific processes.

The models of open systems were substantially simplified in the book (Chapter 5) to allow us to analyze real processes. In principle, open systems having stationary nonequilibrium environments are considered; for example, plasma gasification of coal, plasma stabilization of pulverized coal torch, and the atmosphere’s interaction with solar radiation. Processes in these systems refer to areas of high-energy

chemistry [26] and the nonequilibrium thermodynamics [56, 143], and they are characterized by different temperatures for different components. However, in the MEIS description of these processes, the impact of high-temperature flows (plasma, photon gas) is supposed to reduce only to formation of some active particles, which initiate the corresponding reactions. We take this fact into account by broadening the list of substances in the reacting mixture.

When we study real systems, in which a portion the substances do not participate in exchange with the environment (for example, reactors for heterogeneous catalysis), we include the elements of such substances in material balances in quantities that exceed *a priori* their usage in possible reactions. No other variations to consider specific features of individual groups of substances are introduced into MEIS.

The validity of such arbitrariness in modeling can be substantiated at least to some extent, only when we know specific features of the model and if it is a sufficiently strict model, as discussed in *Equilibrium Encircling*.

I.4. Ideal and Nonideal Systems

The ideal gas, whose internal energy is determined solely by the kinetic energy of its particles, is an initial ideal model. There are only elastic collisions between these particles. Each component of the multi component ideal gaseous mixture behaves as if it occupied the overall volume of the mixture. The chemical potential of the j th component of the ideal gas is determined by the formula

$$\mu_j = \mu_j^0 + RT \ln \frac{Px_j}{\sigma}, \quad (\text{I.1})$$

where μ_j^0 is the chemical potential in the standard state; R is the universal gas constant; T is the absolute temperature; P is the total pressure of the mixture; x_j and σ are the mole quantities of the j th component and the mixture as a whole, respectively.

Formula (I.1) is true for any ideal thermodynamic system, and it may be applied as a definition of an ideal system.

The significance of ideal models is determined by the facts that, first, only ideal models help to establish and explain the basic laws and peculiarities in the behavior of thermodynamic and kinetic systems; and second, the appropriate ideal description of real systems essentially facilitates computational experiments.

As a result of the development of the kinetic theory of ideal gases Clausius and Boltzmann formulated the second law of thermodynamics. The mass action law is also based on the ideality assumption. The book examines the problems of coordination between kinetics and thermodynamics, the convexity conditions for thermodynamic functions and correspondingly the uniqueness of equilibrium points basically for ideal systems. Consideration is given to MEIS modifications that include descriptions of diverse types of ideal systems: ideal gas, ideal plasma, ideal surface gas (models of a mixture of substances adsorbed onto the surface

of solid phase), ideal solution. Studies are carried out on heterogeneous systems containing both ideal and nonideal phases, e.g., condensed phase and ideal gas.

The book demonstrates the high practical efficiency of ideal models and the potential extension of the sphere of their application to the case in which it is impossible to establish whether the assumptions made in construction of these models are fulfilled. Chapter 5 describes an example of determining the maximum water vapor content in the atmosphere, i.e., the point on the curve between the gas and liquid phases. Discrepancy between the mole quantity of saturated vapor calculated by the model of the ideal gas and the results of measurements is less than 0.5%.

At the same time, Chapter 2 is devoted to construction and analysis of MEIS peculiarities; it investigates an impact of different types of nonidealities on specific features in the behavior of chemical systems. Conditions for the convexity of thermodynamic functions are determined for a gas phase that satisfies two-parameter equations of state: van der Waals and Redlich–Kwong. These conditions are discussed for systems with nonlinear balances (energy, entropy) and for nonadditive heterogeneous systems. The convexity condition is shown to be strictly proven only with some simplifying assumptions on the physics of processes. But nonetheless the method of convex mathematical programming allows a satisfactory account of the basic features of a wide scope of applied problems.

It is worth mentioning that the principle one chooses to construct a model influences how well the modeled system's actual peculiarities are represented. Since the law of mass action presumes ideality of the studied processes, the errors arising due to the disparity between the model and the modeled system should be estimated in each specific case; for example, this is true when thermodynamic models constructed on the basis of LMA are applied to analyze nonideal systems. Extreme models based on mathematical programming (MP) methods including MEIS are less sensitive to peculiarities of real objects and in principle can be used to study any complex nonideal system.

I.5. Modeling of Homogeneous and Heterogeneous Systems

The models of heterogeneous (multiphase) systems are obviously much more complicated than homogeneous ones if for no other reason than a wide qualitative variety of the applied functions and equations. For construction and analysis of heterogeneous models one has to take into account physical phenomena of a different nature, such as formation of phase interfaces, ionic dissociation of electrolytes, and gravitation. The interactions among separate components of multicomponent mixtures frequently cannot be neglected and the models for ideal systems become inapplicable.

However, when the heterogeneous system is a mixture of the ideal gas and pure condensed substances, the difficulties caused by absence of the strict convexity of functions to be minimized can be circumvented. One way to do this is to increase the space dimensionality of problem variables from the number of substances in the given list to the number of possible phases formed by these substances. As a

result of such transformation along the axes corresponding to the gas phase the functions will turn out to be strictly convex, and along the axes corresponding to the condensed phases the functions will be linear, thus providing a single-extremum character of the problem solved. It should be noted that the application of models and computer programs based on the assumption about a space with dimensionality equal to number of system substances often lead to divergence of the numerical process or to obviously absurd results.

Introduction of a real gas phase into the model gives rise to complexities because of nonadditivity of thermodynamic functions, even when use is made of the van der Waals equation of the state, the simplest one for real systems being

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT, \quad (I.2)$$

where P is pressure; V is mole volume; and a and b are constants accounting for molecular attraction and repulsion, respectively.

The emerging non-additivity can be revealed, for example, if the Gibbs free energy (enthalpy) G of the gaseous mixture with constant T and P is represented as a sum of “ideal” free enthalpies of individual components and the correction is made for nonideality (excess free enthalpy) for the whole mixture, i.e.,

$$G = \sum_j (G_j^0 + RT \ln P_j) x_j + \sigma \int_{P^0}^P V dP, \quad (I.3)$$

where σ is the total quantity of moles in the mixture; the superscript 0 refers to the standard state of the j th component; and P^0 is the highest pressure at which the mixture can still be considered an ideal one.

When equation (I.2) is used to calculate the integral on the right-hand side of (I.3) and the coefficients a and b are determined by the rules of mixing [170]:

$$a = \sum_i \sum_j a_{ij} \frac{x_i x_j}{\sigma^2}, \quad (I.4)$$

$$a_{ij} = (a_i a_j)^{0.5}, \quad (I.5)$$

$$b = \sum_j b_j \frac{x_j}{\sigma}, \quad (I.6)$$

these coefficients are found to be the functions of composition and in this case a is a nonadditive function. Hence, nonadditivity of G also becomes evident. Nonadditivity of the other thermodynamic functions can be determined in a similar way. However, the idea is clear even without mathematical analysis, as the notion of additive thermodynamic functions is associated in physics with the idea that there is no interaction among the system parts. When interaction is present, the additivity property disappears.

To ease the analysis of real heterogeneous systems by MEIS the authors tried to make their mathematical description similar to descriptions of ideal systems and to express explicitly corrections pertaining to nonideality. Equation (I.3) is an example of such description. A similar equation was applied to describe a gaseous mixture subject to the Redlich–Kwong equation.

We achieved analogy with ideal models when describing diluted liquid solutions by introducing activity coefficients. The free enthalpy of one mole of the j th dissolved substance was represented in this case in the form

$$G_j = G_j^0 + RT \ln \frac{x_j}{\sigma_s} + RT \ln \gamma_j(x), \quad (I.7)$$

where σ_s is the total quantity of moles of the solvent and dissolved substances; γ_j is a rational (referring to the mole fraction) activity coefficient.

Nonadditivity of the total free enthalpy is determined by the correction for nonideality (the third term of the right-hand side of (I.7)).

In Chapter 2 of the book it is shown that for heterogeneous systems with nonadditive phases, the mole thermodynamic functions of the j th component are *not* derivatives of the corresponding system's functions with respect to x_j , i.e.,

$$G_j \neq \frac{\partial G}{\partial x_j}, \quad F_j \neq \frac{\partial F}{\partial x_j}, \quad H_j \neq \frac{\partial H}{\partial x_j}, \quad U_j \neq \frac{\partial U}{\partial x_j}, \quad S \neq \frac{\partial S}{\partial x_j}, \quad (I.8)$$

where F is Helmholtz free energy; H is enthalpy; U is internal energy; S is entropy. Correspondingly, the phase equilibrium conditions for nonadditive systems consists not in the equality of mole free enthalpies of one and the same substance at different phases, but in the equality of derivatives of G with respect to x_j .

This is seen in the expression for the derivative of the Lagrange function

$$L = \sum_{j=1}^n G_j x_j + \sum_{i=1}^m \lambda_i \left(b_i - \sum_{j=1}^n a_{ij} x_j \right), \quad (I.9)$$

where n and m are the number of mixture components and number of material balance equations, respectively; b_i is the i th component of the vector of mole quantities of elements; and a_{ij} is the quantity of moles of the i th element in the mole of the j th component of the mixture.

The derivative of L is

$$\frac{\partial L}{\partial x_j} = \frac{\partial G}{\partial x_j} - \sum_{i=1}^m \lambda_i a_{ij} = 0. \quad (I.10)$$

Since the coefficients a_{ij} are equal for, the components of the vector x , (each x_j corresponds to a different phase of some substance), then the associated derivatives $\partial G / \partial x_j$ are also equal.

Convexity conditions for the thermodynamic functions of nonadditive systems were analyzed on an example of the gas subject to the van der Waals equation making it possible to obtain comparatively simple and qualitatively analyzable relationships.

Chapter 5 of the book offers examples on the efficient application of MEIS of heterogeneous systems for analyzing environmental characteristics of fuel processing and combustion and behavior of harmful anthropogenic emissions in the atmosphere.

I.6. Almost Almighty Thermodynamics

Discussions in the previous sections apparently allow us to state a broader question on the omnipotence of thermodynamics as a whole: its almighty character in our understanding is the “unlimitedness” of its sphere of applications (power).

To be sure, when emphasizing here and later the unlimitedness of the sphere for applications of thermodynamic models, we mean only their possible application to study of a wide variety of processes and phenomena. However, we in no way think that thermodynamics alone can present a comprehensive picture of objects under study. Using the axe, a skilled master can both cut a log and make it into a doll. However, to impart beauty to it for a child, he needs finer tools. This is the case for thermodynamics applications. We cannot say exactly, to what macroscopic systems and processes its methods are inapplicable, and therefore we write about the unlimitedness of the sphere of applications. But at the same time we assert that there are always subtle effects that require other special models besides thermodynamic ones.

The almighty character of thermodynamics was already demonstrated by its founders: Boltzmann and Gibbs. Boltzmann actually utilized the techniques of Markovian random processes and Lyapunov functions to deduce the H -theorem [21]. The H -theorem establishes irreversibility of the final results of processes in isolated macroscopic systems. So, the theorem is based on the assumptions of reversibility and equilibrium. In his work, Boltzmann illustrated the effectiveness of these techniques. According to Polak [140] statistical Boltzmann–Gibbs mechanics that originated from these premises initiated such novel sciences and scientific schools as statistical physics; thermodynamic theory of structure, stability, and fluctuations; nonequilibrium thermodynamics; nonequilibrium chemical kinetics; theory of information; synergetics; and so on.

Gibbs’s book [54] deals with the analysis of complex systems, where a wide variety of forces are involved, such as: chemical, electrical, gravitational, as well as forces of surface tension and elasticity. Concurrently, along with energy conversions, substance transformations and phase transitions can take place. Gibbs scrupulously investigated a set of real processes. For example, a sufficiently complete qualitative picture of hydrogen combustion in oxygen is presented there. Discussion of possible solutions to the derived system of equations results in a clear understanding of the drop in reaction temperature due to water dissociation and availability of limited regions where explosion and burning can take place. The inexhaustible nature of thermodynamic analysis is demonstrated on many other examples in [54]. Among them is the analysis of soap film stability and such a “fine” phenomenon as the sticking of wool hairs to ice crystals formed under the surface of water.

Thermodynamics found very diverse applications in the classical works by Albert Einstein. Einstein was rather skeptical of the development of the quantum mechanics and the statistical physics (even though he certainly had a profound impact on the development); he revised many new concepts of physics in his time,

addressing the “old good” thermodynamics, and he discovered a striking universality of its statements.

In Einstein’s works devoted to the theory of Brownian motion [40, 41, 42] we find two factors of interest for our further analysis. First, when devising the basic relations, he assumes that the motion of suspended particles is uniform motion and does not differ at low concentration from the motion of dissolved substances in a diluted (ideal) solution (pointing to the analogy between physical and chemical phenomena). Second, he substitutes the analysis of such motion by analysis of the state of thermodynamic equilibrium between the motive force (osmotic pressure) and the drag proportional to velocity. He derived a formula for the diffusion coefficient from the equilibrium equation, that coefficient being the key parameter of the most important irreversible process. In the context of the mentioned Boltzmann approach to derivation of the second thermodynamics law (H -theorem) Einstein’s result seems to be a natural extension of thermodynamic principles to substance transfer processes.

In [38] Einstein devises formulas of the statistical Boltzmann distribution and Planck radiation on the macroscopic model that represents a chemically homogeneous gas as a mixture of n chemically differing components, each characterized by its standard mole energy. Assessing the significance of conclusions in the paper he points out that there is no fundamental difference between physical and chemical systems and that the applied macroscopic thermodynamic analysis is adequate for description of radioactive decay, diamagnetism, Brownian motion and other phenomena. Note in addition that in his theory of opalescence in liquids [43]. In fact, Einstein employed the idea of “partial equilibria” (he considered these equilibria to be “partially determined in the phenomenological sense”), which is the principal subject of this book. Based on this idea he explained formation of complex spatial structures in liquids.

In *Theoretical Physics*, by Landau and Lifschitz [122–127] thermodynamics runs through the volumes devoted to the physics of continua, primarily *Hydrodynamics* [123]. In [123] the discussion on thermodynamic relations cover processes of shock wave formation in one-dimensional flows, combustion (chemical reactions), energy and substance transfer in the atmosphere. It will also be recalled that, in his the paper, by Landau [121] discusses coordination of thermodynamics and kinetics for the simplest case of monomolecular chemical reactions.

The author of *Equilibrium Encircling* [58] describes, along with diffusion, another most important irreversible process—heat conduction—in terms of thermodynamics and ideal kinetics. Heat conduction is based on the universally known Fourier law

$$w_u = k(T - T_h). \quad (\text{I.11})$$

The monograph [58] presents transition of the Fourier law to the equation

$$w_u = \varphi_k \left(\exp \left(-\frac{E}{RT} \right) - \exp \left(-\frac{E}{RT_h} \right) \right), \quad (\text{I.12})$$

where w_u is a rate of heat transfer (the stage of energy exchange in the overall reaction mechanism); $\varphi_k \geq 0$ is some intensive quantity; E is mole energy (constant); T and T_h are the respective temperatures of a chemical system and a thermostat exchanging energy with it.

Despite widespread of thermodynamic models in the fundamental science, for the time being, practical application of thermodynamics is very narrow when the situation requires talking into consideration specific features of concrete processes.

As mentioned above, the main examples illustrating capabilities of thermodynamics in the book are the analysis of harmful substance behavior in the atmosphere and the study on environmental characteristics of fuel combustion and processing.

Many experts believe it impossible in principle to apply thermodynamics in atmospheric chemistry because of low temperatures and correspondingly vanishing low rates of chemical reactions, and as a result the majorities of processes do not reach the end and are hampered in their partial equilibrium states. All living creatures, including people, are also in these states, and by the laws of thermodynamics in the oxidizing atmosphere they would convert over a very long period of time to a mixture of water, carbon dioxide, and diluted solution of nitric acid.

The MEIS application itself allows possible states on the path to final equilibrium to be determined, however, it does not solve all problems that may arise. If the totality of processes in which anthropogenic emissions take part are accounted for, the atmosphere should be considered an open heterogeneous system with a heterogeneous external environment (including earth, water, and solar radiation). Additionally, the atmosphere should comprise different groups of substances (some which participate and some which do not in mass transfer to the environment) and be far from equilibrium in the first meaning given in Section I.2. This is so because the processes of high-energy chemistry (photochemical) proceed in the atmosphere. This system involves forces of differing nature: chemical, electrical, gravitational, surface tension (as found on the surface of fog and aerosol droplets), wind pressure, Coriolis, and so on.

Chapter 5, however, shows that the models of closed heterogeneous systems with the equilibrium environment solve a wide scope of problems in forecasting the human-induced pollution of the atmosphere. In so doing the extent of idealization possible (consideration of different forces and phases in a system) depends on specific features of the problem to be solved in each particular case.

This chapter also discusses capabilities of thermodynamics in examples involving the analysis of fuel combustion in boiler furnaces and of fuel processing. It is shown that descriptions of real open heterogeneous systems, in which irreversible processes of diffusion and heat transfer, motion of particles with variable mass, non-stationary flows of reacting mixtures of substances, and other complex effects that take place, can also be substituted in many cases by descriptions of closed thermodynamic systems.

Section 1.3 is fully devoted to illustration of the almighty character of thermodynamics.

I.7. Problem of Getting Maximum Knowledge from Available Information

The problems of constructing models and applying them to study real systems under insufficient and inaccurate initial information are closely related. Preparation of the mathematical description of some classes of systems is only half the work. To obtain useful results on the basis of this description in solving specific problems is its second, and no less important, half.

In [58] the chemical systems were analyzed assuming that complete information on their dynamics comprises the following components: a list of substances, type (formulas) of thermodynamic functions, reaction mechanism, kinetic law, and rate constants. Let us discuss briefly specific features of these components.

Touching on the problem on compiling a list of substances, we will say that one should first note that the complete list of substances for systems of rather large dimensionality cannot be made up, in principle. This is due to the notion that the final equilibrium point for gaseous mixtures is the interior point of the material balance polyhedron (see Section I.9) and it should contain all the substances (even in negligible amounts) that can be formed from the elements available in the initial composition of reagents. For heterogeneous systems all possible gaseous components are to be present. Therefore, even when there are about 10–15 elements, the complete list of substances can reach enormous sizes. It should be remembered that, in the presence of organic substances in reaction mixtures, one and the same molecular formula can be associated with numerous substances of different spatial structures.

In the analysis of real systems such as chemical-technological ones it may turn out to be too complicated to specify both the general list of reagents x and the list of initial reagents y ($y \subset x$). Because of insufficient instrumentation it is often difficult to determine composition of raw material (vector y components), which influences the technological process quality.

It is very difficult to evaluate the errors of calculated composition of an equilibrium mixture caused by incorrectly given composition and dimensionality of x and y . It is apparent that if we are interested in the detailed composition of reaction products and calculations thereof, we should try to increase dimensionality. The aggregate of components x_j and y_j should be chosen carefully on the base of preliminary knowledge about the peculiarities of the process under study. Here it is important to correctly represent a composition of substances in terms of their thermodynamic properties. A group of substances with approve properties can often be represented as a single component of x .

When passing from the study of general properties of the models of chemical systems to the study of real objects, we encounter additional problems relating to the type of thermodynamic functions we must establish. For the analysis of models it is convenient to represent thermodynamic functions as the Lyapunov functions [58]. In so doing, the equilibrium point is conveniently taken in theoretical studies as the benchmark at which the values of these functions are equal to zero or a constant.

Therefore, in [58] use is made of the formulas

$$G = \sum_{j=1}^n c_j \left(\ln \frac{c_j}{c_j^{\text{eq}}} - 1 \right), \quad (\text{I.13})$$

where c_j is the concentration of the j th mixture component, and the index “eq” refers to the final equilibrium state.

In applied studies, formula (I.13) proves to be virtually inapplicable. First, before we do calculations, substance concentrations at the equilibrium point are unknown, and therefore it is difficult to apply (I.13) in computational algorithms. Second, when we use diverse available data banks of thermodynamic properties of substances—data banks that are created on the basis of the third law of thermodynamics or our own calculations of these properties—it is necessary to keep track of the correspondence between the accepted standard states of reaction mixture components. In order for us to construct thermodynamic functions for each substance in the given list, we need no less than two initial values of any thermodynamic parameter, and the type of formula for one such parameter should be set.

Necessity of setting the constants is seen from the Gibbs–Helmholtz equations:

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_v, \quad (\text{I.14})$$

$$H = G - T \left(\frac{\partial G}{\partial T} \right)_p. \quad (\text{I.15})$$

Actually, to determine U and H it is necessary to know the integration constants in addition to type of the function, $F(T)$ or $G(T)$. However, the equality $S(0) = 0$ cannot be employed because of the absence of information about the type of thermodynamic functions at temperatures close to absolute zero. Therefore, the thermodynamic parameters are calculated in this book by means of a system of coordinates that is determined by the third law of thermodynamics, rather than by the equilibrium point of the system studied.

As to the third component of initial information, i.e., reaction mechanism, it should be mentioned that in the analysis of real systems we deal with the conditional macromechanism, including not elementary but overall reactions (stages). However, even for such a mechanism it is usually possible to elucidate only separate fragments. Hence, construction of thermodynamic models on the basis of a list of reagents is seen to be preferable to construction on the basis of information about the mechanism of the studied process.

The kinetic law is imported not only for studying general properties of models and testing the coordination between thermodynamics and kinetics, but for analyzing real systems, at least to simultaneously make thermodynamic and kinetic calculations in some cases. However, it should be remembered that the direct application of LMA to construct thermodynamic models (when it is formulated on

the basis of equilibrium constants of the form

$$\prod_j P_j^{\nu_j} = K_p, \quad (\text{I.16})$$

where ν is a stoichiometric coefficient, and K_p is an equilibrium constant) requires great care, since it is valid only for ideal systems.

Use of the rate constants in the “thermodynamic-kinetic” analysis calls for their coordination with each other (if they are obtained from different sources) and with the thermodynamics of kinetic equations written with the help of these constants.

Specific features of the considered object and the researcher’s objectives (determination of the maximum yield of useful products in chemical reactors, their possible contamination by harmful impurities, composition of reagents in emergency situations, etc.) may call for the researcher to know other diverse information to study real (actually existing) objects, in addition to what is considered in [58]. It may include, for example, conditions of energy and mass transfer in the reaction volume, surface tensions of different phases, activity coefficients of electrolytes, and so on.

Surely, the case in hand implies the simplest dynamics associated with the process run through a sequence of equilibrium states. The goal to reveal such exotic effects as bifurcations, auto-oscillation, waves, etc. changes the character of the information problem.

The next critical problem of “filling” the models with information consists in estimation of errors of initial data and their effect on the results of computational experiments. Specifically it refers to the accuracy of setting the standard values of thermodynamic functions, the values of constants of reaction rates and the accuracy of equations applied to model construction (thermodynamic state, kinetics, diverse interactions between system components). Difficulty of estimating errors in determining different constants originates at least from the fact that each of the constants can be calculated by the specific technique that combines both theoretical calculations and experiments in varying degrees.

Insufficiency of initial information predefines to a great extent the possibility of attaining reasonable accuracy in constructing the model of the studied object and requirements to the quality of results.

The given list of substances directly affects model dimensionality (number of variables and number of balances). Accuracy of setting the different constants should be coordinated at least intuitively with the accuracy of approximation of basic calculated relationships, and with the extent to which nonidealities and interactions occurring in the modeled system will be considered. Preliminary knowledge about actually running processes foster formation of inequality constraints as well.

The relation between the accuracy of initial information and the requirements the calculation results is shown by the example: Suppose we need to estimate potential formation of a hazardous concentration of some harmful ingredient in the atmosphere and let this concentration make up an amount equal to 10^{-12} part of the total amount of substance in the system. Certainly, with the attainable accuracy

of determining standard values of thermodynamic functions (e.g., the free enthalpy G^0) not exceeding 5 to 6 digits such low concentrations can hardly be calculated with a better accuracy than the order of magnitude. However, if under widely varying values of G (and other information) the concentrations of the ingredient sought in most calculations exceed a hazardous value by 2–3 orders of magnitude, it can be asserted that in real conditions the formation of harmful mixtures in terms of the chosen index is highly probable (a *qualitative* estimate!). It is all we can conclude in the case.

From the above explanation it is clear that completeness and quality of initial information has a pronounced effect on the technique of computational experiments carried out with the help of available models: choice of varied parameters, estimation of solution sensitivity, and interpretation of results.

Problems of solving specific problems under insufficient initial information are addressed in Sections I.20 and I.21 and Chapter 5.

I.8. Types of Descriptions: Stationary (Where Do We Stay?), Dynamic (How Do We Run?), Geometrical (Where Do We Run?)

In view of the basic properties of models of chemical systems and clearly stated goal of studies, it is possible to sensibly select in each particular case the how the studied system will be described from among the types mentioned in the section title.

Dynamic description containing functional relationships between coordinates and time provides undeniably the most complete knowledge of evolution. Such a description enables the determination of either the unique trajectory of system motion, if any, or the possibility for emergence of bifurcations, oscillations, waves, odd attractors, etc. Dynamic models offer for each time instant a complete picture of probable characteristics of motion: In what directions and at what rates can the system state change (or “How do we run”?).

However, it often proves important not to know possible trajectories in time, but only to determine either the final process point or some intermediate state with the given properties or the region of states the trajectory can pass through. In these cases it is naturally reasonable to select simpler mathematical descriptions that are better suited for problem characteristics.

The key simplification of models is certainly the elimination of the time variable τ that was proved yet the classical work by Boltzmann [21]. He established independence of thermodynamic states of time and hence the feasibility of constructing the whole “building” of equilibrium thermodynamics without this variable.

When we need to determine only the final equilibrium state, i.e., to answer the question “Where do we stay?”, use is made of traditional thermodynamic models either to solve a closed system of equations of LMA and material balances or to search for the extremum of some thermodynamic function. In both cases

in comparison to application of the kinetic model the differential equations are eventually substituted by algebraic and transcendental ones.

The geometrical problem (“Where do we run?”) can be solved by transformed kinetic equations, in which the derivatives of concentrations with respect to time are replaced by the derivatives of thermodynamic functions with respect to concentrations or some other macroscopic variables (the dimensionless *pseudopotentials*) (see Section 1.5). In [58] the simplest examples of constructing the whole region of thermodynamic attainability from the given initial state are described on the basis of the reaction mechanism and the type of thermodynamic functions.

The use of MEIS is another possible approach. In this case a single calculation results in only one point corresponding to the extremum of some given function of concentrations. However, the multivariant computational experiment presents a rather complete picture of probable events on the path of the studied system to the equilibrium.

Though the geometrical description occupies an intermediate place between the stationary and dynamic ones in volume and quality of knowledge acquired, the computational difficulties caused by its application in MEIS differ little from those arising in calculations by stationary models, but they are much less difficulties than those of dynamic modeling. As mentioned above, this is because we apply simpler equations in geometrical descriptions compared to what we apply in dynamics.

Elimination of the variable τ , simplification of models and computational algorithms allow a more detailed study on individual states and whole regions of attainability using the stationary and geometrical models over the dynamic description. These advantages of nondynamic descriptions are exemplified in Chapter 5 of the book.

I.9. “The Field of Battle”: Balance Polyhedrons

The study of chemical systems implies the study of the specific features (continuity, convexity, etc.) of thermodynamic and other functions sought on the sets of admissible values of variables. Configuration of these sets is first of all determined by *balance polyhedrons*. Basic linear balances reflect the law of mass conservation. Depending on the properties of the considered systems, other linear balances can also be used, for example the balances of electric charges, surfaces, or volumes. In addition to these balances the condition of non-negativity of variables is present.

Nonlinear balances (energy, entropy) and inequality constraints (excluding the constraints on non-negativity) usually only reduce the region where we search for solutions, in a number of cases making it nonlinear, but these balances and constraints do not affect the type of functions sought. Neither does decrease in dimensionality of the polyhedrons caused by reducing a given list of substances (without decreasing the number of phases).

When we study the properties of models, analyze objects that really exist, and develop computational algorithms we shall know the characteristics of polyhedrons: the number of vertices and edges; the change in the form that depends on the

conditions of the problem solution; the type of graph representing the scheme of vertexes connected by edges; specific features of matrices that reflect the structure of this graph, and so on.

A rather detailed analysis of balance polyhedrons was already presented in the monograph *Equilibrium Encircling*. The monograph gives briefly the main information from linear algebra [72], linear programming [33] and convex analysis [146]; it presents the main assumptions on both the area where potential values of variables are set and the properties of functions changing in this area; consideration is also given to the methods of describing the polyhedrons by the systems of equalities and inequalities, including complexes. The monograph also describes the graph of a balance polyhedron. The technique of constructing such polyhedrons and analyzing their properties is illustrated by a reaction of hydrogen combustion in oxygen.

The monograph addresses the properties of polyhedrons as applied, mainly, to the problem of constructing thermodynamic trees (Sections 3.2. and 4.4).

I.10. Roughness and Reliability of Thermodynamics

Understanding the universality of principles and the unlimitedness of areas for thermodynamics application, and the possibility of creating on these basis comparatively simple mathematical models and efficient computational algorithms, does not give an exhaustive answer to how good the pictures obtained with the help of thermodynamic analysis will be. Are these pictures too rough due to lack of description of the studied system evolution with time? May losing the sight of some effects (subtle differences in behavior) that appear in the course of the evolution lead to a description that does not correspond to the reality?

There is no unique answer to such questions in any area of life. In each particular case we have to account for the specific nature of both the object of study and the objectives of a researcher. There is always a need for an explicit statement of the problem that includes clear instructions on what should be determined with full certainty and what mistakes and ambiguities can be neglected.

However, the only general and absolutely correct statement is that, despite all the roughness of thermodynamics, we gain subtle insight into the peculiarities of problems solved with its help, making it possible at all time to obtain useful and reliable results.

Two things determine the roughness of thermodynamic models: on the one hand, the universality itself of thermodynamic relationships creates difficulties when it is applied to specific phenomena; on the other hand, the rigidity of premises associated with the idea of reversibility and equilibrium character of processes based on the idealizing a real situation also contributes to the model's rough character.

We are sure that a "rough" thermodynamic model is practical and reliable, because of the following circumstances: an increase in the dimension and complexity of a system under study, a rise in the number of interactions between system components, and the diverse nature of these interactions—all factors being

equal—increase the chance of a system's transition to the (desired) equilibrium trajectory in the course of its evolution. Indeed it is natural to suppose that if in a rather large system some local volume, one that is an insignificant fraction of its full volume, deviates from equilibrium, the equilibrium environment (i.e., the remaining part of the system) will make this smaller volume return to equilibrium state. A similar picture may appear when the forces (potentials) that characterize one of many interactions between system components deviate from equilibrium values.

To make these assumptions clear let us now introduce the examples that run through this book.

Consider two flows of the substance going through a furnace: fuel-air mixture and plasma, the latter used for lighting the flame. The flows have essentially different temperatures (the environment is in a nonequilibrium state). At a small fraction of plasma in the total flow the temperatures, chemical potentials and pressure assume equilibrium values fast and the process in the system becomes subject to thermodynamic laws.

The atmosphere, which exchange mass and energy with the nonequilibrium environment, includes separate parts (earth, water, radiation) each having different thermodynamic parameters. In the atmosphere, states are also attained that are described in terms of partial equilibria (due to the extremely slow rate of many reactions). The applicability of these terms relates also to the interaction between a relativistic flow of photons and the substance, which was shown by Einstein [39]. The flow of the substance with definite quantities of moles and energy becomes the model of photon gas.

In many cases the thermodynamic relationships are used to easily model the periodic fuel combustion processes (in the fixed-bed furnaces of stoves and boilers) and the chemical reactions in autoclaves. Here it is natural to assume that the parameters of interaction between the system and the environment change so slowly that partial or complete equilibrium can be attained within the system.

Certainly, it is desirable to confirm the correctness of applying thermodynamics in the above and similar cases by at least partial experimental and, if possible, theoretical check. Unfortunately only qualitative analysis is usually available before application of thermodynamic models, which is to a larger extent based on the intuition of a researcher.

In turn such intuition can be well developed only in specialists who understand the formalized relationships between thermodynamic models and different types of microdescriptions and macrokinetics. These relationships are studied in detail in [58] and addressed in Section 1.5 of this book.

I.11. Thermodynamically Admissible Paths

If, when solving a specific problem we are not interested in the whole thermodynamic attainability region, but need only to determine the most favorable states (those with maximum concentrations of useful substances) or, on the contrary, the

most dangerous states (those with the largest fraction of harmful components), it is still necessary to make sure that thermodynamically admissible paths to the states obtained from the calculations exist.

In *Equilibrium Encircling* the notion of such a path is introduced on the basis of a formalized statement on nondecrease of entropy S at spontaneous changes in the isolated system. The assumptions concerning the entropy itself are:

- S is a first-order homogeneous function of the macroscopic variables M_j ; $S(\lambda M) = \lambda S(M)$ for any $\lambda > 0$.
- The value of $S(M)$ can be finite or equal to $-\infty$. The function is continuous and reaches its maximum value at each closed limited compact subset of the domain of definition.
- For the system, consisting of parts

$$S(M) = \sum_j S_j(M_j), \quad (\text{I.17})$$

where $S_j(M_j)$ is the entropy of the part that meets the same conditions as S .

The second condition (on likely values of S) makes essentially easier the analysis of principal peculiarities of the models of thermodynamically attainable regions. However, when we study real objects to calculate entropy we have to use the third law of thermodynamics, according to which the minimum values of S turn out to be equal to zero (see Section I.7).

The latter condition (additivity of entropy) means that energy and entropy related to the interaction of parts are considered negligibly small as compared to the energy of parts themselves.

Equilibrium is the point of global maximum of S in the balance polyhedron. It is assumed that such a point exists. In presence of flows of substance and energy between the system parts, the points of the partial equilibria are do not always occur where the equilibrium of the system as a whole lies.

The thermodynamically admissible path is a continuous trajectory $M = \varphi(\tau)$ if the following four conditions are met:

- (a) $\sum_j a_{ij}^0 \varphi_j(\tau) = 0$ (i.e., $a^0 \varphi(\tau) = 0$) for all $\tau \in [0, 1]$;
- (b) $\sum_j a_{ij} \varphi_j(\tau) = \text{const}$ (i.e., $a \varphi(\tau_1) = a \varphi(\tau_2)$) for all $\tau_1, \tau_2 \in [0, 1]$;
- (c) $\sum_j l_{ij} \varphi_j(\tau) \geq 0$ (i.e., $l \varphi(\tau) \geq 0$) for all $\tau \in [0, 1]$;
- (d) the function $S(\varphi(\tau))$ on the segment $\tau \in [0, 1]$ is nondecreasing.

In the above conditions, a^0 and a_{ij}^0 , a and a_{ij} , and l and l_{ij} are matrices of coefficients in homogeneous and nonhomogeneous balances, nonnegativity conditions, and the matrices' elements respectively.

Transition from isolated systems to the systems that interact with the environment requires replacement of the condition "d" by the condition of a monotonous change in the function, whose physical sense is determined by the fixed parameters of interaction (see Section I.12).

In [58] the author gives examples of constructing admissible paths for the case where the reaction mechanism is set, and for a more general situation in which only a list of reagents is known. The general technique was based on the transformation of the thermodynamic attainability region (a space of admissible paths) to a graph, namely a thermodynamic tree, and enabled one to obtain a number of interesting results (see Sections I.13, 3.2 and 4.4).

The book *Equilibrium Thermodynamics* deals with the problems of admissible paths' existence when modeling actually existing systems of a large dimensionality for both the case of absolute absence of the information on the process mechanism and the case in which there is fragmentary knowledge on the regions passed by the system trajectory in the space of compositions. Our book addresses the problems of determining potential directions of motion in studies of principal peculiarities of thermodynamic and kinetic models and real objects in Sections 1.5, 3.2 and 4.4.

I.12. Thermodynamic Functions

A primary requirement of the set of variables to be applied, including the set of functions, is that it should completely determine the state of the studied system, i.e., it should enable one to frame the system in by closed mathematical description. However, this requirement is certainly not the only one. Being closed, the models applied should also possess an aggregate of valuable qualitative characteristics.

In principle we can construct the formal thermodynamics by building on five variables only: pressure P , volume V , temperature T , internal energy U and entropy S , as well as by two more quantities: heat q and work l , which can be expressed via these variables. However, the vocabulary – at a minimum it contains only the listed terms—does not make it possible to see all the qualitative diversity of thermodynamic systems and processes, nor does it give clear explanations of their specific features or unfold clear and efficient theoretical principles. To perform a conceptual informal analysis of mathematical models of thermodynamics the list of the variables we use has to be essentially extended. Though, for every day communication in the home and in business, people need to know about 3,000 to 5,000 words, Pushkin's language, which can express the subtlest shades of feelings and thoughts, contains about 20,000 units by the estimations of philologists.

It follows from the first and second laws of thermodynamics that, in an isolated system at constant energy, the energy's value in the course of any possible process decreases; at maximum entropy (i.e., at equilibrium state), this energy cannot be used for performance of work or for heat transfer from one part of the system to another. Thus, it becomes clear that to have a full picture of transformations in the isolated system we must introduce variables that could characterize the value of energy and the relationship between energy of individual parts and conditions of interaction with each other. This circumstance made important the use in thermodynamics of such functions as free Helmholtz energy F , enthalpy H , Gibbs energy (free enthalpy) G , chemical potential μ , and some others.

TABLE I.1. Classical conditions of equilibrium

Fixed parameters	Equilibrium criterion
T, V	$\min F$
T, P	$\min G$
S, V	$\min U$
S, P	$\min H$
U, V	$\max S$
H, P	$\max S$

For a clear mathematical analysis of nonisolated systems it is necessary to determine the function (characteristic) that takes an extreme value in the equilibrium state. In thermodynamics these functions and type of extremum (maximum, minimum) are determined for six classical combinations of fixed parameters, given in Table I.1:

To conveniently analyze the uniqueness and stability of solutions of thermodynamic (kinetic) equations the chosen functions should have the form of the Lyapunov functions, i.e., of functions that have the following properties:

$$\Phi(x) > 0, x \neq x_0, \quad (\text{I.18})$$

$$\Phi(x_0) = 0, \quad (\text{I.19})$$

$$\frac{d\Phi(x)}{dx} f(x, \tau) = \sum_{j=1}^n \frac{\partial \Phi(x)}{\partial x_j} f_j(x, \tau) \leq 0, \quad (\text{I.20})$$

where x is a vector of variables of the problem (for example, the mole quantities of substances), and x_0 is a fixed point, in which the right-hand side of the differential equation

$$\dot{x} = f(x, \tau)$$

is identically equal to zero.

The homogeneous functions of the first and zero power also play an important role in thermodynamic analysis. The homogeneous function of power λ is the function $f(x)$ for which the equality

$$f(kx) = k^\lambda f(x) \quad (\text{I.21})$$

is true. Homogeneous functions of the first power ($\lambda = 1$) relative to the amount of a substance are the extensive thermodynamic variables, for example, the above mentioned S, U, H, F , and G . The intensive quantities P, T, μ , mole entropy, mole energy, mole free energy, and mole free enthalpy are of the zero power ($\lambda = 0$).

The homogeneous functions satisfy the Euler theorem

$$\sum_{j=1}^n \frac{\partial f(x)}{\partial x_j} x_j = \lambda f(x). \quad (\text{I.22})$$

This theorem is important for our further analysis.

Chapter 2 of this monograph discusses in detail the composition and specific features of thermodynamic functions and their application to the analysis of models of chemical systems.

I.13. A Thermodynamic Tree and Space of Admissible Paths

Though the thermodynamic Lyapunov functions, set on polyhedrons of material balances, in most cases are either convex or approximated by convex curves with negligible errors, the studies of peculiarities of the surfaces of these functions with respect to large-dimensional systems represent a very complicated problem. The issue is that, as applied to the problems discussed in this book, it turns out to be necessary both to determine the location and properties of the final equilibria points and to find the partial equilibria that correspond to different compositions of reaction mixture, admissible paths, and regions of thermodynamic attainability from the set initial states.

In mathematical programming (MP) (the theory of problems that search for extrema of functions) [19, 94, 142], algorithms are developed to describe the process of movement towards maximum or minimum points, which lie directly on the surface of studied function. In [58] the author suggests a radically different method of solving this problem, one that implies transforming a multidimensional domain of the function into a one-dimensional set—a graph in the form of a tree, called by the authors “a thermodynamic tree”. The authors examine specific features of the function’s behavior already on this graph.

Here, A.N. Gorban introduces the notions of *thermodynamic preorder* and *thermodynamic equivalence*.

Preorder is defined as the condition in which $x_1 \geq x_2$ if there exists a thermodynamically admissible path $\varphi(\tau)$, $\tau = [0, 1]$, such that $\varphi(0) = x_1$, $\varphi(1) = x_2$.

Thermodynamic equivalence is defined as the condition in which $x_1 \sim x_2$ if $x_1 \geq x_2$ and $x_1 \leq x_2$. The states x_1 and x_2 are comparable if $x_1 \geq x_2$ or $x_1 \leq x_2$. Comparable states x_1 and x_2 always belong to one balance polyhedron.

The identification of thermodynamically equivalent states on the balance polyhedron results in a thermodynamic tree or a tree of entropy.

The condition of arcwise connectedness components is another very important notion for description of chemical systems by the “trees”, which was introduced in [58]. The component $D \setminus U$ (U a convex set) that contains the point x_0 is an aggregate of all points x for which there is a continuous path in $D \setminus U$ that connects x_0 and x . Any two points lying in one arcwise connected component $D \setminus U$ can be connected by continuous paths located in $D \setminus U$.

In [58] it is shown that between the components exhibiting arcwise connectedness in the initial polyhedron D and the thermodynamic tree Y there is a one-to-one correspondence. This makes it possible to map the whole set of thermodynamically admissible paths from different initial points (states) and thermodynamic attainability regions on Y and to find on the tree the points with the known composition and extreme concentrations of given substances, as well as to estimate the limits of

change in the composition of reaction mixture at a given class of thermodynamic equivalence.

Chapters 3 and 4 of the present book repeat in brief the principles presented in [58] and an effort is made to further extend the ideas of the “tree” to devise the computational algorithms for analysis of really existing systems of large dimensionality. The main problem here is associated with the huge numbers of vertices and edges of trees that are obtained when modeling multicomponent chemical mixtures.

I.14. From Admissibility to Feasibility

The estimation of what in principle may happen to a studied system is usually not sufficient to obtain a satisfactory result of the studies. It is always desirable to obtain more specific information on the opportunities and conditions of feasibility of one or another probable event. The thermodynamics, as is known, is liberal and allows everything that is not contradictory to its first and second laws. To choose from an admissible set of processes and states those which are practically feasible, some additional nonthermodynamic initial data are needed. Because the latter are quite often unreliable, they have to be varied.

In G.K. Boreskov’s opinion [22], everything allowed by the thermodynamics can be realized. The question is only how some desirable or undesirable state is attained. If it concerns the technological processes, the required results can be achieved either by choosing catalysts, the number of which is unlimited, or by regulating the parameters. If natural processes are the subject of the study, the rate of individual reactions of process mechanism is changed by the nature itself, which possesses an inexhaustible set of control means.

The difficulty, naturally, consists in revealing and describing those methods of process implementation that are used by humans and nature. Unfortunately one can find with certainty only fragmentary data. Mainly we employ assumptions that require further analysis of their reliability.

Sometimes it turns out possible to set a part of the initial information in a probabilistic form. For example, to forecast the air pollution in some region we can estimate the probability of unfavorable combinations of meteorological factors (pressure, temperature, air humidity, wind speed) in terms of accumulation of harmful substances. It is also possible to estimate roughly probabilities of limiting conditions of fuel combustion in energy plants. In some situations we can assume equal probabilities for different sets of initial data. Yet, the dominating cases are those for which we can estimate only the ranges of changes in the factors that affect the course of the process studied.

Additional information is conveniently varied at an extreme formulation of the problems solved, particularly when the problems are described in the form of mathematical programming (MP). In this case within a single general model, for example MEIS, it becomes easy to change composition of variables, form of objective functions, set of equality and inequality constraints, values,

and the list of fixed parameters, formulas for calculation of thermodynamic functions.

The problem of constructing the model that takes into account the specific nature of a concrete studied process turns out physical-technical rather than mathematical. The involvement of additional constraints or variables into the problem statement can certainly result in nonlinear balances, violation of the objective function surface convexity, and some other effects. However, the main difficulty is in the formulation of the initial assumptions on the physics and chemistry of the process. Comparing the results of modeling with the known published data on the processes, similar to those studied, we can correct iteratively these assumptions and achieve plausibility of the final result of the computational studies.

A comprehensive analysis of possible feasibility of complex processes certainly requires employment of other models besides MEIS. Thus, the use of the LMA equations (in thermodynamic form (I.16)) helps us estimate the impact of the process mechanism on the attainable states. Estimation of stability of the analyzed partial equilibria can require direct application of kinetic models. The complexity of LMA and kinetic models mentioned in the previous sections makes us reduce essentially the list of substances for their construction, as compared to the MEIS-based description, which is also a nontrivial problem. Consideration for the impact of heat and mass transfer and hydrodynamics on the process can also call for the appropriate simplified models.

The problems outlined in this section are analyzed in the next sections of the Introduction, in Section 4.5, and in Chapter 5, which is dedicated to the thermodynamics applications.

I.15. Constraints Imposed by the Reaction Mechanism

The monograph *Equilibrium Encircling* gives a theoretical analysis of reaction mechanism impact on thermodynamic attainability regions, and on partial and complete equilibria in chemical systems. The technique applied for the analysis is illustrated on the elementary example of isomerization in a closed system at constant temperature and volume. The applicability of the technique for the analysis of behavior of the open systems with nonequilibrium environment was also shown. Though the suggested algorithm does not possess high computational capabilities, it fosters understanding of the main patterns of equilibrium detour and facilitates correct construction of more complex models and algorithms.

Setting constraints on the process mechanism when we study multicomponent systems calls for solution of a number of complicated problems.

First of all, we encounter the problem of determining the mechanism itself. In [58] “mechanism” means a list of elementary reactions set by stoichiometric equations. If we regard as “elementary” those reactions that go forward in interaction (collision) of species (as it is usual to do), the list of such reactions for real technological and natural processes is usually hard to describe due to its extensiveness. For example, in coal combustion just the components formed out of organic and

mineral parts of coal in more or less noticeable concentrations (assume more than 10^{-8} mole/kg of the mixture) account for several hundreds species; the number of elementary reactions is much larger. Recall that when solving environmental problems we may be interested in estimating concentrations of harmful ingredients when their fractions in the reaction mixture do not exceed 10^{-12} – 10^{-15} . Setting a complete list of elementary reactions here becomes unrealistic.

Equilibrium Encircling emphasizes the possibility of determining the elementary character of reactions phenomenologically based on the form of the kinetic equations for a unit of the reaction mixture volume,

$$\dot{x}_j = \sum_s (\beta_{sj} - \alpha_{sj}) w_s(x, T), \quad (\text{I.23})$$

where β and α are stoichiometric coefficients on the right-hand and left-hand sides of the stoichiometric equation of the s th stage (reaction), respectively; and w_s is a rate of the s th stage. Here the function form $w = f(x, T)$ was supposed to be known. However, such knowledge turns out to be hard to come by even when several tens or hundreds of overall reactions in a real process are regarded as elementary.

Therefore, when studying the large-dimensional systems, we can hope only for the knowledge (still incomplete) of stoichiometric equations of principal overall reactions

$$\sum_j \alpha_j A_j = \sum_j \beta_j A_j, \quad (\text{I.24})$$

where A_j are substance symbols.

The mechanism represented by a system of equations of type (I.24) can obviously be determined as a conditional “overall mechanism.”

The next and apparently to a great extent nonformalized problem consists in putting forward the hypothesis on such a mechanism. Its solution in each specific case should be based on the available preliminary knowledge on the physics and chemistry of the process and depends on the researcher’s skills (see Sections I.20, I.21).

And finally the third problem is associated with formalization of an assumed hypothesis in the form of separate blocks of the mathematical model to be applied.

If MEIS is chosen as a main tool for the study, the choice of a list of substances (the composition of the sought variables) turns out to be the simplest and most natural way to indirectly account for the mechanism.

In [83], attention is given to several algorithms for checking the hypothesis on the process mechanism and to considering the assumed hypothesis in the analysis of the chemical systems’ behavior. In doing so MEIS was used along with the thermodynamic models on graphs specially intended for the analysis of mechanisms of chemical reactions. Further the problem of setting the constraints on the mechanism is analyzed in Sections I.20 and in I.23–I.25 of the Introduction and in the body of the book.

I.16. Constraints on Exchange

As mentioned above, most chemical-technological systems and practically all natural systems are open. Even in cases where the processes taking place in them can be studied using the models of closed systems, we still encounter problems describing the mass-and-energy exchange with the environment.

As examples we can present here the problems of modeling atmospheric pollution and state of indoor air environment.

The components of the atmosphere of any city or region are involved in the various processes of exchange with the heterogeneous environment: mass transfer by the air flows from the neighboring regions, sorption (desorption) by ground surface; solution in the aqueous medium; condensation (evaporation); and energy exchange with solar radiation, water, and terrestrial surface.

The exchange processes in ventilation and air conditioning systems in buildings are distinguished by a similar variety. Here, first of all, absorption and extraction of harmful substances at the boundary surfaces and moisture condensation on the window apertures are of interest. Specific problems can appear when we model air exchange in the production premises and in mines where formation of a large number of harmful and explosive ingredients and significant heat emission are often observed.

The processes in furnaces (combustion chambers) of energy plants include substance transfer (fuel, air, and combustion products) and heat exchange with heating (cooling) surfaces.

When studying the above and many other systems, description of the exchange (interaction) conditions with the environment can be made easier owing to a proper choice of the boundary between the considered system and its environment. Thus, conditionally including into the atmosphere the volumes of water and dry land adjacent to the atmosphere, we can substitute to a greater extent the modeling of the transfer processes by the modeling of the system equilibrium conditions with an increased number of phases. In doing so, those additionally introduced masses (surfaces, energies, etc.) should be large enough to run processes (chemical reactions, sorption, solution, etc.) that involve atmospheric components.

Variation in the system composition at its modeling should certainly be sensibly combined with imposition of additional equality and inequality constraints on the exchange processes. For example, constraints on the rate of oxygen diffusion to the surface of an oxidized substance can be represented in the form of inequality

$$x_{\text{O}_2} \geq x_{\text{O}_2}^b, \quad (\text{I.25})$$

where $x_{\text{O}_2}^b$ is the quantity of O_2 that, according to the mass exchange conditions, can not enter into reaction. The constraint on the endothermal process of nitrogen oxide formation at fuel combustion in a system with fixed P and T is described by the inequality

$$H \leq H^b, \quad (\text{I.26})$$

where H is the system's enthalpy; H^b is the fuel calorific value.

The latter inequality (I.26) can be interpreted as a constraint on the potential range of technological regulation of reaction mixture parameters. The set temperature and pressure can be maintained only when (I.26) is true.

I.17. Constraints on Parameters

We touched on problem of formulating the constraints on parameters in the previous section, as it was relevant to the discussion of the exchange problem we addressed in that section. So, constant temperatures and pressure can be maintained only when the chemical-technological process is run at definite rates of energy and mass transfer between the reacting mixture and the environment. In other words, T and P are regulated by this transfer.

Dependence of parameters on possibilities of regulation can be mathematically expressed by additional constraints imposed along with the parameters determining the interaction of the system with the external environment. For example, for the systems with fixed H and P it often turns out that it is useful to impose the constraints

$$T \geq T^b \quad \text{or} \quad T \leq T^b. \quad (\text{I.27})$$

The first inequality in (I.27) takes into account using practical calculations (see Chapter 5) a possible decrease in furnace temperature due to endothermic reactions of nitrogen oxide formation in them.

The choice of fixed parameters is not always obvious. For example, when studying the stationary process of fuel burning in a boiler furnace, we can assume the pressure and temperature in one of the furnace's points are constant (this is most logical for the combustion completion area). However, in this case, as was explained above, the equilibrium mixture formation can be accompanied by heat absorption that exceeds the enthalpy of the initial fuel. Fixing of H and P in turn can lead to an unrealistically low temperature, at which the endothermic reactions may not be kinetically feasible.

Solution of the specified problems associated with the choice of initial physical assumptions presumes, of course, correct mathematical formalization. An extreme model, for example MEIS, should be constructed so that, on the one hand, there is a possibility for optimization and, on the other hand, all the relationships between the variables that are required by the process physics are met.

Apparently, when determining the number of degrees of freedom f of multi-phase, multicomponent systems of large dimensionality, we cannot use the Gibbs rule of phases directly,

$$f = n - k - r + 2. \quad (\text{I.28})$$

For the systems with a disperse liquid phase in which the surface tension forces should be taken into account, number of degrees of freedom is given by

$$f = n - k - r + 3, \quad (\text{I.29})$$

where n is the number of independent components (substances), k is the number of independent reactions, and r is the number of phases.

Normally, without information (at least without quite full information) on the process mechanism, we can set neither k nor r . Prior to doing the calculations, it would be hard for one to estimate which substances' concentrations will be non-negligibly small, i.e., to estimate, in effect, what the system dimensionality will be.

Obviously, when we use extreme thermodynamic models, the phase rule should be met automatically with accuracy as to the error in calculations due to observance of equilibrium conditions.

Let us point out that, in using MEIS and other models of thermodynamic equilibria, we digress from the classical definition of Gibbs. Namely, we regard "a system component" as not an individual substance, but its amount in some phase. For example, if the water in a reaction mixture is present in gas and liquid phases, its concentration in the two phases is described by two separate variables. Such an extension of the space of variables of the considered problem makes easier its reduction to a convex programming problem.

These problems do not become more complicated in terms of computation when the inequality constraints on the parameters similar to (I.25)–(I.27) are included into the model.

I.18. Constraints on the Regions of Process Running

The problem of formalizing knowledge of the regions through which runs the process of the studied system's relaxation to equilibrium is rather complicated. As is clear from the previous sections, sufficiently full data on both the reaction mechanism and the individual overall stages are hardly obtainable when modeling complex actual systems.

Available published and experimental data in the majority of cases enable us to specify possible values for only a part of the composition vector components in the intermediate points of a process and do not allow the coordinates of these points to be completely determined. Such scantiness of initial information naturally leads to an increase in the number of computation options and in complexity of the computational experiments.

Chapter 5 presents examples of modeling regions of complex process running, a model that is based on a multistaged scheme of calculations. The scheme goes like this. If we are to find a possible extreme concentration of the substance A and know that at the intermediate stages of its formation substances C and B participate successively (B at the stage after C) in the process, then we suppose the functional relationship

$$A^{\text{ext}} = f(B^{\text{ext}}(C^{\text{ext}})) \quad (\text{I.30})$$

to take place.

Proceeding from (I.30) to determine A^{ext} we first calculate C^{ext} . Finding the composition corresponding to the partial equilibrium with an extreme concentration of C is assumed as necessary to finding B^{ext} . And finally the composition with an extreme content of B is used to calculate A^{ext} . MEIS, as an example, can be used to perform all the calculations according to the above scheme.

Each stage of the computational experiment certainly supposes variation of external and internal system parameters that seem for a researcher to be most important in terms of attaining the sought extreme concentration. A rather full picture of relationships between the characteristics of the processes studied and the main influencing factors increase in the number of computations and in difficulties in the analysis of results associated with a larger number of stages. If the subject of the study is a natural process, the researcher determines conditions under which a phenomenon of interest may take place. However, if consideration is given to the chemical-technological process, the scientist then can determine the methods of its regulation that lead to a desired result.

I.19. Stability and Sensitivity

The problems of stability of system motion along admissible paths and sensitivity of solution (partial equilibria that belong to these paths) were not considered at length in either *Equilibrium Encircling* [58] or *Equilibrium Thermodynamics* [81]. At the same time the analysis of these problems is necessary if one is to estimate the realizability of the states that are considered using thermodynamic models.

Though *a priori* it is clear that accuracy of calculating the thermodynamically attainable points and estimating their feasibility depends on the quality of the initial information and real disturbances that are observed at some or another process, formalized statements of the problems are not obvious.

The statement of the sensitivity problem seems to be simpler than the stability problem. In mathematical programming “sensitivity” is taken to mean the extent of change in the objective function as a result of small changes in the parameters of constraints. In linear programming the indices of sensitivity are the changes in the dual estimations (Lagrange multipliers).

As applied to the problems discussed in this book an aggregate of the sensitivity indices used should obviously be essentially larger.

First of all, of interest are the changes in the composition of the studied equilibrium mixtures depending on the completeness (dimensionality) of the set lists of substances (the general list and the initial reagents). As is clear from the previous text, the dimensionality of the variable space determines the possibility of the equilibrium detour, and with increase in this dimensionality the sought extreme concentrations of the reaction mixture components may essentially rise. The problems of analyzing the errors related to the setting of the list of substances are considered in Chapters 2, 4 and 5.

Another important sensitivity index is the change in the calculated composition of the reaction mixture depending on an error in setting the standard values of thermodynamic functions (free enthalpy, entropy, etc.). Two circumstances should be borne in mind when one estimates the impact of the accuracy to which these values are determined on the results of calculations.

The first one consists in the fact that the moving force of chemical reactions is a standard chemical affinity

$$\Delta G^0 = \sum_j v_j G_j^0, \quad (\text{I.31})$$

which represents the difference between the total standard free enthalpies of initial substances and products. It is obvious that a relative error in determining this difference may theoretically turn out to be as large as is wished at the most insignificant deviations of the set values of G_j^0 from the true ones.

The second circumstance is related to the slight slope of the thermodynamic function surface near the equilibrium point, in which its differential equals zero. An insignificant error in determining the magnitude of the function used due to an error in the data on the standard value can lead to a sharp change in the vector x . Since the existence of different phases of one and the same substance is associated with the phases' equilibrium and the equality of chemical potentials, at the points of phase transitions along the corresponding coordinate axis, the relative change of G ($\Delta G_j/x_j$) is negligible and, hence, in this case x may also change sharply.

The problem of searching for the composition may turn out to be rather sensitive to the errors in standard values of the functions if P_j , V_j , and T are large. The high sensitivity is explained by the peculiarities of the logarithmic functions. Fig. I.1, based on the calculation of hydrogen combustion in pure oxygen, shows that with increase in temperature the entropy surface becomes close to the horizontal plane, which complicates essentially the search for an extremum point.

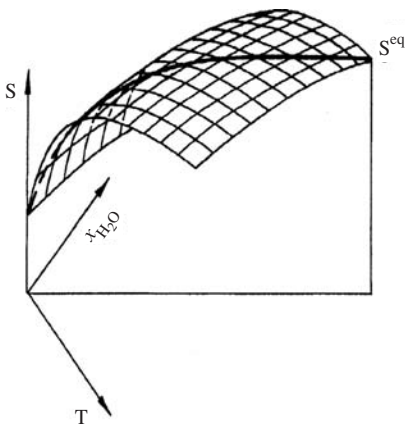


FIGURE I.1. Entropy maximization under conditions $H = \text{const}$, $P = \text{const}$ for the system $\text{H}_2 - \text{O}_2 - \text{H}_2\text{O}$

It is also very important to estimate the sensitivity of solutions to the choice of equations of state of the individual phases of a heterogeneous system and other analytical relationships (for example, for calculation of electrolyte activity coefficients).

Passing to the stability problem let us explain the related practical problem. Suppose we are interested in producing the maximum amount of some substance *A* by a given chemical process at set constraints on its purity. Naturally the question arises: Will the considered process be stable, or will the concentrations of *A* and its purity inadmissibly change due to random variations in the quality of the initial raw material and parameters of the process? Similar problems may emerge when one analyzes natural processes.

At formalization of such problems it is obviously desirable to consider stability by Lyapunov in accordance with the properties of the thermodynamic functions used and in particular to study the stability problems of the autonomous system equilibrium and stability of some of the variables. Here, problems arise of choosing the disturbances, “some of the variables” and many others. They are discussed in Section 4.5.

When analyzing sensitivity problems and stability of solutions to thermodynamic problems we certainly need to take into account the errors and stability of the applied computational algorithms and computations.

I.20. The Art of the Possible: Idealized Models of Real Systems

The above description of the problems that emerge when modeling the regions of attainability and partial equilibrium show quite clearly what the art of a researcher who deals with thermodynamic analysis of specific systems entails. This art should make it possible to explain the most important features of the studied object even with insufficient information using the models of “liberal” thermodynamics (which allow everything that does not contradict its two main laws).

Certainly it is in principle impossible using thermodynamics alone to explain everything that may be of interest to a researcher of one or another phenomenon. A good specialist should possess a set of specialized tools. A good theorist should have a set of different theoretical (mathematical) models. As applied to chemical systems the special models are irreplaceable when calculating the time of relaxation toward equilibrium; when considering the nonequilibrium character associated with distribution of microscopic variables that differ essentially from the equilibrium distribution; and in many other cases. However, it is desirable to extend at most the application of thermodynamic models that are the simplest to use in computational experiments.

In the art of their application, including the areas that seem to be beyond the thermodynamics we can distinguish two constituents:

- 1) the art of constructing a model that implies largely the art of simplification and idealization of real processes;
- 2) the art of carrying out computational experiments using the model constructed.

First, let us dwell on the art of constructing models and emphasize at once that fortunately the well-constructed models find much wider use than the physical assumptions that underlie these models. A small fall outside the limits determined by the initial assumptions is observed in all the cases of modeling reality, since the model is always a description of a real object with some errors, and it's the real object's study through the model is always a deviation from assumptions made by a researcher. However, the extent of violating the limits mainly depends on the model's designer.

Now, using the previous text let us try to set off individual components in the art of idealized description of real systems.

First of all, the choice of the modeled system type itself has the characteristics of nontriviality and necessary for a researcher's skill in accordance with whatever the classification assumed in the thermodynamics is: isolated, open, closed, homogeneous, heterogeneous, ideal, or real.

Normally the studied objects represent open systems. However, if the researcher combines such systems with their environment in a number of cases, it is possible to pass to the description of isolated systems. Neglect of the change in transit energy flow passing through a system often allows for a correct use of the closed system model. Examples of these techniques were mentioned above. Decrease in the number of phases when modeling a heterogeneous system can be illustrated in the example of studying atmospheric processes; in that discussion, formation of harmful substances on the surface of aerosols is described by their emergence in the homogeneous medium. *Equilibrium Thermodynamics* [81] presents examples of real systems descriptions by ideal models: a real gas by an ideal gas; real solutions by ideal solutions; the mixture of adsorbed substance on the surface of solid phase by ideal surface gas.

The next component of the art is the skill of choosing the fixed parameters, i.e., the conditions of interaction between the system and the environment. The nontriviality of this choice was already explained in Sections I.16 and I.17.

Use of equilibrium models for studies of principally nonequilibrium systems certainly calls for intuition. The experience gained in such an art is discussed in many sections of this book.

A most important condition of successful application of thermodynamic models is development of the skill in making up the lists of substances, which supposes in each specific case the skill to guess the hidden peculiarities of the studied object. Certainly, it is necessary to correct preliminarily compiled list if the calculations show that the assumptions were not completely accurate. Simultaneously, it is desirable to work at formalization of the analysis of a substance list's impact on the results of thermodynamic modeling.

Finally, a subject of the art that is hardly subject to general recommendations is consideration of nonthermodynamic factors: conditions of energy and mass exchange, kinetic constraints, and so on.

In concluding this section let us point out that, in any case, the art of modeling should be based on the already available knowledge of the specific subject of study and on the experience derived from its analysis.

I.21. The Art of the Possible: Methods for Calculation of Estimates

Successful computational experiments call, first of all, for a good model or, that which is even better, a set of models. However, this is certainly not enough. The following conditions should also be met:

- minimum required initial information should be prepared;
- efficient computational algorithms should be devised and computer-aided computational system on their basis should be created for laborious multivariant calculations;
- a detailed program of conducting experiments should be elaborated;
- the program should be strictly implemented;
- results of calculations should be analyzed and the analysis should be thorough and comprehensive enough to obtain profound conclusions.

Preparation of initial information includes nonformalized analysis of all accessible preliminary data on the studied object, concrete definition of the models used on their basis (composition of variables, objective function type, system of constraints) and some auxiliary calculations. The calculations, for example, can be necessary to determine the standard values of thermodynamic functions if they cannot be determined from the available data bases. It is clear that the preparatory work requires a researcher's experience and knowledge.

A number of complicated problems are associated with creation of computational algorithms. Though the models discussed in the book relate to the problems of convex programming, cases where the functions to be optimized deviate from strict convexity or linearity are possible, and this increases the requirements on the methods of calculations. Another computational complexity is determined by a very slight slope of optimized function surfaces near the final equilibrium and along the individual axes near the partial equilibria, including the points of phase transitions. The zones of the slight slope, as was mentioned above, can emerge due to peculiarities of logarithmic functions as well.

Finally the principal problem of convergence and stability of computational algorithms arises when thermodynamic models are used for studies of environmental characteristics of natural and chemical-technological processes; estimation of the content of harmful admixtures in materials of high purity; concentrations of highly valuable components in poor ores; and some other problems. Here we have to solve

the systems of algebraic and transcendental equations with a large scatter in the values of sought variables (up to 12–15 orders of magnitudes), i.e., to say figuratively, for example, weigh an elephant and an ant on the same scales. As an example of such “weighing” we can present the problem of estimating dioxin concentration in the air, a dangerous dose of which is usually lower than 10^{-10} kg/kg.

It is clear that even the most efficient algorithms can be successfully used only if a computer-aided computational system is created on their basis and this system provides a user-friendly interface at multivariant calculations and their analysis. For construction of the system it is desirable to apply at most the available packages of routine programs.

The key stage in a specific computational experiment with available models, algorithms realized on computers, and minimum required information is certainly the development of the experiment’s program.

First of all we have to clearly formulate the objectives of the study, determining what values should be determined to have an idea of potential favorable and unfavorable results of the studied process. After the objectives are set we can outline the list of calculations to be made and the areas of variation in the initial information. Each step of the experiment calls for the choice of model and algorithm to be used and determination of sensible accuracy of computations.

To reduce the number of variants to be calculated on computers and make easier the analysis of the obtained information it is important to skillfully combine the use of MP models with elementary analytical relationships. For example in [100] the study of the secondary pollutant formation in the air employed the formula

$$r_{jp} = a_j + b_j \Delta H_p^{0x}, \quad (\text{I.32})$$

where

$$r_{jp} = \frac{x_{jp}^{\text{ext}} - x_j^0}{x_j^0} \quad (\text{I.33})$$

is a response of the atmosphere to the emission of the p th primary pollutant; a_j and b_j are coefficients; ΔH_p^{0x} is the change of enthalpy in reaction of the p th pollutant oxidation; x_{jp}^{ext} and x_j^0 are extreme concentrations of the j th secondary pollutant in the atmosphere polluted with the p th primary pollutant and in the clean (background) atmosphere, respectively.

Formula (I.32) allows one to sharply reduce the volume of thermodynamic calculations when analyzing the secondary pollution of the atmosphere. Actually, in using MEIS it is only necessary to calculate the values of extreme concentrations of the secondary pollutants in the background atmosphere (x_j^0). The technique of deriving and using the relationships (I.32) and (I.33) is presented at length in Section 5.1.

A most subtle point in the analysis of thermodynamic modeling results is estimation of accuracy of the thermodynamic estimates themselves. Determining the accuracy, we should bear in mind that, while involving various constraints in the thermodynamic models, thermodynamics still determines only limiting indices of

the processes. Along with accuracy of the thermodynamics employed, we should estimate the accuracy of the initial information, algorithms, and computational process. These points are discussed in Chapter 5.

I.22. Models of Extreme Concentrations

MEIS was the primary tool of the studies described in *Equilibrium Thermodynamics*. For fixed P and T it has the form of the following problem:

Find

$$\max F(x, y) = \frac{\sum_{j \in J^{\text{ext}}} c_j x_j}{\sum_{j \in J^0} g_j y_j} \quad (\text{I.34})$$

subject to

$$\sum_{j=1}^l M_j y_j = 1, \quad (\text{I.35})$$

$$Ax = b(y), \quad (\text{I.36})$$

$$Ay = b(y), \quad (\text{I.37})$$

$$\alpha_k \sum_{j \in J_k} y_j \leq y_k \leq \beta_k \sum_{j \in J_k} y_j, k \in K, \quad (\text{I.38})$$

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

$$G(x) = \sum_j G_j(x) x_j, \quad (\text{I.40})$$

$$x_j \geq 0, y_j \geq 0, \quad (\text{I.41})$$

where $x = (x_1, \dots, x_n)^T$ is a vector of mole quantities of the reaction mixture components; $y = (y_1, \dots, y_l)^T$ is a vector of mole quantities of the initial reagents, $y \subset x$; J^{ext} is a set of indices of components whose mixture's extreme concentration is to be determined; c_j is a coefficient ranging the harmfulness (or any other property) of the j th component of the vector x , $c \geq 0$; J^0 is a set of initial component indices whose efficient use is of interest; g_j is a coefficient ranging the value of the j th initial reagent, $g_j \geq 0$; M is the mole mass; A is an $m \times n$ -dimensional matrix of contents of elements in the system components; α and β are coefficients; k is an index of inequality (or equality); K is a set of indices of initial reagents, on whose quantities the constraints are imposed; J_k is a set of indices of initial reagents considered in the k th constraint; $D_t(y)$ is the region (the set) of thermodynamic attainability from the initial state; G and G_j are the free enthalpy of the system and a mole of its j th component, respectively; and x^{eq} is the composition of reaction mixture in the point of global (final) equilibrium.

The form of the objective function (I.34) is chosen because we are often interested in: the efficient use of the variable y 's individual components rather than the initial mixture of reagents as a whole. For example, when one studies the

combustion processes it is more important to estimate the economic use capabilities of a deficient fuel than of the air. When the differences in the value of the initial components are not significant, the denominator of the expression in the right-hand side of (I.34) can be taken equal to unity, i.e., we can use a linear objective function.

Equation (I.35) is used to norm the numbers of the initial reagents relative to the unit of their mass. The matrix equations (I.36) and (I.37) express the condition of conservation of a mole quantity of elements for each varied value of y . Inequalities (equalities) (I.38) are used to determine the admissible relationships between the values of different components of the vector y .

Expression (I.39) determines the thermodynamic attainability region at a fixed value of y . The sign \leq within braces is taken to mean, in the thermodynamic sense (see Section I.13): $x_1 \geq x_2$ if it is possible to pass from x_1 to x_2 by the continuous trajectory, along which $G(x)$ is monotonically nonincreasing. It is obvious that in $D_t(y)$ the inequalities $G(x^{\text{eq}}) \leq G(x) \leq G(y)$ are met.

The choice of formulas for computations of individual terms under the symbol of summation on the right-hand side of equality (I.40) depends on the initial physical assumptions on the properties of the considered system, which are discussed in detail in Chapter 2.

The composition of variables of the model (I.34)–(I.41) is represented by two vectors x and $y \subset x$. This is rather important in terms of application, as it allows, based on the thermodynamic analysis, a strictly formalized solution to the problem on optimal composition of the initial reagents. The search for such a composition using the variant calculations may be laborious. Besides, strict optimization gives us a clearer idea on dependence of y^{ext} on the main influencing factors as compared to the variant calculations.

Depending on the peculiarities of the studied system and specific statement of the problem, the model (I.34)–(I.41) can easily be supplemented by different equality and inequality constraints that reflect the conditions of energy and mass transfer, interactions with the environment, and impacts on the reaction mechanism.

A rather detailed analysis of mathematical features of MEIS and the problems of updating these models as applied to different types of thermodynamic systems was presented in the book *Equilibrium Thermodynamics*. The main problem among those considered there consists in reducing MEIS to the problems of convex programming (CP). Its analysis implies consideration of three problems: 1) search for the final equilibrium (x^{eq}); 2) search for extreme concentrations (x^{ext}) at a fixed value of y ; 3) search for the extremum point ($y^{\text{ext}}, x^{\text{ext}}$) of the function (I.34), i.e., solution of a general problem (I.34)–(I.41).

The study of the first of the above problems in fact implies the analysis of thermodynamic function convexity. A strict convexity (linearity by the axes that correspond to the condensed phases) at some simplifying assumptions was proved for additive systems with linear and nonlinear balances. For nonadditive heterogeneous systems strict convexity was proved only for some areas of parameter change, though the areas themselves were rather extensive.

The second problem in the case of the thermodynamic function convexity consists in determination of the extremum of a linear form on the convex set of constraints. Its analysis revealed the conditions of (1) location of the point x^{ext} on the boundary of the thermodynamic attainability region; (2) its coincidence with the vertex that corresponds to the solution of the linear programming problem that is obtained by excluding thermodynamic constraints (I.39) from the model; and (3) degeneration of solutions.

As applied to the third problem it was shown, based on qualitative speculations without strict formalization that at a search for maximum concentrations of the set of substances the objective function will much more likely be concave and the problem reduce to CP. At the objective function minimization we obtain a multi-extreme problem of concave programming.

The above differentiation of mathematical models was carried out in accordance with the probable composition of real systems to be modeled. The systems may contain: ideal gas phase; real gases; plasma consisting of neutral active particles (radicals), ions, and electron gas; pure condensed substances; ideal solutions of neutral substances and solutions of electrolytes; surface gas (two-dimensional gas of adsorbed substances on the surface of adsorbent); substances in colloidal (dispersed) state, with the surfaces of their particles subject to the surface tension forces, and other components.

The brief MEIS analysis presented in *Equilibrium Thermodynamics* shows clearly that many problems still remain unsolved. Further specification of mathematical peculiarities and possibilities of reducing the models of extreme intermediate states to CP problems is important in terms of both improvement of the algorithms applied to calculations and easier interpretation of the computational experiment results.

The next group of problems is associated with extension of MEIS application, in particular, with its applicability to systems with spatially nonhomogeneous structure (see Sections I.23, I.25), concentrated solutions of electrolytes, electrochemical systems with the sources of electromotive forces, and so on.

Chapter 2 of the book is entirely dedicated to the problems of further MEIS development and application.

I.23. Thermodynamics of Combustion

The processes of fuel combustion and atmosphere pollution were presented many times as examples illustrating the problems that arise when modeling complicated chemical systems of large dimensionality. Now we can try to systematize the problems associated with the thermodynamic analysis of these processes. These problems are interesting in terms of both theory and application.

Combustion thermodynamics and kinetics have been studied for more than 100 years. First of all we should refer to a very short but excellent (in terms of profundity) thermodynamic analysis of hydrogen combustion in oxygen, which was presented in the book *On Equilibrium of Heterogeneous Substances*, by Gibbs

[54]. Lacking both information on thermodynamic properties of substances and a computational tool, Gibbs managed to give a rather complete and qualitative picture of the process. Discussing potential solutions of the derived systems of equations he explained both the decrease in the reaction temperature due to water dissociation and the presence of limited regions of explosion and burning.

Classical works on combustion kinetics were performed by N.N. Semenov [151, 152], Ya.B. Zeldovich [174, 175, 176], and others. The book *Fluid Mechanics*, by L.D. Landau and E.M. Lifschitz [123] showed the possibilities of using thermodynamics in hydrodynamic analysis of the combustion process, in particular, for calculation of amplitudes of detonation waves. In the last years intensive studies have been performed on the processes of harmful substance formation during fuel combustion in furnaces and combustion chambers of energy plants and vehicles [137, 165, 30, 169]. The main problem concerns determination of concentrations in the combustion products of nitrogen oxides, sulfur oxides, carbon monoxide, and some other pollutants, using full-scale experiments and kinetic modeling.

The subject of the studies described in *Equilibrium Thermodynamics* [81] was thermodynamic analysis of environmental characteristics of the combustion processes. The objectives of the thermodynamic analysis were: to reveal the efficiency of the thermodynamics application in the study of real objects; to gain experience in the joint application of thermodynamic and kinetic models and full-scale experiments; and to obtain useful application results. The processes of nitrogen and sulfur oxide formation in the stationary processes of the Kansk–Achinsk coal combustion in torch furnaces were considered in detail. The results of the calculations were compared to the known published data and to the characteristics of real boiler units.

The analysis showed that MEIS application made it possible: to understand deeper the physics of the combustion process and suppression of NO_x formation reactions by adjusting combustion modes; to estimate the potentialities of environmental updating of furnaces; and to obtain additional information for choosing concrete methods of decreasing the formation of harmful ingredients in the furnaces.

Increase in dimensionality of the problems to be solved (a list of considered components of the reaction mixture) when using MEIS as compared to kinetic modeling enabled one to find out the interrelations between the decrease in concentrations of some pollutants and increase in the yields of the others (for example decrease of the NO_x fraction in the reaction mixtures and increase in the CO fraction). Along with that the increase in dimensionality of the model allowed one certainly to obtain a more complete idea on the range of the harmful products of fuel combustion, which makes it easier to substantiate the choice of methods for regulation of the processes in furnaces.

At the same time the environmental analysis of combustion processes that was presented in *Equilibrium Thermodynamics* revealed the problems and trends of further development of thermodynamic methods in the studies on the impact of fuel combustion technologies on nature.

First let us emphasize the inexhaustibility of the problems associated with modification of models to simulate the processes in the furnaces of boiler units at modern thermal power plants. These furnaces represent the largest chemical reactors. Several hundred tons of fuel per hour can be burnt in them, their sizes reach 300–400 m² in cross-section and 60–80 m in height. Here, both along the motion of gas or pulverized (in coal burners) mixture (usually vertically) and in the plane perpendicular to the motion, we observe drastic changes in the temperature, reaction mixture composition, and conditions of mass and energy transfer. Difference in the temperature in the vertical direction is usually about 1000 degrees and differences in the horizontal sections are lower by approximately an order of magnitude. Thus, it is clear that powerful furnaces are spatially inhomogeneous structures. The choice of models of such furnaces depends on both the specific features of the combustion process to be modeled and the character of the problem to be solved.

Specific problems arise when we study the coal-burning reaction in the small fixed-bed furnaces of industrial and municipal boilers and stoves. There we observe periodic processes (fuel supply, normal combustion, rabbling, cleaning), for which change leads to sharp alterations in: the solid and gas phases, temperature in the furnace, and conditions of harmful substances formation. Estimation of environmental characteristics of small furnaces represents an important practical problem, since the contribution of these furnaces to environmental pollution is quite considerable.

The problems of the same complexity as those we have at description of periodic combustion in the stationary plants arise certainly when using the equilibrium models to model non-stationary processes in the engines of vehicles. The description of forest fires in terms of thermodynamics is also interesting.

Modeling of combustion in the above types of the processes calls for modification of traditional MEIS, construction of principally new models of spatially inhomogeneous structures and improvement of computational algorithms. Spatial models are shortly discussed in Section I.25 and at length—in Chapters 2 and 3. Section 5.2 is entirely dedicated to the modeling of the combustion processes.

Section 5.3 addresses similar problems of fuel processing.

I.24. Thermodynamics of the Atmosphere

The difficulties of atmospheric thermodynamics are associated with the problem formulation itself, the construction of mathematical models, and with the development of computational algorithms.

The publications that contain thermodynamic interpretations of atmospheric processes date back at least to the early 20th century. The literature then was mainly devoted to explanations of changes in the air parameters, emergence of air flows, formation of clouds and fogs, and some other phenomena. In the context of our discussion, the works by Einstein on interaction of matter and radiation [39] are of interest, as is the article on the theory of opalescence [43], in which

the analysis of partial equilibria (by Einstein's terminology, "incompletely determined in phenomenological sense") is used to explain the blue color of the sky. A clear thermodynamic analysis of atmospheric hydrodynamics is presented in the classical textbook by Landau and Lifschitz [123].

However, up to now the thermodynamics has not been practically used for the analysis of chemical transformations in the atmosphere and atmospheric pollution by anthropogenic emissions. It is widely believed that due to low temperature and hence extremely low rate of reactions the latter do not reach equilibrium and thermodynamic models turn out to be inapplicable in principle in atmospheric chemistry. Therefore, it is studied now mainly by the methods of kinetics and full-scale experiments [12, 31, 36, 74, 128].

Equilibrium Thermodynamics [81] presents the problem of estimating the impact of anthropogenic emissions on air quality. The problem was formulated on the basis of modeling the partial equilibria. Here we also have examples of determining maximum possible water vapor concentration in the atmosphere, limits of carbon dioxide accumulation which account for its solution in the ocean, and forecasting the composition and concentrations of harmful substances, including secondary pollutants for given emissions.

The thermodynamic analysis of the air pollution got its further development in [84, 91, 100, 101]. These works reveal to some extent the advantages of thermodynamic models as compared to kinetic ones. Thus, the thermodynamics allows one in the course of a single computational process to simultaneously find the concentrations of numerous pollutants (substances containing nitrogen, sulfur, chlorine, fluorine, etc.) yet the reactions of their formation turn out often very little studied.

Traditional MEIS, constructed as applied to closed systems with fixed P and T , underwent some definite tests as well as MEIS's spatial modifications that represent the description of chemical component distribution over the edges of a graph, i.e., over the hydraulic circuit [91]. Application of the latter type of the model is associated with a new statement of the problem, i.e., a search not only for the composition of harmful substances, but for their distribution in space (one-, two-, and three-dimensional).

The results of the studies, where possible, were compared to the available published data. Quantitative comparisons were made only for the water vapor content, as there is a great amount of experimental material on this phenomenon. High accuracy has been mentioned before. At the same time, for the present we have to be satisfied with the qualitative estimates of likelihood concerning the picture of other microcomponents' formation. Thus, thermodynamics modeling "confirmed" existence of such known phenomena as acid rain, formation of peroxy acetyl nitrate (PAN), phosgene, and other pollutants experimentally detectable in the atmosphere. The calculated concentrations of nitrogen dioxide appeared to be several orders of magnitude higher than those of monoxide, a result that is also in agreement with the experimental data.

Thermodynamic modeling also revealed the fact that the concentrations of most of the secondary pollutants at the point x^{eq} are practically equal to zero and reach noticeable values only at the partial equilibria points. Certainly, it is impossible

to determine by MEIS to what extent the stationary concentrations of individual substances corresponding to these equilibria are close to their plausible extreme concentrations. Therefore, thermodynamic analysis may succeed only in establishing the probability of dangerous concentrations of a number of pollutants in the atmosphere, which itself is certainly not a matter of small importance.

The comparatively small experience gained in the thermodynamic modeling of human impact on the atmosphere revealed the difficulties related to this modeling and outlined the objectives of further research.

A most interesting problem is the one of describing the processes that occur on a moist aerosol surface, which changes its sizes with time. Here, the need appears for a model of the phenomena of solution, sorption, and surface tension. The aerosol is considered an element of the unified thermodynamic system, i.e., a fixed amount of air.

Principal problems also have to be solved when we analyze photochemical processes that belong to the area of high energy chemistry. Besides, with sufficiently high levels of description strictness they belong to relativistic thermodynamics. Description of the processes in terms of equilibria is related to the nontrivial substantiation of admissibility of the accepted physical assumptions.

The thermodynamic modeling of accumulation of carbon dioxide and other greenhouse gases in the atmosphere deserves extension and development. Here, we first of all need to specify the description of the air's interaction with aqueous surfaces and dry land.

Modeling of the processes of spatial distribution of harmful substances is so far at the initial stage of development. Here we have to determine a set of practical problems that arise, as well as what types of mathematical models we need to apply.

Touching upon the problem of improving the computational algorithms, we should remind ourselves that it is precisely in the study of the atmospheric pollution that the problem of a huge scatter of values of variables is rather topical.

The thermodynamic modeling of atmospheric processes is considered in Section 5.1.

I.25. Thermodynamic Modeling on Graphs

The idea of thermodynamic analysis of kinetics of chemical reactions on graphs unfolds in the *Equilibrium Encircling* [58] which has already been discussed in Section I.13. Based on a graph, i.e., "the thermodynamic tree," a qualitative description of possible changes in the composition of a chemical system and admissible paths from arbitrary initial states is given in [58].

At the same time the idea of graphs as applied to the problems discussed in this book can find other implementations as well. Along with the tree, the closed (cyclic) schemes are also of interest. In any case, transition from a multidimensional to the one-dimensional space provides a number of advantages. The reduction of the sought functions to the functions of no more than two variables allows one

to substantiate strictly the admissibility of applying differential equations (the Pfaffian forms of one or two variables are always holonomic) and equilibrium thermodynamic methods. It is precisely the property of holonomy of infinitesimal increments of functions (the Pfaffian forms) that was used by K. Caratheodory [27] and then by M. Born [23] to give macroscopic substantiation of thermodynamics. In *Fluid Mechanics*, by Landau and Lifschitz [123] there are a number of examples on exclusion of the time variable from the description of one-dimensional flows and solutions of typical dynamics problems by thermodynamic methods (such as determination of amplitudes of different macroscopic quantities in the wave processes).

Addressing MP, one may assume that application of graphs essentially increases it's the method's potential. Thus, the choice of MP methods can be interpreted as the choice of a rule to be used at each step of the computational process to determine the motion trajectory on the surface of the maximized (minimized) function in the domain of its definition. When transforming this multidimensional domain to a graph the choice of a rule becomes at least, in some cases, more visible.

Efficiency of the multidimensional space transformation into a graph was revealed yet by Kirchhoff. Having obtained the formulas of current distribution in a round plate [111], he experimentally tested his theoretical conclusions on the electric circuit, i.e., on the scheme that has a graph form, for which he derived his laws of current distribution. Such a test supposed agreement between the values of variables that characterize electric fields at the points of a multidimensional region and on the graph. Having established for passive circuits the equivalence of the system of equations that describe the network conservation laws and the problem of search for the minimum heat production, Kirchhoff in fact showed the possibility of solving the extreme problems on graphs [108]. For complex circuits, he suggested that the spanning tree be determined on these circuit's graphs [112], which could be used to determine the system of independent loops.

Maxwell solved the problem of current distribution on graphs by the *method of potentials* [129] and showed the equivalence of the latter to Kirchhoff's method. It is interesting that Maxwell's development of the method of potentials for loops almost coincided in time with Gibbs's introduction of the method of potentials into thermodynamics as applied to multidimensional spaces.

The problems of modeling thermodynamic systems on cyclic graphs were posed in [79] and considered in detail in *Equilibrium Thermodynamics* and later in [85]. These works suggest three types of models:

- extreme thermodynamic models of flow (current) distribution in hydraulic and electric circuits;
- graphical extreme models of chemical processes that are intended for determination of final equilibria and based on the representation of a process in the form of an oriented graph whose arcs correspond to the flows of substances entering into some reaction or another, and the nodes are the points where the flows merge and separate;

- spatial MEIS modifications that are based on the representation of multidimensional, inhomogeneous spatial systems in graph form.

The models of hydraulic circuits were extended to circuits with multiphase chemically reacting flows. The topicality of researching such circuits is determined by the need to solve many applied problems. For example:

- hydraulic calculations of chemical reactors;
- calculation of operation modes for extended steam pipelines under conditions of potential formation of condensate;
- determination of conditions of sedimentation of heavy hydrocarbons in oil and gas pipelines;
- calculations of communications of energy plants with energy carriers of complex composition.

Graphical models of chemical reactions were tested by the analysis of some small-dimensional systems, for example synthesis of methanol from the mixture of carbon monoxide and hydrogen. It was revealed that these models could be applied to study the impact of the reaction mechanism on the composition of final products.

Based on the spatial MEIS, two problems were solved in [91]: distribution of harmful substances in the vertical air column of the isothermic atmosphere; and determination of relationships between the pollution of outdoor air and indoor air.

A preliminary analysis of the mathematical peculiarities of the suggested models was carried out: The criteria of extremeness were determined; the possibilities of reducing the problems solved to the convex programming problems were revealed; and the need was shown to describe the relationships between the head losses and flow rates in the flows with chemical transformations and phase transitions by algebraic equations of no lower than the third power.

The studies to be planned for the future in thermodynamic modeling on graphs are: determination of new areas of efficient application of graphical models; modification of the models according to the chosen purpose; analysis of their peculiarities and development of necessary computational algorithms; and solution of the applied problems.

It is interesting to apply the models of heterogeneous hydraulic circuits to the studies of ventilation and air conditioning systems on residential, public, and industrial premises. This problem is rather topical in terms of its application. We now know that the traditional method of reducing the concentration of harmful substances in buildings, a method that consisted of increasing the exchange ratio, may lead to a reverse effect due to the heavy pollution of “cleaning” air. To choose the optimal methods of air conditioning it is necessary to combine the hydraulic calculations of ventilation with the analysis of change in chemical composition of the atmosphere.

Development of graphical models of chemical reactions implies the elaboration of methods for determining partial equilibria with extreme concentrations of the given substances, i.e., the construction of models competing with MEIS, and the

application of these models to determine reaction mechanisms—optimal in terms of yield of some substances.

The problems of constructing models for analysis of substance distribution in two- and three-dimensional atmospheres, as well as for the analysis of combustion processes in spatially inhomogeneous systems, seem of top priority in the studies of spatial MEIS modification.

The study of computational algorithms based on the idea of the thermodynamic tree is certainly extremely interesting, as we mention in Section I.13.

The problems of graph-based modeling are discussed at length in Chapter 3 and Section 4.4.