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Thermodynamic Equilibria and Extrema

Analysis of Attainability Regions and Partial Equilibria

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In memory of a remarkable personality,
physicist-chemist, and historian of science,
Lev Solomonovich Polak

Preface

The authors are very glad to see the publication of *Thermodynamic Equilibria and Extrema* in English and would like to express their gratitude to everybody who contributed to this end.

The book is devoted to the analysis of attainability regions and partial equilibria in physicochemical and other systems. This analysis employs the extreme models of classical equilibrium thermodynamics. Consideration is given to the problem of choosing, from the set of equilibrium states belonging to the attainability regions, that equilibrium corresponding to the extreme values of a property of interest to a researcher. For example, one might desire to maximize the concentration of target products of a chemical reaction. The problem of coordinating thermodynamics and kinetics is very important in the analysis presented.

At a glance, it may seem that the objects of study in thermodynamics (the science of equilibria) and kinetics (the science of motion toward equilibrium) coincide only in the case of complete and final equilibrium. In reality, joint application of thermodynamics and kinetic models gives a clearer understanding of the regularities of the kinetics involved.

Relativity of the notions of rest and motion was already firmly established in mechanics when the principles of equilibrium were formulated by Galilei, D'Alembert, and Lagrange. Historically, the theories of motion and equilibrium states are related. It is precisely the study of gas kinetics that led Clausius and Boltzmann to the main principles of thermodynamics. The systematic analysis of these principles in the classic book by Gibbs, *On the Equilibrium of Heterogeneous Substances* [54], demonstrated the feasibility of substituting the models of rest for the models of motion when studying various physicochemical processes. The classics of thermodynamics, Gibbs [54], Planck [139], Einstein [43], and Sommerfeld [158], showed that, in passing from descriptions of processes to descriptions of equilibrium states, it is possible to use the notion of partial equilibrium (they used different terminology) as well as complete equilibrium. L.D. Landau and E.M. Lifshitz in [125] emphasized the importance of studying partial (incomplete) equilibria in chemical systems where reactions often do not reach the end.

The regions of thermodynamic attainability and possible effects on the path of physicochemical systems toward final equilibrium were thoroughly analyzed in the

1980s by V.I. Bykov, A.N. Gorban, and G.S. Yablonsky [58, 59, 60]. The essence of the problem was most clearly revealed in the book by A.N. Gorban, *Equilibrium Encircling (Equations of Chemical Kinetics and Their Thermodynamic Analysis)* [58]. This volume used models of closed system equilibria to describe all of the following: macroscopic kinetics and thermodynamics; thermodynamic analysis of chemical and biological system relaxation toward equilibrium; and nonstationary and nonequilibrium processes, including those in open systems.

The problems arising in kinetics are interpreted on the basis of Lyapunov functions, Markov random processes, topology, and graph theory. A geometrical technique was developed to pass from the search for the Lyapunov function extremum on the material balance polyhedron to the search for extremum on the graph—a thermodynamic tree.

Using the principles formulated in [58], B.M. Kaganovich, S.P. Filippov, and E.G. Antsiferov [82, 83] constructed and studied thermodynamic models and computational algorithms that would find, for a given function, points where extreme values will occur in the attainability region. The most detailed discussion of these models is given in the book *Equilibrium Thermodynamics and Mathematical Programming* [181]. Unlike *Equilibrium Encircling*, in [81] consideration was given not to the equations of motion but to possible states; that is, the conventional thermodynamic approach was applied. This approach was extended to the analysis of a number of processes in the fields of themal energy, chemical technology, and nature.

The current volume expounds the basic principles of both *Equilibrium Encircling* and *Equilibrium Thermodynamics*, and synthesizes the ideas of these books. Twenty years worth of work on the thermodynamic analysis of kinetics of macroscopic systems is summarized in this book, and areas for further study are outlined.

There are twice as many authors for this English edition as there were in the Russian edition. The authors of the Russian edition were A.N. Gorban, B.M. Kaganovich, and S.P. Filippov. The findings of the “new” authors were heavily used in the Russian text of the present book. These authors contributed enormously to the preparation of the English edition. In particular, they helped to eliminate many inaccuracies in the original text.

The authors owe much to many discussions they held with a remarkable physicist, chemist, and historian of natural science, L.S. Polak. The successful performance of many of the studies in this book is due to these conversations. Professor Polak immediately understood and approved the basic mathematical *model of extreme intermediate states* (*MEIS*) applied by the authors, including versions of this method intended for analysis of hydraulic and chemical circuits. The remarks of L.S. Polak on the authors’ interpretation of the history of the development equilibrium principles were extremely valuable.

The main MEIS versions were also discussed with L.I. Rosonoer, who assisted the authors in constructing the model of systems with variable extents of reaction completeness.

E.G. Antsiferov created the first algorithms for calculation of partial equilibria that correspond to extreme concentrations of given substances [7]. Further development of these algorithms was based on his idea of a two-stage search for the extreme state of a thermodynamic system: stage one being initial calculation of the optimal level of thermodynamic function, and stage two the further search for location of the extreme point on the surface of this level. E.G. Antsiferov contributed greatly to the analysis of mathematical features of the problems considered in this book and, in particular, to the study of the convexity of thermodynamic functions.

A.P. Merenkov and S.V. Sumarokov helped greatly in the first work on thermodynamic analysis of multi-loop hydraulic systems, substantiation of the extremality criteria in hydraulic circuit theory, and creation of heterogeneous circuits theory.

The authors believe it is their duty to pay tribute to the memory of V.Ya. Khasilev, the founder of hydraulic circuit theory, whose ideas were interpreted in terms of thermodynamics.

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Contents

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 microdiscription 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 brunches 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 *plasmochemical 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 jth component of the ideal gas is determined by the formula

$$\mu_j = \mu_j^0 + RT \ln \frac{Px_j}{\sigma}, \tag{I.1}$$

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 jth 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

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

where P is pressure; V is mole volume; and a and b are constants accounting for moleculare 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.,

$$G = \sum_j \left(G_j^0 + RT \ln P_j\right) x_j + \sigma \int_{P^0}^{P} VdP, \tag{I.3}$$

where σ is the total quantity of moles in the mixture; the superscript 0 refers to the standard state of the jth 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]:

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

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

$$b = \sum_j b_j \frac{x_j}{\sigma}, \tag{I.6}$$

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 jth dissolved substance was represented in this case in the form

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

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 jth component are *not* derivatives of the corresponding system's functions with respect to x_j, i.e.,

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

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

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

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

The derivative of L is

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

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

$$w_u = k\,(T - T_h)\,. \tag{I.11}$$

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

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

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

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

where c_j is the concentration of the jth 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:

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

$$H = G - T \left(\frac{\partial G}{\partial T} \right)_P. \tag{I.15}$$

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

$$\prod_j P_j^{\nu_j} = K_p, \tag{I.16}$$

where v 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_i; $S(\lambda M) = \lambda S(M)$ 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

  $$S(M) = \sum_j S_j\left(M_j\right), \tag{I.17}$$

  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) $\sum_j a_{ij}^0 \varphi_{\mathrm{j}}(\tau) = 0$ (i.e., $a^0\varphi(\tau) = 0$) for all $\tau \in [0, 1]$;
(b) $\sum_j a_{ij} \varphi_{\mathrm{j}}(\tau) = \text{const}$ (i.e., $a\varphi(\tau_1) = a\varphi(\tau_2)$) for all $\tau_1, \tau_2 \in [0, 1]$;
(c) $\sum_j l_{ij} \varphi_{\mathrm{j}}(\tau) \geq 0$ (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:

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

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

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

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

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

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

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

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 $D \backslash U$ (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 $D \backslash U$ that connects x_0 and x. Any two points lying in one arcwise connected component $D \backslash U$ can be connected by continuous paths located in $D \backslash U$.

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,

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

where β and α are stoichiometric coefficients on the right-hand and left-hand sides of the stoichiometric equation of the sth stage (reaction), respectively; and w_s is a rate of the sth stage. Here the function form $w = f\left(x, T\right)$ 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

$$\sum_j \alpha_j A_j = \sum_j \beta_j A_j, \tag{I.24}$$

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

$$x_{O_2} \geq x_{O_2}^b, \tag{I.25}$$

where $x_{O_2}^b$ 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

$$H \leq H^b, \tag{I.26}$$

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

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

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 multiphase, multicomponent systems of large dimensionality, we cannot use the Gibbs rule of phases directly,

$$f = n - k - r + 2. \tag{I.28}$$

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

$$f = n - k - r + 3, \tag{I.29}$$

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

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

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

$$\Delta G^0 = \sum_j \nu_j G_j^0, \tag{I.31}$$

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 $\left(\Delta G_j/x_j\right)$ 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.

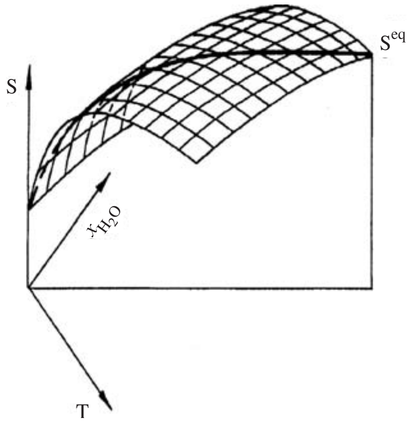

FIGURE I.1. Entropy maximization under conditions H = const, P = const for the system $H_2 - O_2 - H_2O$

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

$$r_{jp} = a_j + b_j \Delta H_p^{0x}, \tag{I.32}$$

where

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

is a response of the atmosphere to the emission of the pth primary pollutant; a_j and b_j are coefficients; ΔH_p^{0x} is the change of enthalpy in reaction of the pth pollutant oxidation; x_{jp}^{ext} and x_j^0 are extreme concentrations of the jth secondary pollutant in the atmosphere polluted with the pth 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

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

subject to

$$\sum_{j=1}^{l} M_j y_j = 1, \tag{I.35}$$

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

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

$$\alpha_k \sum_{j \in J_k} y_j \leq y_k \leq \beta_k \sum_{j \in J_k} y_j, k \in K, \tag{I.38}$$

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

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

$$x_j \geq 0, \ y_j \geq 0, \tag{I.41}$$

where $x = \left(x_1, \ldots, x_n\right)^T$ is a vector of mole quantities of the reaction mixture components; $y = \left(y_1, \ldots, y_l\right)^T$ 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 jth 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 jth 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 kth 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 jth 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^{ext}, x^{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. Liftschitz [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 m^2 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 Liftschitz [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 Liftschitz [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 Kichhoff'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.

1

Principles of Equilibrium and Extremality in Mechanics and Thermodynamics

> A bearded sage once said that “there’s no motion.”
> His colleague strode before him. Stricken mute,
> He could no stronger argue or refute;
> All praised the cunning answer with devotion.
> Odd episode! But, men, I recollect
> An old example from my mental journal
> The sun before us strides in steps diurnal
> Yet stubborn Galileo stands correct!
>
> *A.S. Pushkin*

1.1. Principles of Equilibrium and Extremality in Mechanics

Thermodynamics theory, like physics in general, developed from mechanics, and though the appearance of thermodynamics is associated with the analytical theory of heat [51] and the kinetic theory of gases [21], its roots penetrate deep into mechanics. Therefore, prior to an analysis of the thermodynamic principles, it is useful to discuss the basic principles of mechanics.

At the end of the 1960s the the beginning of the 1970s Heisenberg included mechanics and thermodynamics along with statistical physics in the four closed theories (models) of the modern physics. The two remaining are special theories of relativity and quantum mechanics. By “closed” Heisenberg meant the possibility of an exhaustive and noncontradictory explanation for all the phenomena that relate to the subject of a relevant theory.

The main principles of mechanics and thermodynamics that allow a description of the whole set of their applications can be called the *principles of equilibrium and extremality*.

Not dwelling on Archimedes formulation of the equilibrium laws as applied to individual mechanisms and a body (his own, in this case) submerged in liquid, the story of the development of equilibrium principles should begin with Galileo Galilei, who employed the notion of uniform motion for formulation of his inertia law. This motion can be seen as a continuous sequence of states in each of which the forces that act on the system are in equilibrium. It also becomes clear from the inertia law that the description (a model) of a uniform motion can be replaced by the description (a model) of a state of rest, i.e., an equilibrium state. D'Alembert introduced inertial force to describe the equilibrium state, which made it possible to consider the nonuniform mechanical motions as those passing only through such states.

It is natural to interpret the second and third laws of Newton in equilibrium terms. The second law determines equilibrium between the driving force and inertia force of the system at issue and the third law—equilibrium between the action and counteraction.

However, a strictly formalized presentation of mechanics as a science on equilibria and extrema was given by Lagrange in his famous "Mechanique analytique" [118]. He chose the equation of mechanical system equilibrium

$$\sum_j c_j(x)dx_j + \sum_i \lambda_i(\varphi)d\varphi_i = 0, \tag{1.1}$$

which was based on the principles of Galilei and d'Alembert, as the starting point for reconstructing all Newtonian mechanics.

The variables c, x, λ and φ are, respectively, a driving force, a coordinate, an unidentified multiplier (a bond resistance force) and bond deformation, and i and j are indices of driving forces and bonds.

Equation (1.1) is interesting for our analysis in many respects, and we will refer to it many times in this book. First of all, it is used to reveal the interrelations among the principles of *conservation*, *equilibrium*, and *extremality*.

To reveal conservation of some quantity, let us note that each sum in the left-hand side of (1.1) has the dimensionality of energy (or work). Hence, at an infinitesimal deviation of a system from its equilibrium state, the work expended on its travel is equal to zero and the energy remains unchanged. The interpretation of the (1.1) represents the *principle of virtual work* (PVW).

Analyzing his equation, Lagrange revealed the connection between the equilibrium and extremality principles from the fact that, if a left-hand side of (1.1) represents a total differential of some function, the solution to the equilibrium search problem coincides with the solution to the problem of finding the extremum of this function. The extreme problem has the following form:

Find

$$\operatorname{extr}\left(L = \sum_j c_j(x)x_j + \sum_i \lambda_i(\varphi)\varphi_i\right), \tag{1.2}$$

where L is the function that was subsequently called a Lagrange function.

The assumption that an infinitesimal change in the function is a total differential in terms of physics means the mutually unique correspondence between the system's state determined by the values x_j and φ_i, and the value of function and, hence, the potentiality of its field and equality,

$$\oint dL = 0. \tag{1.3}$$

To facilitate further physical interpretation of the Lagrange equation, we transform it to the form

$$dT - d\Pi = 0, \tag{1.4}$$

where T and Π are kinetic and potential energy of the system, respectively.

The possibility of such a transformation is obvious: The work of the driving forces c_j is done through kinetic energy, and bond deformations affect the potential energy of the system. Naturally, the differentials of these energies have different signs as a decrease in one corresponds to an increase in the other. The systems for which equations (1.3) and (1.4) are met and the energy conservation laws are reduced to the constancy of the sum $T + \Pi$ are called *conservative* systems, because no energy is dissipated in them.

In writing equation (1.1) Lagrange divided the forces applied to the mechanical system into two groups: 1) those bringing the system to a motion (c_j), and 2) those resisting to this motion (λ_i). The idea appeared to be excellent from a mathematical viewpoint, as it allowed one both to formulate the problems of search for the extremes of type (1.2) and to pose the problems of a conditional extremum. In the latter case, the total work of driving forces is an objective function and the expressions for the work of the bond deformation make up a system of constraints. Thus, Lagrange's formulation of the equilibrium problem underlay the description of modern problems of mathematical programming (MP) [19, 94, 142], which can be defined as a mathematical theory of extrema.

Note that it seems natural to use MP in thermodynamic studies as thermodynamics is a science about extrema and equilibria.

Formulation of the equilibrium problems in MP terms facilitates their physical-mathematical interpretations. So, it becomes clear that the solution to an equilibrium problem corresponds to the saddle point of function L. Since the driving forces c_j try to move the system as far as possible from the initial state, and the resistance forces λ_i try to decrease the bond deformations, the equilibrium between c_j and λ_i corresponds to maximum work of the former and minimum work of the latter. Hence follows the possibility of dividing MP problems into ones of direct (maximization) and dual (minimization) problems, and the term "dual estimates" used by mathematicians as applied to λ_i become clear.

Based on the works by Maupertuis and Euler, Lagrange integrated (1.2) with respect to time and formulated mathematically a basic extreme principle of physics—a *principle of least action* (PLA):

$$\delta J = \delta \int_{\tau_1}^{\tau_2} L d\tau = \delta \int_{\tau_1}^{\tau_2} (T - \Pi) d\tau = 0, \tag{1.5}$$

where δ is a function variation, J is an action, and τ is time.

Those who developed variation (extreme) principles of mechanics [124, 141] introduced the key (in terms of thermodynamics) notions of reversible equilibrium processes into the science, though they did so without providing appropriate terms. Euler showed that PLA was met only for motion without friction, which, as is now known, causes irreversibility. Planck was the next to call the PLA a universal principle of equilibrium processes [139].

The most important property of the equilibrium systems was discovered by Jacob Bernoulli, who showed that if any curve had the property of having either a maximum or a minimum, then any infinitesimal part of the curve had this property. This principle can be considered a prototype for formulations of extreme principles in the theory of optimal control (by Pontryagin, Bellman, etc.). It follows from the principle that any state can be fixed in an equilibrium process. A prehistory of its attainment does not matter. Further optimal behavior of the system is determined only by this state. In the modern textbooks of macroscopic thermodynamics [20, 115, 117], equilibrium processes are usually defined as infinitely slow and quasistatic. However, a property they possess (revealed in mechanics)—that of possibily setting off any intermediate state from a continuous curve of the process—is of principal importance for the modern analysis of thermodynamic models.

The Lagrange derivation of equation (1.5), optimal motion trajectory of a mechanical system (PLA), from equation (1.1), optimal equilibrium state (PVW), and further study of the properties of these trajectories in mechanics, extended the understanding of interrelations between the models of rest and motion (first revealed by Galilei), and principal capabilities of thermodynamic modeling based on elimintation of the time variable.

The use of a Lagrange function taking an extreme value for systems in equilibrium states in the equations of motion in the form of difference between kinetic and potential energy ($T - \Pi$) allowed Helmholtz to define it as a "kinetic potential" or as a "free energy of the system". The latter definition is of an explicitly thermodynamic character. Its essence is in the fact that for useful (efficient) movement, a system need not use all the kinetic energy, but only the part that remains free from the work of bond deformation.

Mathematically the PLA development and application is associated with the creation of the calculus of variations (CV), which is the study of the extreme trajectories of system motion. The ideology of CV can also be useful for mathematical analysis of thermodynamic problems.

1.2. Principles of Equilibrium and Extremality in Thermodynamics

Thermodynamics, unlike mechanics, entails the study of systems undergoing transformations of substances and energy, as well as dissipation of the latter. It considers functions (heat q and work l) whose changes, as the system passes from one state to another, depend on the path of the transition, and hence, heat and work'a infinitesimal changes are not total differentials. Therefore, for thermodynamic systems the admissibility of the Lagrange assumption on correspondence between the problems of search for equilibrium and search for extremum falls far short of being obvious.

The efforts put forth in reducing to mechanics wrote a number of important pages in the history of the initial period of thermodynamic theory. Emergence of thermodynamics is associated with the development of the kinetic theory of gases. In the course of this development, in the 1860s, Clausius discovered the existence of a function, i.e., *entropy*, that is monotonically nondecreasing in isolated systems. Clausius, Boltzmann, and other researchers endeavored to explain this property of entropy—the property of irreversibility of the natural processes. Their explanation was based on the principles of mechanics, first among them, on the principle of least action (PLA). However, their efforts showed the principal impossibility of reducing thermodynamics to mechanics and explaining the asymmetry of changes with respect to time in thermodynamic systems by the models of conservative mechanic systems.

Clausius, Maxwell, Boltzmann, and Gibbs showed that the nature of irreversibility can be revealed by passing from a deterministic to a probabilistic interpretation of physical laws.

Boltzmann, being unfortunately unfamiliar with the works of Russian mathematicians, in fact applied the technique of Markov random processes and the Lyapunov functions [140] to study the regularities of gas movement in a closed vessel. He chose as a base equation the kinetic equation for a gas consisting of particles of one kind. The equation was later assigned his name and has the form

$$\frac{\partial f}{\partial \tau} + v\frac{\partial f}{\partial r} + \frac{1}{m}F\frac{\partial f}{\partial \vartheta} = \int (f'f_1' - ff_1)u\sigma(u, \vartheta)d\Omega d\vartheta_1, \tag{1.6}$$

where $f(\vartheta, r, \tau)$ is a function of distribution of gas molecules (particles) by velocities v and coordinates r; ϑ and r are vectors ($d\vartheta = d\vartheta_x d\vartheta_y d\vartheta_z$, $dr = dxdydz$); $F(r, \tau)$ is the force acting on the particle (can depend on the velocity as well); m is particle mass; $u = |\vartheta - \vartheta_1|$ is a relative velocity of colliding particles; σ is a differential effective cross-section of particle scattering into the solid angle $d\Omega$; ϑ is an angle between a relative velocity and the line connecting the particles. A prime on a function f in (1.6) indicates the state of the particles after collision and the absence of a prime indicates their state before the collision; the index 1 indicates particles colliding with those subject to distribution f.

The first term on the left-hand side of (1.6) is a change in the density of the number of particles in the element of a phase volume $d\vartheta dr$ per time; the second and third terms characterize the changes in the distribution function due to movement of particles in space and the action of external forces, respectively. The integral of collisions on the right-hand side of (1.6) determines the change in f. This change is related to the particles' departure from the element of phase volume at the so-called "direct collisions" and replenishment of the volume with the particles that underwent "reverse" collisions.

Generally, the equation (1.6), *the Boltzmann kinetic equation*, reflects the balance of the number of particles in the element of phase volume. The balance is maintained at a change in $f(\vartheta, r, \tau)$ due to the motion of particles under the action of external forces and collisions among them. Note that this equation takes into account only paired collisions and is true only for not too dense and not too rarefied gases.

For a gas in statistical equilibrium the integral of collisions vanishes and the *Maxwell distribution* by the velocities of particles

$$f(\vartheta, r) = A \exp\left(-\frac{m\vartheta^2}{2}\frac{1}{kT}\right), \tag{1.7}$$

becomes the solution to equation (1.6) in absence of a potential field, where k is a Boltzmann constant, A is a constant determined from the condition of normalization (the total number of particles for all possible states is equal to the total number of particles in the system), and T is the absolute temperature.

For a system in the external potential field, the Maxwell distribution is replaced by the more general *Boltzmann distribution*,

$$f(\vartheta, r) = A \exp\left(-\left(\frac{m\vartheta^2}{2} + U(r)\right)\frac{1}{kT}\right), \tag{1.8}$$

where $U(r)$ is a potential energy of a particle in the external field.

After we integrate the distribution function (1.8) by all the impulses of particles, we can represent the Boltzmann distribution in the form of an equation that is used to determine the density of the number of particles in the point r as

$$n(r) = n_0 \exp\left(-\frac{U(r)}{kT}\right), \tag{1.9}$$

where n_0 is a density of the number of particles that corresponds to the point in which $U(r) = 0$.

For a mix of gases with particles of different mass, the Boltzmann distribution shows that the distribution of partial densities of particles for each component does not depend on the other components. The Gibbs distributions [55] together make up the generalization of the Boltzmann distribution for nonideal systems.

Along with the interrelation revealed between the kinetics of gases and equilibrium statistical distributions, Boltzmann's analysis of the kinetic equation resulted in another very important conclusion for a closed and noncontradictory description of thermodynamics. He formulated it in the form of the H-theorem, according to which, for an isolated system, there is an H-function that monotonically decreases with time:

$$H = \int h(r, \tau)dr = \iint f(\vartheta, r, \tau)\ln f(\vartheta, r, \tau)d\vartheta dr, \tag{1.10}$$

where $h(r, \tau)$ is a spatial density of the H-function, which means the local density of entropy (S) with reversed sign and $f(\vartheta, r, \tau)$ satisfies the kinetic equation (1.6):

$$\frac{\partial H}{\partial \tau} = \iint (1 + \ln f)\frac{\partial f}{\partial \tau}d\vartheta dr. \tag{1.11}$$

Substituting $\frac{\partial f}{\partial \tau}$ from (1.6) into (1.11) and symmetrizing the obtained expression with respect to the distribution function of colliding particles in direct and reverse collisions it can be shown that

$$\frac{\partial H}{\partial \tau} \leq 0. \tag{1.12}$$

The H-function equals the gas entropy with a reverse sign and divided by k, therefore, the H-theorem expresses the *law of entropy increase in isolated systems*, i.e., it can be considered a formulation of the second law of thermodynamics. Mathematically, the inequality (1.12) is equivalent to the more widely spread expression

$$dS \geq 0. \tag{1.13}$$

The detailed conclusions and analysis of the presented relationships (1.6)–(1.12) can be found in special monographs; for example, in the fifth [125] and tenth [127] volumes of *Theoretical Physics*, by Landau and Lifschitz. Here we use these relationships to find the interrelations between the descriptions of motion and rest (equilibrium).

Bearing in mind that the equations of equilibrium distributions (1.7)–(1.9) have no time variable τ and, hence, the equilibrium state can be determined from a simple calculation of probabilities, Boltzmann concluded that it was possibile to exclude the notion of time from thermodynamics as a science of equilibrium. From the tendency of systems that satisfy the kinetic equation (1.6) to the minimum of the H-function (1.10) having the properties of a Lyapunov function, and, hence, towards the maximum of S, another conclusion follows relating to convergence of thermodynamic problems to the mathematical problems of the search for extrema. This conclusion is very important to our analysis.

Assuming, along with the Markov character[1] of the random motion process that underlies the derivation of the equation (1.6), the entropy additivity of the studied thermodynamic system, it is easy to explain the third[2] great Boltzmann equation:

$$S = k \ln w. \tag{1.14}$$

Indeed, if system entropy is a function of state probability (a fact that is clear from the previous text), and if the entropies of individual parts of this system do not depend on the entropies of the others (also true, since the effects on a subsystem's state due to interactions between particles within is much stronger than interactions with other subsystems), the following relationships turn out to be clear:

$$S = f(w), \tag{1.15}$$

$$S = \sum_j S_j, \tag{1.16}$$

$$w = \prod_j w_j. \tag{1.17}$$

Equation (1.14) follows from (1.15)–(1.17).

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[1] The Markov character is that which describes how the evolution from a fixed state is independent of the history of its attainment.

[2] The two others are (1.6) and (1.9).

Besides S, the other characteristic thermodynamic functions (those which take extreme values under certain conditions of system interaction with the environment) are also additive. These functions are internal energy U, enthalpy H, free energy of Helmholtz F, Gibbs energy (free enthalpy) G. The mathematical interdependencesies of U, H, F, and G with entropy are found using the differential equations of thermodynamics.

The following equations [54] were chosen by Gibbs as the fundamental thermodynamics equations (that is, they can be used to find all other necessary relationships):

At independent S, V, and x,

$$dU = TdS - PdV + \sum_{j=1}^{n} \mu_j dx_j; \tag{1.18}$$

at independent S, P and x,

$$dH = TdS + VdP + \sum_{j=1}^{n} \mu_j dx_j; \tag{1.19}$$

at independent T, V, and x,

$$dF = -SdT + VdP + \sum_{j=1}^{n} \mu_j dx_j; \tag{1.20}$$

at independent T, P, and x,

$$dG = -SdT + VdP + \sum_{j=1}^{n} \mu_j dx_j, \tag{1.21}$$

where P is pressure, V is volume, μ is chemical potential, x is a mole quantity, and $j = 1, \ldots, n$ is an index of each component of the system.

As in the Lagrange equation of equilibrium (1.1), each term in equations (1.18)–(1.21) has dimensionality of energy (work). Each type of work done in the system is determined by taking the product of corresponding potentials using conjugated coordinates.

Whereas Boltzmann drew on the example of ideal gas systems to show how it was possible to pass from descriptions of motion (kinetics) to those of equilibrium state, Gibbs extended those equilibrium principles to complex multiphase systems.

There have been a countless multitude of proofs to the trustworthiness of first the principles of equilibrium macroscopic thermodynamics presented systematically by Boltzmann and Gibbs. The theory has shown the highest scientific efficiency for more than a century.

However, the validity of using the thermodynamic principles of equilibrium and extremality for description of any macroscopic nonequilibrium and irreversible processes (including the motions of a huge number of particles) has not yet been strictly proved. Indeed, when Boltzmann derived and used his kinetic equation (1.6) he supposed that motion and collision of individual particles obeyed the laws of classical mechanics and were thus reversible, but he considered the final result of the process to be irreversible, i.e., attainment of a state with a minimum value of H-function (or a maximum of entropy[3]). Thus, his conclusion on the isolated systems' tendency toward equilibrium turned out formally contradictory to the initial assumptions of his work (which is thus referred to as "Boltzmann's paradox").

Gibbs in his book *Statistical Mechanics* [55], what was specially intended to rationally substantiate macroscopic thermodynamic theory, also started with an *a priori* assumption on equilibrium distributions of probabilities of microscopic variables (for example, particle energy).

In the context of the difficulties in substantiating the applicability of thermodynamic models to the studies of many real macroscopic systems the interpretation of equilibrium thermodynamics suggested by T.A. Afanasieva-Ehrenfest [2], C. Caratheodory [27] and M. Born [23] and based on the Pfaffian form technique, is rather interesting.

The Pfaffian form

$$d\Pi = \sum_i X_i dx_i,\ X_i = f_i(x) \tag{1.22}$$

is a generalized notion of the function differential, but in a general case its change depends on the trajectory of transition from one point to another in the space of independent variables x. Hence, it may appear that

$$\oint d\Pi. \tag{1.23}$$

Transition from the equation with the Pfaffian form to a differential equation becomes possible in the case of a Pfaffian forms *holonomicity*, i.e., the existence of such functions $\alpha(x)$ (integrating factors) for which

$$df = \alpha(x) d\Pi \tag{1.24}$$

is a total differential. Pfaffian forms of no more than two variables are always holonomic. In thermodynamics the most important transformation of a Pfaffian form to the total differential is given by

$$\frac{1}{T} dq = dS, \tag{1.25}$$

where is $1/T$ an integrating factor.

It is precisely the possibility of transformation (1.25) that allows us, in a number of cases, to explain the validity of formulating the equilibrium conditions for thermodynamic systems in the form where the left- and right-hand sides are equal to zero in the fundamental Gibbs equations (1.18)–(1.21). Besides, we start to better understand the significance of the inequality (1.13) with its left-hand side

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[3] It is impossible to simultaneously change the signs of velocities for a huge number of particles that make up a macroscopic system.

being a total differential of the function that has all the properties of potentials. Indeed, it represents the basic extreme thermodynamic principle, which asserts the irreversibility of natural processes (the tendency to the entropy maximum, i.e., the second law of thermodynamics). Hence, the behavior of this function can be described by the models of equilibrium processes.

Certainly, it should be noted that the macroscopic substantiation of thermodynamics by Caratheodory and Born does not imply its reducibility to mechanics. In particular, the approach developed by them does not allow standard values of thermodynamic functions (a mole, free energy, chemical potential, etc.) whose statistical character is to be calculated.

A principal possibility of describing one or another problem in terms of equilibrium thermodynamics allows the specific thermodynamic models to be constructed using the equations analogous by form to the equilibrium equations of classical mechanics. The thermodynamic potentials' values, calculated on the basis of the principles of statistical physics or experimental data, can be substituted into these equations similar to the manner that mechanical forces values are substituted. Further, in this book we use the formalism of mechanics in the construction of our models many times, certainly bearing in mind the need to decide on the admissibility of such a technique in each specific case.

1.3. Thermodynamics and Models of Motion

Let us endeavor to derive the thermodynamic equations of some motion processes of macroscopic systems based on the principle formulated in the previous section, i.e., let us determine whether, if the studied system can be described in terms of thermodynamic equilibria, it then becomes possible to apply the equations similar in form to the mechanics equations. Here we mean chemical transformations and transfer processes (diffusion, thermal and electric conductivity, motion of viscous and ideal liquids, radiation). The relationships discussed below can be strictly substantiated only by using the Boltzmann kinetic equation and the statistical principles. The "macroscopic" derivations of these relationships are useful here, as the subject of the present book is a macroscopic modeling of various physical-chemical processes, and macrodescription of relations among the processes studied becomes important for such a modeling.

Of special interest here is the use of the Lagrange equilibrium equation (1.1), which underlies mathematical programming. This is because the thermodynamic models we suggest are formulated in terms of mathematical programminf as well.

Figure 1.1 presents a conventional scheme of ties among thermodynamics and the divisions of theoretical physics. A starting point of the scheme is certainly the classical mechanics. It "feeds" all the other physical sciences. Thermodynamics is a field of study connected directly with mechanics, statistical physics and kinetics. The latter here embraces both microscopic kinetics (based on the Boltzmann equation) and macroscopic kinetics (comprising chemical kinetics and transfer processes). Unlike thermodynamics, which studies the states of rest of macroscopic systems, kinetics deals with the study of motion toward these states. In

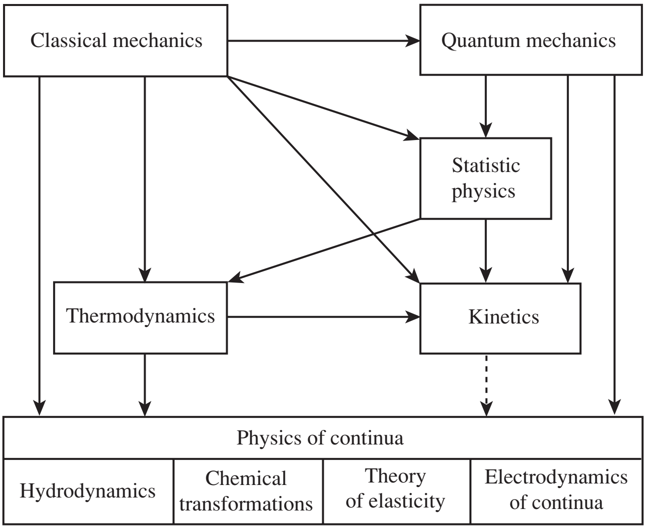

FIGURE 1.1. Relations of thermodynamics to other divisions of theoretical physics.

fact, kinetics is generally defined as a science of system relaxation in the direction of equilibrium. Thus, the models of motion and rest belong to one and the same science—mechanics—when applied to conservative systems. For nonconservative systems accounting for the huge number of particles is imported, and therefore the motion and the rest are considered by distinctly different sciences.

The possible ways to use the macroscopic models to pass from one scince (kinetics) to the other (thermodynamics) are presented below. The results obtained are intended to be used theoretically in the general area of thermodynamics application for a continuous media (see Fig. 1.1). The thermodynamic model as presented here, unlike traditional treatments, includes chemical transformations, though only for macroscopic descriptions of chemical systems. Practical applications of thermodynamic models coincide with those of macroscopic physics and chemistry.

The Law of Mass Action

Let us analyze the relationships between macroscopic models of motion and rest starting with the "mechanical" derivation of the main law of ideal chemical kinetics—the *law of mass action* (LMA).

We write the equilibrium equation for a complex chemical reaction that takes place at fixed T and P in a form analogous to the Lagrange equation (1.1):

$$\begin{aligned}&\sum_{j=1}^{l} G_j\left(y, x_p\right) dy_j + \sum_{j=l+1}^{n} G_j\left(y, x_p\right) dx_j\\&\quad+\sum_{i=1}^{m}\lambda_i d\left(b_i - \sum_{j=1}^{l} a_{ij} y_j - \sum_{j=l+1}^{n} a_{ij} x_j\right) = 0\end{aligned} \qquad (1.26)$$

where G_j is molar Gibbs energy of the jth reagent; $y = y(y_1, \ldots, y_l)$ and $x_p = (x_{l+1}, \ldots, x_n)$ are vectors of mole quantities of initial reagents and reaction products, respectively; a_{ij} is a mole quantity of the ith element in a mole of the jth component; and b_i is the mole quantity of the ith element in the system.

Since the "bonds" (constant values b_i) in a chemical system are undistortable, the last sum in the left-hand side of equation (1.26) is identically equal to zero. Hence, the equation

$$\sum_{j=1}^{l} G_j\left(y, x_p\right) dy_j + \sum_{j=l+1}^{n} G_j\left(y, x_p\right) dx_j = 0. \tag{1.27}$$

turns out to be valid.

Making the assumption that the detailed equilibrium principle is observed, we pass from differentials to final differences and from the latter to stoichiometric coefficients. Summing up these coefficients for all stages, in place of (1.27) we obtain

$$\sum_{j=1}^{l} G_j\left(y, x_p\right) \nu_j + \sum_{j=l+1}^{n} G_j\left(y, x_p\right) \nu_j = 0, \tag{1.28}$$

where ν_j is a stoichiometric coefficient positive for the reaction products and negative for the initial reagents.

For the ideal system the following relations are met:

$$G_j\left(y, x_p\right) = G_j^0 + RT \ln\left(P\frac{y_j}{\sigma}\right),\ j = 1, \ldots, l; \tag{1.29}$$

$$G_j\left(y, x_p\right) = G_j^0 + RT \ln\left(P\frac{x_j}{\sigma}\right),\ j = l+1, \ldots, n; \tag{1.30}$$

$$\sigma = \sum_{j=1}^{l} y_j + \sum_{j=l+1}^{n} x_j, \tag{1.31}$$

where G_j^0 is a standard value of molar Gibbs energy and; R is universal gas constant. Therefore, equation (1.28) can be transformed to the form:

$$\sum_{j=1}^{l} G_j^0\nu_j + RT\sum_{j=1}^{l} \nu_j \ln\left(P\frac{y_j}{\sigma_j}\right) + \sum_{j=l+1}^{n} G_j^0\nu_j + RT\sum_{j=l+1}^{n} \nu_j \ln\left(P\frac{y_j}{\sigma_j}\right) = 0. \tag{1.32}$$

Taking into account the signs of ν and introducing the notation

$$\Delta G^0 = \sum_{j=l+1}^{n} G_j^0\nu_j - \sum_{j=1}^{l} G_j^0\nu_j,$$

we then make elementary transformations of the equation (1.32), obtaining:

$$\sum_{j=l+1}^{n} \nu_j \ln\left(P\frac{x_j}{\sigma}\right) - \sum_{j=1}^{l} \nu_j \ln\left(P\frac{y_j}{\sigma}\right) = -\frac{\Delta G^0}{RT},$$

$$\prod_{j=l+1}^{n}\left(P\frac{x_j}{\sigma}\right)^{\nu_j} \prod_{j=1}^{l}\left(P\frac{y_j}{\sigma}\right)^{-\nu_j} = \exp\left(-\frac{\Delta G^0}{RT}\right). \tag{1.33}$$

Since

$$\frac{Px_j}{\sigma} = P_j, \tag{1.34}$$

where P_j is a partial pressure of the jth component, the equation for the reaction equilibrium constant K_p directly follows from (1.33):

$$K_p = \prod_{j=1}^{n} P_j^{\nu_j} = \exp\left(-\frac{\Delta G^0}{RT}\right), \tag{1.35}$$

i.e., a "thermodynamic" formulation of law of mass action (LMA).

To pass to the "kinetic" formulation of LMA, we assume that the concentrations of system components are equal to their partial pressures, i.e., $P/\sigma = 1$. That such an assumption is possible is obvious, since the sizes of the system (a total mole quantity) do not affect the mechanism of reaction. The assumption made, equation (1.33) can be replaced by the equivalent equation,

$$\prod_{j=l+1}^{n} \left(x_j\right)^{\nu_j} \prod_{j=1}^{l} \left(y_j\right)^{-\nu_j} = \exp\left(-\frac{\Delta G^0}{RT}\right), \tag{1.36}$$

Taking into account that, in the equilibrium state, the rate of the forward reaction,

$$w^+ = k^+ \prod_{j=1}^{l} y_j^{\nu_j} \tag{1.37}$$

is equal to the rate of the reverse one,

$$w^- = k^- \prod_{j=1+1}^{n} x_j^{\nu_j}, \tag{1.38}$$

i.e.

$$w^+ = w^- = w, \tag{1.39}$$

we obtain the relationships

$$\frac{k^+}{k^-} = \prod_{j=l+1}^{n} \left(x_j\right)^{\nu_j} \prod_{j=1}^{l} \left(y_j\right)^{-\nu_j} = K_p, \tag{1.40}$$

That, together with equation (1.35), testify to the equivalence of the chemical equilibrium principle to the law of mass action.

Arrhenius Equation

Now let us try to use the Lagrange equation to clear out the type of equations that determine the constant rates of reactions (k) that enter into the expressions (1.37) and (1.38).

Let us assume that nearing equilibrium the reaction rate w becomes constant $\left(\frac{dx}{d\tau} = \text{const}\right)$ and equal to a mole quantity of the activated complex x_{com} that is formed per unit time. Then the equation of the chemical system equilibrium will have the form

$$\sum_{j=1}^{n-1} G_j\left(y^a, x_{\text{com}}\right) dy_j + G_{\text{com}}\left(y^a, x_{\text{com}}\right) dx_{\text{com}} = 0, \tag{1.41}$$

where y is a mole quantity of the initial reagents taking part in the reaction. For the above reason this equation does not include the differential of bond deformation. Using the assumptions made when deriving LMA, we pass from (1.41) to the expressions

$$\sum_{j=1}^{n-1} G_j\left(y^a, x_{\text{com}}\right) \nu_j + G_{\text{com}}\left(y^a, x_{\text{com}}\right) = 0 \tag{1.42}$$

and

$$\sum_{j=1}^{n-1} \left(G_j^0 + RT \ln\left(P\frac{y_j^a}{\sigma}\right)\right) \nu_j + G_{\text{com}}^0 + RT \ln\left(P\frac{x_{\text{com}}}{\sigma}\right) = 0, \tag{1.43}$$

where $\sigma = \sum_{j=1}^{n-1} y_j^c + x_{\text{com}}$, and y_j^c is the overall mole quantity of the ith reagent in the initial state of the system. Based on the positivity of x_{com} $(x_{\text{com}} > 0)$ and negativity of ν_j at $j = 1, \ldots, n-1$ $(\nu_j < 0)$ and satisfaction of the equality

$$\frac{P}{\sigma} = 1,$$

(the above made assumption) it follows from (1.43) that

$$x_{\text{com}} = w = e^{-\frac{\Delta G^0}{RT}} \prod_{j=1}^{n-1} \left(y_j^a\right)^{-\nu_j}, \tag{1.44}$$

where

$$\Delta G^0 = G_{\text{com}}^0 - \sum_{j=1}^{n-1} G_j^0 \nu_j.$$

Since, according to LMA,

$$w = k \prod_j \left(y_j^c\right)^{\nu_j}, \tag{1.45}$$

it follows from (1.44) and (1.45) that

$$k = \exp\left(-\frac{\Delta G^0}{RT}\right) \prod_{j=1}^{n-1} \left(y_j^a\right)^{\nu_j} \prod_{j=1}^{n-1} \left(y_j^c\right)^{-\nu_j}. \tag{1.46}$$

Assuming that an activated complex is formed adiabatically (entropy does not change) we can pass from the equation (1.46) to the expression

$$k = \exp\left(-\frac{E}{RT}\right)\prod_{j=1}^{n-1}\left(y_j^a\right)^{\nu_j}\prod_{j=1}^{n-1}\left(y_j^c\right)^{-\nu_j}, \tag{1.47}$$

where E is an activation energy.

Finally, by introducing the notation

$$z = \prod_j \left(y_j^a\right)^{\nu_j}\prod_j \left(y_j^c\right)^{-\nu_j}, \tag{1.48}$$

we arrive at the generally accepted formulation of Arrhenius' law

$$k = z\exp\left(-\frac{E}{RT}\right). \tag{1.49}$$

The obtained relationships (1.48) and (1.49) to a certain extent reflect the real regularities. Thus, it is seen from (1.48) that pre-exponential multiplier z decreases rapidly with an increase in reaction order (rise of ν_j), which is certainly true. However, here it is appropriate to emphasize that such "mechanical" conclusions by no means imply reducibility of thermodynamics and kinetics to mechanics. For example, in this case when deriving equation (1.49) the standard Gibbs mole energies were used as constant values in the initial equations. The values of these energies can be determined only by the principles of statistical physics. Either the kinetic theory of gases, statistic relationships, or quantum chemistry methods may be needed, depending on the order of reactions and phase composition of the reacting medium to estimate with practical accuracy values z that depend on both the energy of interacting molecules and their orientation in space.

The usefulness of mechanical interpretations in the cases similar to that at issue is revealed when different macroscopic variables and relationships are combined into single closed models of complex physical-chemical systems. For example, in order to qualitatively estimate the "impact" of thermodynamics on kinetics of chemical processes, the Arrhenius equation, derived in terms of equilibria (mechanical and thermodynamic), can be used to include activated complexes, given as individual variables, in thermodynamic models of chemical systems.

Diffusion

Einstein established the main relationships for stationary diffusion at negligible concentrations of a diffusing substance in terms of a thermodynamic equilibrium between the forces affecting the moving flow. He did so in his classical works on Brownian motion [40–42]. Einstein considered as forces the osmotic pressure (a driving force) and the resistance force proportional to the velocity of particles. Here, following the idea of Einstein's proof, we show the diffusion equation derivation using the notion of chemical potential, widely applied later in the book, instead of the notion of osmotic pressure.

Let us suppose that the driving force is a derivative of the chemical potential of diffusing substance by the motion coordinate (l). Set off mentally a cross section in the moving flow and denote by indices 1 and 2 the mole quantities of moving particles (x) before and after the cross section. Then the change in the chemical potentials associated with change in x will be found from the expression

$$\frac{\Delta\mu}{RT} = \left[\left(\ln x_1 + \ln\left(\frac{P}{\sigma}\right)\right) - \left(\ln x_2 + \ln\left(\frac{P}{\sigma}\right)\right)\right] x_2 = x_2 \ln\frac{x_1}{x_2} \quad (1.50)$$

In formulating equation (1.50) it was supposed that due to a small concentration of the diffusing substance, σ on both sides of the set-off cross section would remain the same. Now let us transform the expression in brackets in the right-hand side of (1.50):

$$x_2 \ln\frac{x_1}{x_2} = x_2 \ln\left(1 + \frac{\Delta x}{x_2}\right) \approx x_2 \frac{\Delta x}{x_2} = \Delta x.$$

Hence,

$$\Delta\mu = RT\Delta x. \quad (1.51)$$

Passing from the final difference Δx to the differential dx we can write the condition of the thermodynamic equilibrium,

$$-RT\frac{dx}{dl} = a\Delta x w, \quad (1.52)$$

where a is a coefficient of proportionality and w is a diffusion rate.

Einstein assumed the coefficient a to be equal to Nz (N being Avogadro's number and z, a particle's resistance to motion) and determined z based on the assumption that the diffusing particles have the form of a sphere with radius r that exceeds essentially the radius of molecules in the solution (a carrier fluid). Under these assumptions

$$z = 6\pi\eta r,$$

where η is a dynamic viscosity.

From (1.52) it follows that

$$\Delta x w = -\frac{RT}{a}\frac{dx}{dl}. \quad (1.53)$$

The left hand-side of equation (1.53) represents the mole quantity of the substance that passes through the cross section perpendicular to the fluid's motion per second, i.e., a diffusion flow (J), and the multiplier before the derivative in the right-hand side equals the diffusion coefficient D. Hence, equation (1.53) is equivalent to the known equation of the Fick molecular diffusion law,

$$J = D\nabla x. \quad (1.54)$$

Darcy–Weisbach Equation

The hydrodynamics equation that determines head losses due to friction at liquid motion in pipes is the *Darcy–Weisbach equation*. It has the form:

$$h = \lambda l \frac{w^2 \rho}{2d}, \tag{1.55}$$

where λ is a hydraulic friction coefficient, d and l are diameter and length of the pipe, w is an average velocity of the liquid motion, and ρ is density.

The equilibrium formulation of equation (1.55) is obvious. It reflects the equality of a driving force (head) to a resistance force.

Hydraulic Shock in Pipelines

In the previous examples the description of motion was reduced to descriptions of rest (equilibrium) as applied to the stationary processes. Now let us find from the equilibrium equation the pressure amplitude in a non-stationary wave process that occurs at fast valving off a pipeline along which the liquid moves. N. Zhukovsky solved this problem by the equations of ideal liquid motion in 1898 [178]. The assumption on the ideality is obvious since a very steep increase in the pressure does not allow the friction forces to manifest themselves.

For a PVW (principle of virtual work)-based formulation of the problem, assume additionally that during an infinitesimal period of time $d\tau$, the shock wave resulting from an instant braking of the flow propagates at a distance dl, where beyond the wave front the radius of the pipe increases and its walls become deformed. Then the Lagrange equilibrium equation can be written in the form

$$\begin{aligned} &\pi\,(r+\delta r)^2 P dl - (\rho + \delta\rho)\,\pi\,(r+\delta r)^2 dl \frac{dw}{d\tau} dl \\ &-2\pi\,(r+\delta r)\, dl P d(\delta r) + \lambda d\varphi = 0 \end{aligned} \tag{1.56}$$

where P is maximum pressure in the pipeline, approximately taken to be equal to pressure increment; r and δr are the pipe radius and its increase due to shock, respectively; ρ and $\delta\rho$ are initial density of the liquid and its increase due to compression, respectively; λ is a Lagrange multiplier, here interpreted as a stress in the pipe wall caused by its deformation; and φ is deformation.

The first term on the left-hand side of equation (1.56) is an infinitesimal work of the pressure force that acts on the liquid; the second term, the work of the inertial force; the third, the pressure work related to a pipe radius increase; and the fourth, the work of the forces that appear in the wall due to its deformation.

Assuming that: 1) the work of the wall resistance (the third term) and the work of its deformation are negligibly small as compared to the first two terms in (1.56); 2) δr and $\delta\rho$ are also negligibly small; and 3) an absolute value of dw equals an initial velocity of the liquid flow, and taking into account the equality of the derivative

$\frac{dl}{d\tau}$ to the shock wave velocity c, we obtain a simpler form of equation (1.56):

$$Pdl - \rho cwdl = 0. \tag{1.57}$$

Thus, follows the Zhukovsky equation for the hydraulic shock

$$P = \rho cw. \tag{1.58}$$

Certainly, if we tried to formulate equation (1.58) having expressed the velocity of the shock wave (sonic) c, as was done by Zhukovsky, in the form of a function of the elastic properties of liquid and wall, we would not only fail to simplify expression (1.56), but we would have to specify the expressions for deformation of the walls and stresses in them. Thus, the initial equilibrium equation would become "more thermodynamic" owing to the consideration for the forces of different nature.

However, even at an abstraction level chosen for the hydraulic shock description, i.e., at the assumption that the shock wave velocity equals the sonic velocity in a free fluid, the presented example illustrates a pool of equilibrium model capabilities. It shows that the models of "rest" appear to be efficient not only for analyses of stationary processes but for the study of typical dynamics problems as well. If we are interested in the results of a non-stationary process (for example, shock wave amplitudes) rather than in the time of its duration, the equilibrium models (and the relevance to extreme models) turn out to be rather convenient because of the simplicity and clearness of their construction and interpretation. Additionally, we note that when deriving (1.58) we implicitly use the assumption on the equilibrium dynamics, i.e., on the equilibrium of each state in the non-stationary process.

Ohm's Law

For direct current Ohm's law is known to have the form

$$U = RI, \tag{1.59}$$

where U is the voltage applied to an electric circuit section; R is resistance, which depends on the conductor material, its geometry and temperature; and I is current.

Similar to the Darcy-Weisbach equation for liquid flow, equation (1.59) reflects the equilibrium (equality) of the driving force (U) and the resistance force (IR). The linear dependence between I and U is explained by the linear dependence between the friction force that acts on the charge carriers and their velocity, which is directly proportional to the current.

Radiation

To estimate the energy of gas radiation, let us use the macroscopic thermodynamic proof by Einstein as presented in one of his 1914 papers [38]. In this paper he used a conditional model that reflects chemically homogeneous gas in the form of a mixture of n different components, each characterized by its mole energy ε_j.

Following the idea of Einstein's proof we use the notation of this book as applied to the system maintained at a constant temperature and pressure.

When following the detailed balancing principle (Einstein used, but did not introduce an appropriate term) for each reaction of formation (loss) of a component with energy other than the low (zero) level, we can write the equality

$$G_j^0 + RT \ln \frac{x_j}{\sigma} = G_0^0 + RT \ln \frac{x_0}{\sigma}, \tag{1.60}$$

where lower index 0 refers to the component with zero energy level.

From (1.60) it follows that

$$x_j = x_0 \exp\left(-\frac{G_j^0 - G_0^0}{RT}\right). \tag{1.61}$$

Assuming that the entropies of all the components are equal (the fluctuations of electrons in the atoms are reversible) we can pass from (1.61) to the Boltzmann distribution equation

$$x_j = x_0 \exp\left(-\frac{\varepsilon_i}{RT}\right). \tag{1.62}$$

Such an incidental macroscopic derivation of the Boltzmann distribution by Einstein is rather curious; however, it also does not allow one to consider the macroscopic substantiation of thermodynamics that is possible. Indeed, equations (1.60)–(1.62) include those quantities that can be determined only using the statistic regularities.

Using equation (1.62) determining the value x_j, Einstein wrote the expression for an average energy of the conditional mixture components

$$\overline{\varepsilon} = \frac{\sum\limits_{j=0}^{\infty} \varepsilon_j x_j}{\sum\limits_{j=0}^{\infty} x_j}. \tag{1.63}$$

Assuming that ε_j can take only discreet values proportional to $Nh\nu$ (h is a Planck constant, ν is a frequency of radiation), we can pass from (1.63) to the expression

$$\overline{\varepsilon} = \frac{\sum\limits_{j=0}^{\infty} jNh\nu x^0 e^{-jh\nu/kT}}{\sum\limits_{j=0}^{\infty} x^0 e^{-jh\nu/kT}} \tag{1.64}$$

(in the exponent $k = \dfrac{R}{N}$).

For further transformation of equation (1.64) we use the equation for a power series expansion:

The numeration is

$$Nh\nu x^0 e^{-h\nu/kT}\left(1 + 2e^{-h\nu/kT} + 3e^{-2h\nu/kT} + \cdots\right) = \frac{Nh\nu x^0 e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2}.$$

The denominator is

$$x^0\left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \cdots\right) = \frac{x^0 e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)}.$$

Thus we obtain the Planck equation for a monochromatic radiator (resonator),

$$\overline{\varepsilon} = \frac{Nh\nu}{e^{h\nu/kT} - 1}. \tag{1.65}$$

Taking into account that the ratio of the irradiated energy to the energy of a radiator is proportional to ν^2 (see, for example, [49]) and integrating by ν, we write the expression

$$u = \int_0^\infty \frac{ah\nu^3 d\nu}{e^{h\nu/kT} - 1}. \tag{1.65a}$$

Having substituted

$$x = \frac{h\nu}{kT},$$

we find

$$u = bT^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} = \sigma T^4.^4 \tag{1.65b}$$

This is the Stephan-Boltzmann equation for emissivity of an absolutely black body.

Einstein evaluated the significance of the methodical approach to the derivation of $\overline{\varepsilon}$, noting that it followed from an approach recognizing no principal difference between physical and chemical phenomena. In his opinion this macroscopic thermodynamic approach was suitable for description of radioactive decay, diamagnetism, Brownian motion, and other phenomena. These statements of Einstein apparently may serve as a logical conclusion to this section illustrating the “almightniness” of thermodynamics.

1.4. Partial Thermodynamic Equilibria

The analysis of mechanical and thermodynamic equilibria that was presented in the previous section of the chapter supposed that there was but one equilibrium

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[4] For the method of finding the integrals (1.65b) see in [65].

point in a system. However, as we stated in the Introduction, the capabilities of thermodynamic analysis increase enormously in the transition from the search for the *only* point of the complete (final) equilibrium to the study of the *whole* thermodynamic attainability region, one that may include a continuous infinite set of partial (by some parameters) equilibria. It is precisely when formulating the principally new problems that cannot be solved with manual calculation and traditional approaches that the greatest effect is achieved by the use of modern computers. In this case we use not only their computational capabilities, but the potentialities they offer in analyzing qualitatively complicated problems.

Let us consider the expediency of stating the problem of search for partial equilibria in more detail. The traditional analysis of thermodynamic equilibria is associated either with determination of extrema of the appropriate function or with solution of the LMA equations. However, when studying the technological and natural processes, normally we are not interested in the extreme values of entropy or free energy but in the extreme concentrations of useful and harmful substances formed in the course of a process. For example, when we compare different oil refinery technologies it is important for us to know what maximum amount of light hydrocarbons (petrol or kerosene) can be produced from a unit of the initial raw material. When we study the environmental characteristics of the fuel combustion processes, the variables we seek are extreme concentrations of nitrogen oxides, sulfur oxides, carbon monoxide, benzpyrene, and other harmful substances. Such compositions may correspond not to the point of final equilibrium, but to *partial* equilibria that take place when the individual reactions slow down for some reasons or do not run at all.

In Table 1.1 there are the examples of final equilibria calculations for several processes of coal processing and methanol synthesis from the mixture of carbon monoxide and hydrogen. They show that there are practically no target products of these

Table 1.1 presents extreme concentrations of the indicated substances. These are substances that can form in reactors as a result of a naturally run process or a specially arranged process in with relations among the rates of separate interactions are artificially changed (for example, in the use of catalysts).

Substance transformation in atmospheric pollution is perhaps the best example of topicality of the problem of a search for partial equilibria as applied to the study of natural phenomena. It is widely believed by specialists that thermodynamics is principally irrelevant to atmospheric chemistry. Indeed, the traditional methods of searching for final equilibria do not allow one to determine the results of the atmospheric processes. For example, according to these methods, all living nature in the oxidizing medium should turn mainly into carbon dioxide, water, and dilute solution of the nitric acid [22]. This does not happen, however, the only reason being the presence of extremely slow reactions under ambient conditions.

The concentrations of main atmospheric pollutants also turn out to be practically equal to zero in the final equilibrium state. It is seen in Table 1.2 that actually observable dangerous concentrations of these substances in the air correspond to the intermediate partial equilibria.

TABLE 1.1. The final thermodynamic equilibrium (eq) and extreme intermediate state (ext) of fuel processing processes, mole/kg

Reaction mixture composition	Temperature of the process, K			
	500		800	
	eq	Ext	eq	ext
A: Coal pyrolysis. Initial composition: $CH_{0.833}O_{0.233}N_{0.011}S_{0.0016}$, $P = 0.1$ MPa; max C_6H_{14}				
C_6H_{14}	0.0000	3.5430	0.0000	3.5430
C_K	51.4000	31.2800	51.4300	31.2800
CH_4	6.7140	0.0000	4.3430	0.0000
CO	0.0002	0.0000	0.8437	0.0000
CO_2	1.4120	6.8910	2.9130	6.8910
COS	0.0000	0.0936	0.0005	0.0936
H_2	0.2301	0.0000	8.8180	0.0000
H_2O	11.0500	0.0000	7.2050	0.0000
H_2S	0.0936	0.0000	0.0931	0.0000
N_2	0.3564	0.3570	0.3560	0.3570
NH_3	0.0011	0.0000	0.0019	0.0000
B. Coal hydrogenation. Initial composition: $CH_{0.833}O_{0.233}N_{0.011}S_{0.0016}) + 0.66H_2$; $P = 15$ MPa; max C_6H_{14}				
C_6H_{14}	0.0000	8.4840	0.0000	8.4800
C_K	31.0300	0.0000	30.6000	0.0000
CH_4	23.6600	0.0000	23.3500	0.0000
CO	0.0000	0.0000	0.0535	0.0000
CO_2	0.4663	4.2560	1.1510	4.2800
COS	0.0000	0.0000	0.0001	0.0000
H_2	0.0478	0.0000	2.0640	0.0000
H_2O	11.9200	0.0009	10.5000	0.0297
H_2S	0.0867	0.0000	0.0866	0.0000
N_2	0.3268	0.3308	0.3205	0.3308
NH_3	0.0079	0.0000	0.0205	0.0000
O_2	0.0000	2.0860	0.0000	2.0460
SO_2	0.0000	0.0867	0.0000	0.0867
C: Methanol synthesis. Initial mixture (in moles): $CO + 2H_2$; $P = 2$ MPa; max CH_3OH				
CH_3OH	0.0000	29.3900	0.0000	14.6500
C_K	10.1000	0.5949	7.1830	4.0310
CH_4	18.3200	1.0570	18.2800	9.4010
CO	0.0001	0.0000	0.3652	0.2439
CO_2	2.7840	0.1628	5.3780	2.8840
H2	0.1306	0.0260	5.7640	3.7700
H2O	25.6400	1.4900	20.0900	10.5500

TABLE 1.2. Equilibrium and extreme concentrations of some pollutants in the atmosphere

Substance		Gibbs energy	State, mole/kg		
Name	Formula	J/mole	Initial	Equilibrium	Extreme*
Benzpyrene	$C_{20}H_{12}$	245377	0.00	0.00	$4.65 \cdot 10^{-4}$
Peroxy acetyl nitrate	CH_3COONO_3	−220359	0.00	0.00	$3.98 \cdot 10^{-3}$
Trichlor ethane	$C_2H_3Cl_3$	−240257	$3.43 \cdot 10^{-7}$	0.00	$5.30 \cdot 10^{-7}$
Hydrocarbons	C_2H_4	−12922	$1.70 \cdot 10^{-9}$	0.00	—
CFC-12	CF_2Cl_2	−575676	$1.72 \cdot 10^{-8}$	0.00	$1.03 \cdot 10^{-7}$
	$CFCl_3$	−377308	$1.72 \cdot 10^{-7}$	0.00	$2.06 \cdot 10^{-7}$
Methane	CH_4	−130107	$5.83 \cdot 10^{-3}$	0.00	—
Carbon monoxide	CO	−169407	$7.00 \cdot 10^{-6}$	0.00	—
Carbon dioxide	CO_2	−457182	$1.20 \cdot 10^{-2}$	$1.79 \cdot 10^{-2}$	$1.79 \cdot 10^{-2}$
Carbonyl sulfide	COS	−210718	$5.83 \cdot 10^{-8}$	0.00	$7.00 \cdot 10^{-7}$
Chlorine	Cl_2	−66450	0.00	$6.44 \cdot 10^{-7}$	—
Hydrogen	H_2	−38905	$1.92 \cdot 10^{-5}$	0.00	—
Water vapor	H_2O	−298051	1.04	1.05	1.05
Hydrogen peroxide	H_2O_2	−205732	$6.42 \cdot 10^{-9}$	0.00	—
Sulfuric acid	H_2SO_4	−821886	0.00	$7.00 \cdot 10^{-7}$	$7.00 \cdot 10^{-7}$
Hydrochloric acid	HCl	−147978	$1.17 \cdot 10^{-8}$	$3.02 \cdot 10^{-7}$	$1.59 \cdot 10^{-6}$
Hydrogen chloride	HF	−325045	0.00	$2.06 \cdot 10^{-7}$	—
Nitrous acid	HNO_2	−154133	$7.70 \cdot 10^{-13}$	$1.17 \cdot 10^{-12}$	$7.9 \cdot 10^{-2}$
Nitric acid	HNO_3	−213410	$5.01 \cdot 10^{-8}$	$5.73 \cdot 10^{-8}$	$1.38 \cdot 10^{-1}$
Hydroperoxyl	HO_2	−58563	$2.30 \cdot 10^{-12}$	0.00	—
Nitrogen	N_2	−57072	26.79	26.79	—
Nitrogen pentoxide	N_2O_5	−92682	$2.90 \cdot 10^{-10}$	0.00	$4.33 \cdot 10^{-2}$
Nitrogen oxides	NO	28487	$5.90 \cdot 10^{-12}$	$6.17 \cdot 10^{-15}$	$6.55 \cdot 10^{-2}$
	NO_2	−37345	$4.19 \cdot 10^{-9}$	$4.27 \cdot 10^{-9}$	$1.18 \cdot 10^{-1}$
Oxygen	O_2	−61110	7.19	7.18	—
Ozone	O_3	70613	$1.39 \cdot 10^{-6}$	0.00	—
Sulfur oxides	SO_2	−370743	$6.42 \cdot 10^{-7}$	0.00	$7.00 \cdot 10^{-7}$
	SO_3	−472315	0.00	$2.17 \cdot 10^{-14}$	—

* Extreme concentrations are calculated for different objective functions, i.e. belong to different states of the system.

These examples show that expanding the application of thermodynamic analysis and increasing its value as an informational tool is possible only if the analysis is extended to the entire region of thermodynamic attainability of physical-chemical systems and the partial equilibria making up this region.

The properties of partial equilibrium states are completely similar to those properties of the final equilibrium state (x^{eq}). First of all, they correspond to the extrema of some thermodynamic functions (determined by the conditions of the system interaction with the environment). However, unlike the extremum that corresponds to x^{eq} these extrema are conditional, i.e., they take place if no physical-chemical process can run after the system has attained a given partial equilibria. If such processes turn out to be impossible in terms of thermodynamics and additional prohibiting conditions become unnecessary, the considered equilibrium coincides with x^{eq}.

For partial equilibria, as well as for x^{eq}, the requirement is met as regarding their attainability from the initial state of the system by the trajectory along which the characteristic function (that takes the extreme value in the point x^{eq}) monotonically does not increase. Similar to x^{eq}, the partial equilibria in accordance with Boltzmann's idea (see Section 1.2) can be found from a simple calculation of probabilities without studying the actual course of the process in time. Hence, the relations of classical equilibrium thermodynamics can also be used in the search for these equilibria.

Note that when we solve practical problems, partial rather than final equilibria are calculated; this is because the lists of reactions or substances we would normally consider are never complete.

Dependence of the thermodynamic attainability regions of a chemical system, i.e., sets of equilibria attainable from it's the system's initial state, on the conditions of the processes run will be shown in the example taken from *Equilibrium Encircling*.

In [58] consideration is given to the reacting system that consists of three isomers: A_1, A_2 and A_3. Since in isomerization reactions the number of species does not change the law of mass conservation for this system can be written in the form

$$x_1 + x_2 + x_3 = |y| = \text{const}, \quad x_j \geq 0. \tag{1.66}$$

The assumptions were made that each of the system components is an ideal gas and in the state of final equilibrium their mole amounts are equal, i.e.,

$$x_1^{\mathrm{eq}} = x_2^{\mathrm{eq}} = x_3^{\mathrm{eq}}. \tag{1.67}$$

The algorithm for studying the equilibria attainable from the set y is illustrated by Fig. 1.2, taken from [58] with some changes. Each triangle presented in the figure is a material balance polyhedron that meets condition (1.66). The triangles are equilateral, their heights are equal to $|y|$ and sides to $2\sqrt{3}\,|y|/3$. The vertices are the states in which the system contains only one component. The initial composition is determined by the vector $y = (0, 0, 1)^T$ (vertexA_3). Figure 1.2a shows the point of equilibrium x^{eq}, line

$$G = \left(G_j^0 + RT\ln(0.5P)\right) y \tag{1.68}$$

(graphically constructed for T, $P = \text{const}$) and zones of thermodynamic unattainability from vertex A_3: A_1ab and A_2bc (shaded). The nonshaded part of the figure represents the attainability region. Determination of the latter in this case is obvious since line (1.68) due to condition (1.67) touches the edges at their mid points and these contact points are the points of minimum free Gibbs energy at edges.

The attainability regions in Figures 1.2 *a–d* are shown for four given mechanisms of the process (depending on the catalysts chosen or some other effects on the system):

a) $A_1 \rightleftarrows A_2 \rightleftarrows A_3$;
b) $A_2 \rightleftarrows A_1 \rightleftarrows A_3$;
c) $A_1 \rightleftarrows A_2 \rightleftarrows A_3 \rightleftarrows A_1$;
d) $A_1 \rightleftarrows A_2, \quad A_1 \rightleftarrows A_3, \quad A_1 + A_2 \rightleftarrows 2A_3$

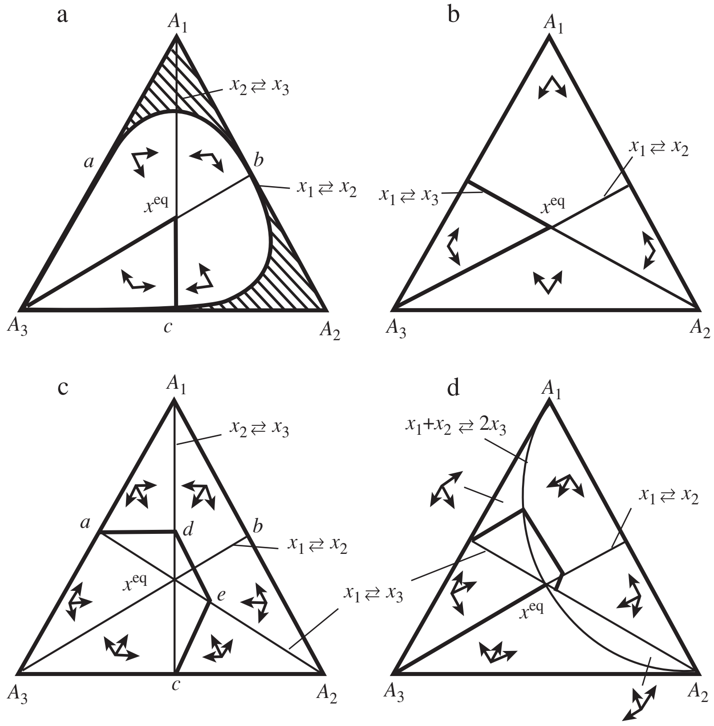

FIGURE 1.2. A graphical interpretation of the algorithm of search for attainable states of a thermodynamic system at a given mechanism of the process.

Let us consider construction of a set of possible equilibria for the mechanism c. To determine the possible direction of the reaction near vertex A_3set off two sections (of a triangle): $A_3x^{eq}a$ and $A_3x^{eq}c$ on the polyhedron of constraints. In the section $A_3x^{eq}a$, there can be reaction $A_3 \to A_1$ until the equilibrium line $x_1 = x_3$ is attained, and reaction $A_1 \to A_2$ until the equilibrium line $x_1 = x_2$ is attained. In the section $A_3x^{eq}c$ there can be the following chemical transformations: $A_3 \to A_2$ (the limiting line$x_2 = x_3$), and $A_2 \to A_1$ (the limiting line$x_1 = x_2$). After the transition from A_3 to one of the states on the section ax^{eq}, we arrive at section$A_1x^{eq}a$, where processes $A_3 \to A_2$ and $A_1 \to A_3$ may take place. Possible directions of transformations in each of the sections are indicated in Fig. 1.2 with arrows. On attainment of the section dx^{eq}, as a result of transformation on the set of compositions $A_1x^{eq}a$, we appear in section $A_1x^{eq}b$, where there can be a motion to the equilibria $x_1 = x_2$. This line will also be attained at subsequent transitions from $A_3x^{eq}c$ to $A_2x^{eq}c$, and from $A_2x^{eq}c$ to $A_2x^{eq}b$. Thus, the whole set of equilibria A_3adecA_3 that are attainable from A_3 is determined for the case of process mechanism c. Similarly the accessible sets are determined at mechanisms a, b and d. It is clear that in all the cases these sets turn out to be smaller than the full attainability region A_3abc that is observed when there are no constraints on the mechanism of reactions.

Some time after the above work was done, a similar algorithm of search for the attainable equilibria was considered in the papers by R. Shinnar et al. [154, 155].

The possibility of finding the thermodynamic attainability regions suggests another tempting area of inquiry: the problem of determining in these regions the points that correspond to extreme concentrations of harmful or useful substances of interest to a researcher. An analysis of this problem—one that goes beyond the traditional methods of equilibrium thermodynamics—is the subject of the study presented next.

1.5. A Thermodynamic Analysis of the Chemical Kinetics Equations

The main content of this book is reduced to a direct application of equilibrium (thermodynamics) models for the analysis of various natural and technological systems. However, thermodynamics can also be used to interpret and transform the motion equations. When so used, it allows reserchers a deeper understanding of motion equations and an easier solution to them. Such a thermodynamic method—studying the kinetics of chemical reactions—unfolds in the book *Equilibrium Encircling*.

Equilibrium Encircling contains a brief comparative analysis of formalisms of kinetics and thermodynamics, it reveals the interrelations between these formalisms; and it offers the conditions of coordinating the kinetic and thermodynamic models. The possibility of simplifying the motion equations (excluding "fast" variables, use of local potentials) is based on the thermodynamic principle of *entropy maximum*. The applicability of the principle of detailed balancing in macroscopic kinetics under condition of microreversibility has been substantiated; the idea of analyzing the direct problems of kinetics when incomplete information is only available, basing the analysis on thermodynamic principles, has been put forward. The method of *balance polyhedron transformation* into a one-dimensional continuum, i.e., a thermodynamic tree, has been suggested. The method makes it possible to determine the substance compositions attained in the course of a chemical process. The technique has been developed to determine a multitude of steady states in open systems.

The geometrical technique of constructing thermodynamic trees used in the *Equilibrium Encircling* can be applied in thermodynamic modeling. It is discussed in Sections 3.2 and 4.4. This section presents briefly the contents of the second, third and sixth chapters of the book by A.N. Gorban [58], which are devoted to coordinating kinetics with thermodynamics, and to applying thermodynamic principles to the analysis and solution of the kinetic equations. Understanding the contents of these chapters is necessary if the reader is to correctly construct and use the thermodynamic models discussed below.

Assumptions, Notions, and Nomenclature Used

Except for a few exceptions, *Equilibrium Encircling* addresses the ideal systems whose kinetics follow the law of mass action. Complex reactions in these systems represent an aggregate of simple (elementary) ones. Each elementary reaction is set by its stoichiometric equation

$$\alpha_1 A_1 + \alpha_2 A_2 + \cdots + \alpha_n A_n \rightleftarrows \beta_1 A_1 + \beta_2 A_2 + \cdots + \beta_n A_n, \qquad (1.69)$$

where A_j are symbols of the substances; α_j, β_j are stoichiometric coefficients–integers that show how many molecules of A_j are involved in one act of the elementary reaction as an initial reagent (α_j) and as a product (β_j). Both forward and reverse reactions are written in (1.69). For the reverse reaction β_j is the number of molecules A_j taking part in one act of reaction as an initial reagent; α_j is the number of molecules A_j that are produced in one act of the reaction as a product.

Each elementary process r is assigned to its stoichiometric vector γ_r with components $\gamma_{rj} = \beta_{rj} - \alpha_{rj}$. Additionally, the elementary process is characterized by an extensive quantity $V_r \geq 0$ (i.e., the volume of the process), and the intensive quantity $w_r \geq 0$, the process rate. The value V that characterizes the size of the region in which the process takes place is called a volume conventionally. In specific cases V_r can be a volume, a surface area, or the number of active centers of catalysts.

The rates of the forward (w^+) and reverse (w^-) reactions based on the LMA are determined from the equations

$$w^+ = k^+(T) \prod_{j=1}^{n} c_j^{\alpha_j}, \qquad w^- = k^-(T) \prod_{j=1}^{n} c_j^{\beta_j}, \qquad (1.70)$$

where c_j is a concentration of the jth substance, and $k^{\pm}$ are the rate constants.

The *rate of the stage* (the reverse elementary reaction (1.69)) is

$$w_s = w_s^+ - w_s^-. \qquad (1.71)$$

The thermodynamic ideality of the considered system is determined by the form of the expression for the chemical potential,

$$\mu_j = \mu_j^0 + RT \ln c_j. \qquad (1.72)$$

Note, that in equations (1.70) and (1.72) and below in this section, unlike in the rest of the book, along with the main variable (x), concentration c_j is the mole quantity of the jth component. Specifically, c_j is the number of species (moles) of the jth component in a unit of V. This is to preserve the form of analytical relationships used in the *Equilibrium Encircling*. Following the rigor (found ib that book), for the antilog in (1.72), instead of c_j we are right to use the dimensionless ratio $\frac{c_j}{c_j^0}$, where c_j^0 is a concentration of the jth component in a standard state that is taken to be equal to unity. In this case, the correspondence of equation (1.72) to equations (1.29) and (1.30) becomes clear. In those equations the antilogs are the ratios of partial pressures to the ideal gas' standard pressure, considered to be equal to unity.

The Schemes of Formal Thermodynamics and Kinetics

Before discussing the problems of coordinating the motion models with equilibrium models let us briefly consider the models themselves, i.e., formal descriptions of thermodynamics and kinetics.

Suppose that the subject of a study is isolated systems. The study of the nonisolated system with equilibrium environment is reduceable to the analysis of a minimum isolated system, including the given one. The thermodynamic description of the system, if specified, comprises the followings: the list of macroscopic variables, a system of balance equations, a system of balance inequalities, and entropy as a function of macroscopic variables.

Denote the macroscopic variables as M_j $(j = 1, \ldots, n)$, and the vector with components M_j as M. The values of variables M_j completely determine the system's states. The choice of the main macroscopic variables for a specific system is far from a trivial problem, but if the choice is made correctly we can consider any macroscopic quantity a function of M. Let us identify vector M and a system's state.

Balance equations can be homogeneous:

$$\sum_i a_{ij}^g M_j = 0, a^g M = 0, \tag{1.73}$$

or nonhomogeneous:

$$\sum_i a_{ij} M_j = b_i = \text{const}, aM = b = \text{const}. \tag{1.74}$$

The balance of electric charges (the electric neutrality equation) can exemplify equations of the first type. Presence of the relationships of type (1.73) means that the variables M_j are not independent. Examples of equations of the second group are balances of mass, energy, surface, etc. The values of the right-hand sides of (1.74) in the isolated system do not change with time. If it is possible to pass from M^1 to M^2, then $aM^1 = b = aM^2$.

As a rule, besides balance equations, there are balance inequalities; for example, conditions of nonnegativity of variables (concentrations, volumes, etc.) expressed in general use:

$$M \geq 0. \tag{1.75}$$

Recall that the inequality $x \geq 0$ for the vector x implies $x_j \geq 0$ for all coordinates x.

The system of balance equations (1.73) and (1.74), and balance inequalities (1.75) define a convex set in Euclidean space R^n, which is a balance polyhedron D.

Entropy S is a homogeneous function of the first order of macroscopic variables M_j : $S(kM) = kS(M)$ for any k larger than zero. It reaches maximum in the domain D and is twice continuously differentiable. Equilibrium is the point of global maximum of S in a balance polyhedron. It is supposed to be an interior point of D. The metastable state represents a local maximum of S in D. Often, but not always, the condition of concavity [72] is met:

$$x^T \left[\frac{\partial^2 S}{\partial M_i \partial M_j} \right] x \leq 0,\ x \in R^n,\ ax = 0,\ x \neq 0,\ S(M) > -\infty. \tag{1.76}$$

The condition $ax = 0$ means that x belongs to the balance plane that passes through zero. In D the conjugate variables $\mu_j(M) = -\dfrac{\partial S(M)}{\partial M_j}$ are determined. In the equilibrium point

$$\mu_j \left(M^{\text{eq}} \right) = \sum_i \lambda_i a_{ij}, \tag{1.77}$$

where λ_i are the uncertain Lagrange multipliers. One of the explanations of expression (1.77) consists in the fact that the scalar product $M, \mu \left(M^{\text{eq}} \right) = \sum\limits_j M_j, \mu_j \left(M^{\text{eq}} \right)$ is constant on any balance polyhedron.

There can be different options of the assumed entropy properties – both stronger and weaker than those presented – but all the equilibrium thermodynamics versions suppose observance of its second law: Entropy does not decrease at spontaneous changes in the isolated system. The notion of a thermodynamically admissible path serves to formalize of this law.

As was mentioned in the Introduction, the function $M = \varphi(\tau)$, $\tau \in [0, 1]$, is called a *thermodynamically admissible path* if the following four conditions are met:

1. $\sum\limits_j a^g_{ij} \varphi_j(\tau) = 0,\ a^g \varphi(\tau) = 0$, for any $\tau \in [0, 1]$.
2. $\sum\limits_j a_{ij} \varphi_j(\tau) = \text{const},\ a\varphi(\tau_1) = a\varphi(\tau_2)$, for any $\tau_1, \tau_2 \in [0, 1]$.
3. $\sum\limits_j \varphi_j(\tau) \geq 0, \varphi(\tau) \geq 0$, for any $\tau \in [0, 1]$,
4. The function $S\left(\varphi(\tau)\right)$ on the section $\tau \in [0, 1]$ is nonincreasing.

Let us define thermodynamic preorder and thermodynamic equivalence. $M^1 \geq M^2$ if there is the thermodynamically admissible path $\varphi(\tau)$ that $\varphi(0) = M^1$, $\varphi(2) = M^2$. $M^1 \approx M^2$ if $M^1 \geq M^2$, and $M^2 \geq M^1$. The comparable states M^1 and M^2 always belong to one balance polyhedron. The thermodynamically equivalent states are identified in D by the graph referred to in *Equilibrium Encircling* as a *thermodynamic tree* or an *entropy tree*.

The quantities used in thermodynamics are divided into categories of *extensive* and *intensive*. All extensive quantities (like system entropy) are homogeneous functions of the first power. The intensive values have zero power of homogeneity. For the latter $f(kM) = f(M)$ at any $k > 0$. The extensive quantities include S, U, H, G, F, V, x, and the intensive ones include T, P, density ρ, specific volume v, derivatives of thermodynamic functions with respect to M_j.

The following property of homogeneous functions is often used in thermodynamics. Let $f(M)$ be a homogeneous function of power λ: $f(kM) = k^\lambda f(M)$ for $k > 0$. We calculate by two methods the derivative with respect to the function

$f(kM)$ at $k = 1$:

$$\left(\frac{df(kM)}{dk}\right)_{k=1} = \sum_j M_j \frac{\partial f(M)}{\partial M_j},$$

and, going the other way, using homogeneity, we obtain

$$\left(\frac{df(kM)}{dk}\right)_{k=1} = \left(\frac{dk^\lambda}{dk}\right)_{k=1} f(M) = \lambda f(M).$$

Finally, for the homogeneous function of the power λ, we obtain the Euler equation

$$\sum_j M_j \frac{\partial f(M)}{\partial M_j} = \lambda f(M) \tag{1.78}$$

In particular, for extensive f,

$$\sum_j M_j \frac{\partial f(M)}{\partial M_j} = f(M), \tag{1.79}$$

and for intensive f,

$$\sum_j M_j \frac{\partial f(M)}{\partial M_j} = 0. \tag{1.80}$$

It is supposed that in additive thermodynamic systems that have

$$S(M) = \sum_k S_k(M_k), \tag{1.81}$$

the entropies of parts S_k meet the same conditions as S of the system. Namely, they have a point of maximum, they are differentiable, and so on. For each fixed state of one part, the balance equations and inequalities of the system (1.73)–(1.75) turn into balance equations and inequalities of the other parts. For example, if we suppose that the state of one part is given, we can determine the balance polyhedrons and equilibria of the others.

Parts of additive systems can be supposed noninteracting though this is not an absolutely correct supposition. Energy and entropy of an interaction are considered negligibly small as compared to energy and entropy of the parts, but admissible are the flows of substance, energy, and other extensive variables from one part to another, as long as this is not prohibited by the balance relationships. Due to these flows, the point $M^{1\text{eq}} + M^{2\text{eq}}$ is not always the equilibrium of the system that consists of two parts. To describe this feature, we can use the phrase: "parts interacting through flows."

In isolated systems those states that take place somewhere besides along the thermodynamically admissible path can also be achieved. These are, for instance, the metastable states that result from fluctuations. However, here we consider the dynamics of the processes that take place by the continuous paths. Far from the points of phase transitions, such a constraint is quite justified.

Now let us pass to the description of kinetics. Consider that, formally, the kinetic description of a system, if given, is specified as: the list of macroscopic variables, the system of balance equations and inequalities, the mechanism of transformations—the list of elementary processes and the rate functions of the elementary processes. In the same manner as in the thermodynamic description it is supposed that the values of macroscopic variables M_j determine the state of the system. The balance equations and inequalities in the kinetic description completely coincide with (1.73)–(1.75) in the thermodynamic model.

From here the differences start. A fixed basis should be chosen in the space of vectors M. Each vector of the basis e_j is correlated to the symbol A_j. M_j is the jth coordinate in this basis.

The mechanism is the list of elementary processes each set by its stoichiometric equation of the form (1.69), the rth elementary process is assigned its stoichiometric vector γ_r with components $\gamma_{rj} = \beta_{rj} - \alpha_{rj}$, the process volume V_r and the rate w_r.

The kinetic equations have the form

$$\frac{dM}{d\tau} = \sum_r \gamma_r V_r w_r, \tag{1.82}$$

where τ is time.

It is supposed that the following conditions of balance conservation are met:

$$\sum_j a^g_{ij}\gamma_{rj} = 0, a^g\gamma_r = 0, \text{ for any } r; \tag{1.83}$$

$$\sum_j a_{ij}\gamma_{rj} = 0, a\gamma_r = 0, \text{ for any } r; \tag{1.84}$$

if

$$\sum_j M_j \geq 0, \text{ for any } r \;\; V_r w_r \sum_j \gamma_{rj} \geq 0. \tag{1.85}$$

Equations (1.83), (1.84) and inequalities (1.85) mean that for each elementary process the balance equations and inequalities are true. According to (1.83) and (1.84) the directions of vectors γ_r pass through zero. It is supposed that $w_r(M)$ are continuously differentiable in the whole domain of definition.

Coordination Between Kinetics and Thermodynamics

Let the macroscopic variables, balance equations and inequalities be set, entropy $S(M)$ be found, and the kinetic equations (1.82) be constructed. Let us consider that the kinetic description is coordinated with thermodynamics if the domain of definition S and w coincide and entropy $S(M(\tau))$ does not decrease on the solutions to the kinetic equations $M(\tau)$.

To determine the conditions of coordination, obviously it is necessary to transform the right-hand sides of equations (1.82), for the variables w_r entering into them were presented in the form of the functions of some thermodynamic quantities.

The transformation is possible owing to the autonomy (independence from τ of the right-hand sides) of the system (1.82)).

Supposing that concentrations c_j are macroscopic variables, we can use for the transformations the equation (1.72), from which we will find, that

$$c_j = \text{const} \cdot \exp\left(\frac{\mu_j}{RT}\right). \tag{1.86}$$

From μ_j it is convenient to pass to the dimensionless *pseudopotentials*

$$m_j = \frac{\mu_j}{RT} = -R^{-1}\frac{\partial S}{\partial c_j}. \tag{1.87}$$

Based on (1.87) and the LMA equation (1.70), the expression for the elementary process rate (1.69) can be presented in the form

$$w_r = \varphi_r \exp\left(\sum_j \alpha_{rj} m_j\right). \tag{1.88}$$

Having illustrated the method of transforming the rate equation with the example of the variable c, we return to the common symbol of macroscopic variables M.

Now we check if the function $G = \int m dM$ is a Lyapunov function of the system (1.82). For certainty let us write the conditions of G decreasing along the solutions.

The derivative of G with respect to time, due to (1.82), is

$$\dot{G} = \sum_r V_r \varphi_r \sum_j m_j \gamma_{rj} \exp\left(\sum_j \alpha_{rj} m_j\right). \tag{1.89}$$

Let us represent G as a derivative of the auxiliary function of one variable λ. For the fixed state, we assume

$$\theta(\lambda) = \sum_r V_r \varphi_r \exp\left(\sum_j \left(\lambda\alpha_{rj} + (1-\lambda)\beta_{rj}\right) m_j\right). \tag{1.90}$$

Then $\dot{G} = -\theta'(1)$. We can try to interpret $\theta(\lambda)$ in the following way: For each $\lambda \in [0, 1]$ consider the system of stoichiometric equations obtained by "combining" forward and reverse processes. These would be:

$$\alpha_{rj}(\lambda) = \lambda\alpha_{rj} + (1-\lambda)\beta_{rj}, \; \beta_{rj}(\lambda) = \lambda\beta_{rj} + (1-\lambda)\alpha_{rj}. \tag{1.91}$$

Keeping the values V_r and φ_r, we substitute on the right-hand side of (1.90) the rate $w_r(\lambda)$ as calculated by equation (1.88), but we would replace α_{rj} by $\alpha_{rj}(\lambda)$ in (1.91) in the final equation:

$$\theta(\lambda) = \sum_r V_r w_r(\lambda). \tag{1.92}$$

In particular, $\theta(1) = \sum\limits_r V_r w_r$.

If for any state from the domain of definition w the inequality $\theta'(\lambda) \geq 0$ is true, the function $G\,(M(\tau))$ is nonincreasing on the solutions of kinetic equations (1.82) and has the properties of the Lyapunov function. The reverse is also true, since $\dot{G} = \theta'(1)$.

Now note that $\theta''(\lambda) > 0$ everywhere; therefore, to satisfy the inequality $\theta'(\lambda) \geq 0$, it is sufficient to have such $\lambda < 1$ so, that $\theta(\lambda) \leq \theta(1)$.

Production of entropy, a derivative of S due to the system (1.82) is

$$\dot{S} = R\theta'(1),$$

and the condition of coordination can be written as follows: $\theta'(\lambda) \geq 0$ for any state from the domain of definition S.

We formulate several sufficient conditions for coordinating kinetics and thermodynamics. If for any state the inequality $\theta(1) \geq \theta(0)$ is satisfied, i.e.,

$$\sum_r V_r \varphi_r \exp\left(\sum_j \alpha_{rj} m_j\right) \geq \sum_r V_r \varphi_r \exp\left(\sum_j \beta_{rj} m_j\right), \tag{1.93}$$

then $\theta'(\lambda) \geq 0$. In particular if for any state $\theta(1) = \theta(0)$, i.e.,

$$\sum_r V_r \varphi_r \exp\left(\sum_j \alpha_{rj} m_j\right) = \sum_r V_r \varphi_r \exp\left(\sum_j \beta_{rj} m_j\right), \tag{1.94}$$

then $\theta'(\lambda) \geq 0$. Expression (1.93) is an *inequality of coordination* and (1.94) is a *condition of balance*.

Let us interpret the expressions (1.93) and (1.94). Compare with each system of elementary processes the reverse process; that is:

$$\alpha'_{rj} = \beta_{rj}, \quad \beta'_{rj} = \alpha_{rj}, \quad V'_r = V_r, \quad \varphi'_r = \varphi_r,$$

and

$$w_r = \varphi_r \exp\left(\sum_j \alpha_{rj} m_j\right).$$

The primed variables relate to the reverse system. The inequality of coordination means that the sum of flows for the reverse system does not exceed in each state the sum of flows for the initial system:

$$\sum_r V_r w_r \geq \sum_r V'_r w'_r. \tag{1.95}$$

The condition of balance consists in the fact that these sums of flows are equal. It is true for the equilibrium points: complete and partial (at supposition that at attainment of the latter all the processes in the system cease).

The presented conditions of coordination and balance show clearly the convenience of using dimensionless pseudopotentials:

$$m_j = -R^{-1}\frac{\partial S}{\partial M_j} = \frac{\mu_j}{RT} \tag{1.96}$$

(as compared with (1.87) the symbol c here is replaced by the common symbol of macroscopic variables M). Here in the case of measuring M in moles the thermodynamic Lyapunov function G is also measured in moles and this function can be directly applied to check the conditions of coordination between the kinetics and thermodynamics (see the equations (1.82), (1.89), (1.93), and (1.94)).

Emphasize that neither inequality of coordination nor the condition of balance are necessary for the entropy monotonical change with time. They are sufficient. The necessary and sufficient is only the inequality $\theta'(\lambda) \geq 0$.

The mechanism of transformations is called reversible if each elementary process in it has a reverse one: for each r there exists such p that $\alpha_{rj} = \beta_{pj}, \beta_{rj} = \alpha_{pj}$. In the reversible mechanisms the inverse processes are combined, by writing

$$\alpha_{s1}A_1 + \cdots + \alpha_{sn}A_n \rightleftarrows \beta_{s1}A_1 + \cdots + \beta_{sn}A_n. \tag{1.97}$$

A couple of processes (1.97) is called a stage. Let V_s^+, w_s^+ be a volume and rate of the forward process and V_s^-, w_s^-—those of the reverse one. Then kinetic equations for the reversible mechanism can be rewritten in the form

$$\dot{M} = \sum_s \gamma_s \left(V_s^+ w_s^+ - V_s^- w_s^-\right), \tag{1.98}$$

where s is the number of stage, γ_s is a stoichiometric vector of stage that coincides with stoichiometric vector of the forward process: $\gamma_{sj} = \beta_{sj} - \alpha_{sj}$; V_s^+ normally equals to V_s^-. Note that any mechanism can be written as a reversible one if several elementary processes with a zero rate are added to it.

The contribution of the s th stage to the entropy production is

$$-\left(\mu, \gamma_s\right) V_s \left(w_s^+ - w_s^-\right) = -V_s \sum_j \gamma_{sj}\mu_j \left(w_s^+ - w_s^-\right). \tag{1.99}$$

If the contribution of each stage to the entropy production is nonnegative, kinetics is coordinated with thermodynamics stage-by-stage. Note that presence of magnetic fields violates the microreversibility and stage-by-stage coordination [125]. In this case we have to return to the balance condition (1.94) or inequality of coordination (1.93), in which all the elementary processes take place simultaneously.

The condition of stage-by-stage coordination (detailed balancing principle) consists in the fact that

$$\left(\mu, \gamma_s\right) w_s \leq 0 \tag{1.100}$$

for all stages s. A sufficient condition for (1.100) is the possibility of presenting w_s in the form

$$w_s = \varphi_s \left(\exp\left(\sum_j \alpha_{sj} m_j\right) - \exp\left(\sum_j \beta_{sj} m_j\right)\right), \tag{1.101}$$

where $\varphi_s \geq 0$. The value φ_s is called a *kinetic multiplier of the stage* and the difference of exponents in brackets (1.101) is called a *thermodynamic function of rate* or the *function of Marcelin-De Donder*.

The kinetic law (1.101) allows a new definition of w_s^+ and w_s^-:

$$w_s^+ = \varphi_s \exp\left(\sum_j \alpha_{sj} m_j\right); w_s^- = \varphi_s \exp\left(\sum_j \beta_{sj} m_j\right). \tag{1.102}$$

It should be emphasized the neither the inequality of coordination (1.93) nor the condition of balancing (1.94), nor the representation of w_s in the form of the thermodynamic function (1.101), nor, finally, the division of w_s into w_s^+ and w_s^- (1.102) are not invariant, even with respect to a simple transformation, that maintains a set of thermodynamically admissible paths: $S' = \lambda S\,(\lambda \geq 0)$. At such a transformation $m'_j = \lambda m_j$. The conditions of coordination $\theta'(\lambda) \geq 0$ and the condition of stage-by-stage coordination (1.100) are invariant to it.

Let us call the vector of pseudopotentials μ^p *thermodynamically admissible* if for any stoichiometric vector γ_s,

$$\operatorname{sign}\left(\mu^p, \gamma_s\right) = \operatorname{sign}(\mu, \gamma_s). \tag{1.103}$$

The vector of pseudopotentials μ^p is thermodynamically admissible if it can be presented in the form

$$\mu^p = f\mu + \chi, \tag{1.104}$$

where $f > 0$ is a positive scalar intensive quantity ($f(\lambda M) = f(M)$ at $\lambda > 0$), and χ is a vector of intensive quantity, i.e., it is orthogonal to all $\gamma_s : (\gamma_s, \chi) \equiv 0$. Representation of (1.104) is sufficient and, at some additional conditions of nondegeneracy, is also a necessary condition of the thermodynamic admissibility of μ^p.

The physical sense of the orthogonality conditions of the vectors γ_s and χ, i.e., satisfaction of the identity $(\gamma_s, \chi) \equiv 0$ can be explained by the equality

$$\sum_j \mu_j dc_j = 0. \tag{1.105}$$

which is satisfied at the equilibrium point of the thermodynamic system.

It is obvious that the orthogonality of potentials and stoikhiometric vectors follows from the orthogonality of potentials and concentrations.

The stage-by-stage coordination (1.100) will be satisfied if at any s

$$w_s = \varphi_s\left(\exp\left(\sum_j \alpha_{sj}\mu_j^p\right) - \exp\left(\sum_j \beta_{sj}\mu_j^p\right)\right) \tag{1.106}$$

for the thermodynamically admissible vector of pseudopotentials μ^p. The thermodynamic admissibility μ^p is observed, for example, at monotonic nondegenerate substitution of entropy: $S' = F(S)$, $\dfrac{dF}{dS} > 0$.

The general formal scheme for coordination of kinetics and thermodynamics as illustrated in *Equilibrium Encircling*, gives examples of: chemical reactions in the homogeneous isolated system; interaction with an inertia-free mechanical system; contact with a thermal reservoir; simultaneous interaction with a thermal reservoir; and a mechanical system. Consideration is given to four classical conditions of chemical kinetics. They are: U, $V = \text{const}$; T, $V = \text{const}$; H, $P = \text{const}$ and T, $P = \text{const}$. A detailed analysis of the main model system of thermodynamics and kinetics, i.e., of ideal gas, is also presented in cited book.

Note the representation of the Fourier heat conduction equation

$$q = \lambda (T - T_T) \tag{1.107}$$

is, in form, similar to the equation of the chemical reaction rate (1.101):

$$w_t = \varphi_t \left(\exp\left(-\frac{E}{RT} \right) - \exp\left(-\frac{E}{RT_T} \right) \right), \tag{1.108}$$

which was given in *Equilibrium Encircling* and is very interesting as regards the subject of this book.

In (1.107) and (1.108) q is a density of heat flow; λ is a coefficient of heat conductivity; T and T_T are temperatures of the system and the reservoir exchanging heat with the system, respectively; w_t is the rate of the heat exchange stage replacing q in the chemical-kinetic interpretation; φ_t is some intensive quantity; E is a constant that has dimension energy/mole.

To be certain in the equivalency of the equations (1.107) and (1.108) it is sufficient to divide $e^{-\frac{E}{RT}} - e^{-\frac{E}{RT_T}}$ into $T - T_T$, assuming with regard to continuity that, at $T = T_T$, the quotient equals $\frac{E}{RT^2} e^{-\frac{E}{RT}}$. This quotient is positive at $T > 0$, $T_T > 0$ and, hence, transition from (1.08) to (1.107) implies multiplying φ_t by the positive function of temperatures T, T_T. The stoichiometric vector of the heat exchange stage

$$EA_s \to EA_T \tag{1.109}$$

(indices s and T refer to the system and reservoir, respectively) has two nonzero components: $\gamma_s = -E$, $\gamma_T = E$. The kinetics equations for the interconnected system interacting with an infinite reservoir can be written in the form

$$\left. \begin{aligned} \dot{x} &= V \sum_s \gamma_s \varphi_s (x, U, V) \exp\left(\sum_j \alpha_{sj} m_j (x, U, V) \right), \\ \begin{pmatrix} \dot{U} \\ \dot{U}_T \end{pmatrix} &= V_s \begin{pmatrix} -E \\ E \end{pmatrix} \varphi_s \left(\exp\left(-\frac{E}{RT} \right) - \exp\left(-\frac{E}{RT_T} \right) \right), \end{aligned} \right\} \tag{1.110}$$

where x is a vector of mole quantities of reagents, U is an internal energy of the system, and V_s is a "volume" of the contact area of the system and reservoir.

The balance equations and inequalities for (1.110) are:

$$\left. \begin{aligned} &a)\ U + U_T = \text{const}; \quad b)\ V = \text{const} \geq 0; \\ &c)\ V_T = \text{const} \geq 0; \quad d)\ \sum_j a_{ij} x_j = \text{const}; \quad e) x_j \geq 0. \end{aligned} \right\} \tag{1.111}$$

The thermodynamic Lyapunov function $G(x, U, U_T, V, V_T)$ is constructed again as $-\frac{S_\Sigma}{R}$, where S_Σ is an entropy of the interconnected system, i.e.,

$$G(x, U, U_T, V, V_T) = -\frac{S(x, U, V) + S_T(U_T, V_T)}{R}. \tag{1.112}$$

Its derivative by virtue of the system of equations (1.110) is non-positive, if kinetics is coordinated with thermodynamics.

Thermodynamics and Composing Kinetic Equations

The third chapter of *Equilibrium Encircling* shows how the conditions of coordinating kinetics and thermodynamics can be used for transformation and solution of kinetic equations. The most popular method of studying the dynamics of somewhat complex objects is to divide the motions into fast and slow ones with subsequent exclusion of the fast ones. As a result we obtain the system of equations that describe the evolution of slow variables.

The basis for the analysis stated in [58] is the assumption that, if the choice of macroscopic variables was made correctly, the system relaxes fast; by this we mean that distribution of probabilities of microscopic variables, as a small period of time passes, is determined to a high accuracy by the values of macroscopic variables. The Markov ergodic circuits (processes) with finite number of states make up the model of a *microdescription*.

The description is reduced by the Lyapunov functions, done so on the basis of the principle of a conditional maximum of entropy at given values of the macroscopic variables. Here we use the Legendre transformation of the thermodynamic Lyapunov function $H(x)$ in a new function:

$$G(\mu) = (\mu, x(\mu)) - H(x(\mu)) = \sum_j \mu_j x_j(\mu) - H(x(\mu)), \tag{1.113}$$

which is applied in mechanics and thermodynamics, where

$$\mu = \nabla_x H, \quad \mu_j = \frac{\partial H}{\partial x_j}, \tag{1.114}$$

$$\frac{\partial G}{\partial \mu_j} = x_j + \sum_i \frac{\mu_i \partial x_i}{\partial \mu_j} - \sum_i \frac{\partial H}{\partial x_i}\frac{\partial x_i}{\partial \mu_j} = x_j. \tag{1.115}$$

Using the conjugate coordinates x and μ we can write the necessary conditions of extremum in the problems with linear constraints

$$\begin{aligned} &H(x) \to \min, \\ &\sum_j l_{ij} x_j = M_i, \quad i = 1, \dots, m, \quad x_j \geq 0 \end{aligned} \tag{1.116}$$

where x is a complete vector of variables, $M$is a vector of slow variables, $M \subset x$. Applying the method of Lagrange multipliers we obtain the system of equations that expresses the necessary conditions for (1.116):

$$\mu_j = \sum_i \lambda_i l_{ij}, \quad j = 1, \dots, n, \quad \sum_j l_{ij} x_j = M_i, \quad i = 1, \dots, m, \tag{1.117}$$

where λ_i are uncertain multipliers. As is seen the necessary conditions of extremum are expressed by the system of equations, one part of which is linear in coordinates x and the other in conjugate coordinates μ.

Now, we pass from the function $H(x)$ to the function of slow variables $H(M)$. Let the Legendre transformation $G(\mu)$ be given, the transformation $x \to \mu$ have a smooth reverse transformation, i.e., equation (1.115) is satisfied and it is known that for some open set of values of the vector $M = (M_1, \dots, M_m)$ the problem (1.116) has only one solution, and the point of minimum $x^{\min}$ and, hence, $H^{\min}$ smoothly depend on M, i.e., $H^{\min} = H(M)$. Denote $\mu_{M_j} = \dfrac{\partial H(M)}{\partial M_j}$. μ_M is a vector with coordinates μ_{M_j}. We find out what information on the function $H(M)$ can be obtained based on $H(x)$, $G(x)$, and without solving any equations. Based on the value of the vector μ_M find vector μ in the appropriate point of the conditional minimum

$$\mu_j = \sum_i \mu_{M_i} l_{ij}. \tag{1.118}$$

Thus, obtain

$$x\left(\mu_M\right) = \left(\nabla_\mu \;\; G(\mu)\right)_{\mu_j = \sum\limits_j \mu_{M_j} l_{ij}}. \tag{1.119}$$

Using the given $x\left(\mu_M\right)$ determine $M\left(\mu_M\right)$ and $H\left(M\left(\mu_M\right)\right)$:

$$M_i\left(\mu_M\right) = \sum_j l_{ij} x_j\left(\mu_M\right), \quad H\left(M\left(\mu_M\right)\right) = H\left(x\left(\mu_M\right)\right). \tag{1.120}$$

Finally we find the Legendre transformation of the function $H(M)$ and label it by $G\left(\mu_M\right)$:

$$G\left(\mu_M\right) = \left(\mu_M, M\left(\mu_M\right)\right) - H\left(M\left(\mu_M\right)\right) = G\left(\mu\left(\mu_M\right)\right). \tag{1.121}$$

Thus, without solving any equations, based on the functions $H(x)$ and $G(x)$, we determine the dependences $\mu\left(\mu_M\right)$, $x\left(\mu_M\right)$, $M\left(\mu_M\right)$, $H\left(M\left(\mu_M\right)\right)$, and $G\left(\mu_M\right)$. Note that at the assumptions made the reversibility of the transformation $M \to \mu_M$ follows from the reversibility of the transformation $x \to \mu$. Moreover, the function $M\left(\mu_M\right)$ is constructed in an explicit form. Convexity of $H(M)$ follows from convexity of $H(x)$.

We pass to the problem of excluding "fast" variables. Let an autonomous system of differential equations

$$\dot{x} = F(x) \tag{1.122}$$

be set with smooth right-hand sides. A balance polyhedron is given by the equations and inequalities (1.116).

Suppose that in the region of initial conditions x^0, the solutions $x(\tau)$ to (1.122) behave in the following manner: Vector $x(\tau)$ approaches the value determined by the values of slow variables M; after that, x can be determined accurately to be a function M and the function itself the same for all initial conditions.

Thus, for each value of M there is $x = x^{\mathrm{eq}}(M)$ such that, if $M\left(x^0\right) = M^0$, then $x(\tau)$ appears fast in a small neighborhood of $x^{\mathrm{eq}}(M^0)$, and eventually gets close to $x^{\mathrm{eq}}(M)$.

Normally, rigorous substantiation of the assumptions made in situations of real complexity fails, and this fact is probably the weakest point in the method of excluding fast variables suggested in [58]. This method's initial assumptions are related to the assurance that the change in macroscopic variables can be described by the system of autonomous differential equations of the first order. If the change cannot be described thus, then a list of macroscopic variables should probably be added, based on the physical features of the described process.

If the function $x^{\mathrm{eq}}(M)$ is known, we can write

$$\dot{M} = lF\left(x^{\mathrm{eq}}(M)\right), \quad \dot{M}_j = \sum_i l_{ij} F_i\left(x^{\mathrm{eq}}(M)\right). \tag{1.123}$$

Generally speaking this equation can be used only on limited intervals of time. On the right-hand side of (1.123), $lF\left(x^{\mathrm{eq}}(M)\right)$ still does not accurately coincide with $lF\left(x(\tau)\right)$. This inaccuracy may lead to an accumulation of errors in computations and, as a result, to a great discrepancy between the solution of (1.123) and the true value of $M\left(x(\tau)\right)$ over a rather long computation time. The exception occurs in the case where, according to (1.123), $M(\tau)$ strives to the only stable, fixed point as $\tau \to \infty$. If the solution to (1.123) and the true values of $M\left(x(\tau)\right)$ do not diverge much in the time during which the solution to (1.123) enters a small neighborhood of the fixed point, equations (1.123) can be used as $\tau \to \infty$ as well.

The function $x^{\mathrm{eq}}(M)$ for a separate system cannot be constructed uniquely, however, the arbitrariness is small in the same sense as the neighborhood of $x^{\mathrm{eq}}\left(M\left(x(\tau)\right)\right)$ is small where, after some short time interval, the motion occurs.

If the Lyapunov function $H(x)$ that decreases along trajectories (solutions) is known for the system (1.122), we can try to construct the dependence $x^{\mathrm{eq}}(M)$ as a solution to the problem

$$H(x) \to \min, \quad lx = M.$$

This way seems natural but the function H may appear to be very sensitive to the changes in the slow variables and to be not very sensitive to the changes in the fast variables. In this case the construction of $x^{\mathrm{eq}}(M)$ as a point of the conditional minimum H will not necessarily lead to the desirable result. In applications, the system (1.122) normally depends on a number of parameters. It seems most sensible to use a Lyapunov function that does not depend on them, if one exists. This is particularly important in the case where, among the parameters, there are parameters whose value determines the possibility of dividing the variables into fast and slow ones.

Thus, when excluding fast variables, we will suppose that the problem (1.116) has the only solution; the minimum point $x^{\mathrm{eq}}(M)$ and the function $H(M)$ smoothly depend on M. Given the value $\mu_M = \nabla_M H(M)$, we can find $\mu\left(\mu_M\right)$ and $x\left(\mu\left(\mu_M\right)\right)$ (see (1.119)–(1.121)). As a result, we obtain

$$\dot{M} = lF\left(\nabla_\mu G\left(\mu\right)\big|_{\mu=\mu_M l}\right), \tag{1.124}$$

where $\mu_M l$ is the product of the vector of line μ_M by matrix l:

$$(\mu_M l)_i = \sum_j \mu_{M_j} l_{ij};$$

$\nabla_\mu\ G$ is a vector with components $\frac{\partial G}{\mu_i}$, the derivatives are taken at the point $\mu = \mu_M l$.

The right-hand sides of equations (1.124) are defined as functions of μ_M. To set them as functions of M, we have to make the Legendre transformation, find the function $H(M)$ through $G\left(\mu_M\right)$ in (1.121) and, thus,

$$\mu_M(M) = \nabla_M H(M).$$

It is impossible to make this in an explicit form for such a general case. Setting the right-hand sides of kinetic equations as functions of conjugate variables seems a natural and a very convenient method (see, for example, the kinetic law (1.101)). If, originally, the right-hand sides of (1.122) are defined as functions of μ, that is,

$$\dot{x} = \Psi(\mu),$$

then equations (1.124) acquire a particularly simple form:

$$\dot{M} = l\Psi\left(\mu_M l\right). \tag{1.125}$$

$H(M)$ is the Lyapunov function for (1.124); its derivative with respect to time by virtue of system (1.124) is nonpositive. Indeed,

$$H(M) = \left(\mu_M, l\Psi\left(\mu_M l\right)\right) = \left(\mu_M l, \Psi\left(\mu_M l\right)\right) \le 0,$$

as $(\mu, \Psi(\mu)) = \dot{H}x \le 0$.

When necessary, we can easily further exclude the variables from (1.124) using the function $H(M)$. The right-hand sides of the obtained equations will be set as functions of conjugate variables and the function of minimum will again appear to be the Lyapunov function. We emphasize that (1.125) does not include the functions H and G in the explicit form at all—they appear only in the cases where it is necessary to find the relation between variables M and μ_M or x and μ.

Convexity of H, strictly speaking, was not used anywhere, however, the natural area of applying the described formalism is in the systems with convex Lyapunov functions $H(x)$. Otherwise there can exist many extrema.

In *Equilibrium Encircling* the presented method of excluding fast variables is also applied to probabilistic systems, the processes of which are described by Markov ergodic circuits. Probabilistic models turn out to be necessary when it is important to observe the principle of detailed balancing in a studied system.

The principle does not follow from the presence of a global equilibrium point that corresponds to the maximum of total entropy of the system. A condition for its observance is microreversibility, which can be described as a random Markov processes.

In *Equilibrium Encircling* there is also a brief analysis of macroscopic kinetic (dynamics) equations that are written in a unified form suggested by L.I. Rozonoer [148]. This form can be used to analyze and solve equations of chemical kinetics, Markov chains, and dynamics of average values (mathematical expectations).

The general form of the kinetic equations is:

$$\left.\begin{aligned} \dot{M}_j &= \left[\frac{\partial \Phi(X,Y)}{\partial Y_j} - \frac{\partial \Phi(X,Y)}{\partial X_j}\right]_{x=\mu(M),y=0} \\ \dot{M} &= \left[\nabla_y \Phi(X,Y) - \nabla_x \Phi(X,Y)\right]_{x=\mu(M),y=0} \end{aligned}\right\} \tag{1.126}$$

where $\Phi(X, Y)$ is kinetic function, and $\mu(M)$ is a potential. The derivatives of (1.126) are taken at the point $X = \mu(M) = -\nabla_M S$, $Y = 0$. The function S, implying entropy in the problems discussed here in the given formal presentation, is called a “structural function”.

For the equations of chemical kinetics with kinetic law (1.101), the function Φ is represented as a sum by stages $\sum\limits_s \Phi_s$

$$\Phi_s(X,Y) = V(X+Y)\varphi_s(X+Y) \cdot \begin{pmatrix} \exp\left(\sum\limits_j \left(\alpha_{sj}X_j + \beta_{sj}Y_j\right)\right) \\ + \exp\left(\sum\limits_j \left(\beta_{sj}X_j + \alpha_{sj}Y_j\right)\right) \end{pmatrix} \tag{1.127}$$

where V and φ_s are presented as functions of pseudopotentials: $V(m, \text{const})$, $\varphi_s\ (m, \text{const})$, $V(X+Y)$, $\varphi_s(X+Y)$ are the values of these functions at $m = X + Y$. Here the function Φ is symmetrical: $\Phi(X, Y) = \Phi(Y, X)$.

Equations (1.126) can be rewritten in the following form:

$$\dot{M} = -\left[\nabla_z \Phi\left(Z, \mu(M) - Z\right)\right]_{z=\mu(M)}. \tag{1.128}$$

From (1.128) follows the statement underlying the method of local potential—a unique variation principle for the equations of macroscopic dynamics. Let $T > 0$ and $M(\tau)$ be a smooth function τ on the section $[0, T]$. Construct by $M(\tau)$ the function of $\varphi_\tau(Z)$–a local potential

$$\varphi_\tau(Z) = \Phi\left(Z, \mu\left(M(\tau)\right) - Z\right) + \left(M(\tau), Z\right). \tag{1.129}$$

The function $M(\tau)$ is the solution of (1.128) if and only if for any $\tau \in [0, T]$ among the critical points $\varphi_\tau(Z)$ there is a point $Z = \mu\left(M(\tau)\right)$such that

$$\left[\nabla_z \varphi_\tau(Z)\right]_{z=\mu(M)} = 0. \tag{1.130}$$

This is another form of (1.126). If the local potential $\varphi_\tau(Z)$ is a convex function this statement can be a basis for effective computational methods that employ well-developed algorithms of convex programming [19, 94, 142]. Particularly this relates to the problem of search for a steady state. The point M is fixed for (1.126) if and only if among the critical points of the function

$$\varphi_{s\tau}(Z) = \Phi\,(Z, \mu(M) - Z) \tag{1.131}$$

there is a point $Z = \mu(M) : [\nabla_z \varphi_{s\tau}(Z)]_{z=\mu\ (M)} = 0$.

In *Equilibrium Encircling* examples are given of the use of equations (1.126) and the method of local potential for the analysis of linear laws of conservation, law of mass action, equations of chemical kinetics, Markov chains and average values, and the relation of microreversibility with nonlinear Onsager reciprocal relationships. Three conditions of "thermodynamic character" have been formulated for regular (with concave $S(M)$ and convex $\Phi(x, y)$) systems: existence of the Lyapunov function, uniqueness and stability of the equilibrium.

Localization of Steady States of Open Systems

This problem addressed in Chapter 6 of *Equilibrium Encircling* is of special interest from the standpoint of this book. Indeed, most of the natural and technological systems that make up the subject matter of the studies discussed here are open systems. In order to study the systems by models of closed systems presented in subsequent chapters it is necessary to understand the *Equilibrium Encircling* chapter abstracted below.

For closed systems with an equilibrium environment, thermodynamic Lyapunov functions can be constructed. Provided the functions are convex and the values of balances are fixed, there is only one positive equilibrium point. If a system and an equilibrium environment exchange matter, the situation does not essentially change. The Lyapunov function can be constructed again and so on. Dynamics can change qualitatively if the studied system exchanges matter or energy with the nonequilibrium environment. Here, it is naturally supposed that the environment is a rather big system whose state, practically speaking, does not change on the time intervals of interest to us. Otherwise, if we were to combine the system with its environment we would obtain an isolated system tending toward its equilibrium.

Consider homogeneous and heterogeneous open systems with $V = \text{const}$ that exchange matter and energy with the nonequilibrium environment whose state is supposed to be constant.

First, write the equations of change in composition and energy with time for the homogeneous system

$$\dot{x} = V \sum_s \gamma_s w_s(c, T) + \upsilon_{\text{ent}} c_{\text{ent}} - \upsilon_{\text{out}} c_{\text{out}}, \tag{1.132}$$

$$\dot{U} = \varphi\,(T_{\text{ent}} - T) + \upsilon_{\text{ent}} u\,(c_{\text{ent}} T_{\text{ent}}) - \upsilon_{\text{out}} u(c, T), \tag{1.133}$$

where υ is flow rate; c is concentration; φ is coefficient of heat transfer; u is internal energy density; $T = T(x, U, V)$; indices "ent" and "out" refer to the input and output flows, respectively.

Equations (1.132) and (1.133) are written with the assumption of ideal mixing (continuous stir), which will be assumed later, as well. Under the isothermal conditions we can assume $T = T_{\text{ent}}$ and neglect equation (1.133).

According to the written equations all the substances are removed from the system with the same rate. For applications, however, an important case is one in which a part of the substances exists only inside the system is important. Heterogeneous-catalytic systems can be a good example of this. In this case we can distinguish in the system two groups of substances and three groups of reactions: reactions inside the first group of substances (taking part in the mass transfer to the environment); reactions with participation of substances of both groups and reactions inside the second group (not going beyond the system). It is natural to suppose that the substances of the first and second groups form different phases. Sometimes it makes sense to set off the third phase, i.e., the phase of an interface between the first two.

We mark the values relating to the first group of substances with superscript 1 and those relating to the second group by superscript 2 to write

$$
\begin{aligned}
\dot{x}^1 &= V^1 \sum_s \gamma_s^1 w_s^1 \left(c^1, T\right) + V^{12} \sum_\sigma \gamma_{\sigma 1}^{12} w_\sigma^{12} \left(c^1, c^2, T\right) + \upsilon_{\text{ent}} c_{\text{ent}}^1 - \upsilon_{\text{out}} c^1, \\
\dot{x}^2 &= V^{12} \sum_\sigma \gamma_{\sigma 2}^{12} w_\sigma^{12} \left(c^1, c^2, T\right) + V^2 \sum_z \gamma_z^2 w_z^2 \left(c^2, T\right), \qquad (1.134) \\
\dot{U} &= \varphi \left(T_{\text{ent}} - T\right) + \upsilon_{\text{ent}} u^1 \left(c'_{\text{ent}}, T_{\text{ent}}\right) - \upsilon_{\text{out}} u^1 \left(c, T\right),
\end{aligned}
$$

where $\left(\gamma_{\sigma 1}^{12}, \gamma_{\sigma 2}^{12}\right)^T$ is a stoichiometric vector of the stage that involves the substances of both groups; $\gamma_{\sigma 1}^{12}$ is made up of stoichiometric coefficients of the first group; $\gamma_{\sigma 2}^{12}$ is made up of stoichiometric coefficients of the second group; V^{12} characterizes the region of phase contact; subscripts s, z, σ relate to reactions in the first phase, the second phases, and to reactions that involve substances of both phases, respectively.

The particular cases (1.134) in which flow rates are large is considered most often. Here, it is normally supposed that $c^1 = c_{\text{ent}} = \text{const}$, $T = T_{\text{ent}} = \text{const}$ and the subsystem (1.134) for c^2 is written separately:

$$
\dot{x}^2 = V^{12} \sum_\sigma \gamma_{\sigma 2}^{12} w_\sigma^{12} \left(c^1, c^2, T\right) + V^2 \sum_z \gamma_z^2 w_z^2 \left(c^2, T\right). \qquad (1.135)
$$

It is well known that in the systems described by equations (1.132)–(1.135) there can be several steady states. The thermodynamic analysis does not allow their exact number to be determined or even their approximate number to be assessed. It is only possible to indicate the region that contains all steady states. This region is sought based on the following simple considerations. The terms in the right-hand sides of the equations (1.132)–(1.134) are divided into two groups: the "thermodynamic" terms, which do not include the transfer rates, and the "transfer" terms, which do include them. The thermodynamic terms contribute negatively to the derivative of the thermodynamic Lyapunov function, therefore, at a stationary point, the contribution of the "transfer" terms to the derivative should be positive. These considerations should be supplemented by the analysis of balance relations.

To study the system (1.132), (1.133) we choose the free Helmholtz energy divided into RT_{ent} as the Lyapunov function G:

$$G = \frac{U - T_{\text{ent}} S(x, U, V)}{RT_{\text{ent}}}.$$

The derivative of G due to (1.132) and (1.133) is

$$\begin{aligned}\dot{G} = -V \sum_s w_s \ln \frac{w_s^+}{w_s^-} - \frac{\varphi\,(T - T_{\text{ent}})^2}{RTT_{\text{ent}}} + \sum_j m_j(c, T)\left(\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j\right) \\ + \frac{(T - T_{\text{ent}})\,\upsilon_{\text{ent}} u(c, T)}{c_{\text{ent}} T_{\text{ent}}} - \frac{\upsilon_{\text{out}} u(c, T)}{RTT_{\text{ent}}}\end{aligned} \tag{1.136}$$

In the steady state $\dot{G} = 0$, therefore, for any stationary point $\left(c^0, T^0\right)$

$$\begin{aligned}\sum_j m_j\left(c^0, T^0\right)\left(\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j^0\right) \\ + \left(T^0 - T_{\text{ent}}\right)\left(\upsilon_{\text{ent}} u\left(c_{\text{ent}}, T_{\text{ent}}\right) - \upsilon_{\text{out}} u\left(c, T^0\right)\right) \geq 0\end{aligned} \tag{1.137}$$

The inequality (1.137) provides an estimate of the region of steady states of the system. In the stationary point both $\dot{x} = 0$ and $\dot{U} = 0$ and the contributions of thermodynamic terms of $\dot{x}$ and $\dot{U}$ to $\dot{G}$ are negative; therefore, instead of (1.137), two inequalities can be written:

$$\sum_j m_j\left(c^0, T^0\right)\left(\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j^0\right) \geq 0, \tag{1.138}$$

$$\left(T^0 - T_{\text{ent}}\right)\left(\upsilon_{\text{ent}} u\left(c_{\text{ent}}, T_{\text{ent}}\right) - \upsilon_{\text{out}} u\left(c, T^0\right)\right) \geq 0. \tag{1.139}$$

The inequality (1.139) means that flow of energy transferred by the material flow and the flow related to heat conductivity have different signs. This is obvious and follows from the energy conservation law. The inequality (1.138) is more interesting. Its physical sense consists of the fact that the entropy flow related to the material flow is negative. In the steady state the flow of negative entropy from outside should compensate for the entropy production in the system. Banning the reactions, i.e., leaving in the initial equations for x only the transfer terms, the left-hand side of the inequality (1.138) will equal $-\dfrac{dS}{d\tau}\dfrac{1}{R}$. Indeed, we write the system of equations

$$\dot{x} = \upsilon_{\text{ent}} c_{\text{ent}} - \upsilon_{\text{out}} c_{\text{out}}.$$

We find the derivative of $S(x, U, V)$:

$$\frac{\partial S}{\partial x_j} = -Rm_j, \quad \frac{dS}{d\tau} = -R \sum_j m_j(c, T)\left(\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j\right).$$

Here we use the circumstance that, in the steady state, $\dot{U} = 0$. Note that the expression obtained for $\dot{S}$ does not coincide with the difference of entropies of input and output flows. This is due to entropy increase at mixing.

To find the relationship between υ_{ent} and υ_{out} use the balance relation

$$\sum_j a_{ij}\left(\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j^0\right) = 0. \tag{1.140}$$

which is satisfied in the steady state. Hence,

$$\upsilon_{\text{out}} = \upsilon_{\text{ent}} \frac{\sum\limits_j a_{ij} c_{j\text{ent}}}{\sum\limits_j a_{ij} c_j^0}. \tag{1.141}$$

For calculations introduce the function $f(c, T)$ equal to the density of the Helmholtz energy divided by *RT*:

$$f(c, T) = \frac{U - TS}{RTV}, \qquad \frac{\partial f(c, T)}{\partial c_j} = m_j.$$

Using f, the inequality (1.138) acquires the form

$$\sum_j \left(\frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}} - c_j^0\right) \frac{\partial f\left(c^0, T^0\right)}{\partial c_j^0} \geq 0. \tag{1.142}$$

The inequality has a simple geometrical sense. Consider the region of concentrations c in which $f\left(c, T^0\right) \leq f\left(c^0, T^0\right)$. Draw a hyperplane of support via the point c^0. This hyperplane divides the set of all c into two half-spaces so that in one of them,

$$\sum_j \left(c_j - c_j^0\right) m_j \left(c^0, T^0\right) \geq 0, \tag{1.143}$$

while in the other, this inequality does not hold. The inequality (1.142) means that the vector $\frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{\text{ent}}$ lies in the half-space where (1.143) is satisfied.

Note that the convexity of the function $f(c, T)$ does not guarantee the convexity of the region of c^0 for which (1.142) is satisfied. From (1.142) we can pass to the inequalities with convex functions if we assume a constant pressure and use the Gibbs energy G instead of the Helmholtz energy. This substitution provides conservation of all the intensive values.

Since

$$G = \sum_j x_j \mu_{xj},$$

inequality (1.138) can be presented in the form

$$\upsilon_{\text{ent}} \sum_j \mu_{xj} c_{j\text{ent}} - \upsilon_{\text{out}} \frac{G(x, T, P)}{V} \geq 0. \tag{1.144}$$

Here the first term is a rate of the free enthalpy inflow to the system with the mixing losses deducted. The inequality itself means that this inflow exceeds the amount of free enthalpy carried away by the material flow—part is spent on chemical reactions.

For ideal systems

$$\sum_j \left(m_j^0\left(T^0\right) + \ln c_j^0\right)\left(\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j^0\right) \geq 0. \tag{1.145}$$

At fixed T^0, c_{ent}, ν_{ent} and ν_{out}, the left-hand side of (1.145) is a concave function since the matrix of the second derivatives is diagonal with negative elements along the diagonal:

$$\frac{d^2\left[\left(\ln c_j + m_j^0(T)\right)\left(\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j\right)\right]}{dc_j^2} = -\frac{\upsilon_{\text{ent}} c_{j\text{ent}}}{c_j^2} - \frac{\upsilon_{\text{out}}}{c_j}.$$

The region of possible values c^0 that corresponds to the inequality (1.145) is convex. This region contains the detailed balancing point c^{eq} that meets the balance relations

$$\sum_j a_{ij}\left(\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j^{\text{eq}}\right) = 0. \tag{1.146}$$

Indeed, the vector with components $m_j\left(c^{\text{eq}}, T^0\right)$ is orthogonal to all vectors γ for which $\sum_j a_{ij}\gamma_j = 0$. According to (1.146) the scalar product of vector $m_j\left(c^{\text{eq}}, T^0\right)$ by the vector with components $\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j^{\text{eq}}$ equals zero and the point c^{eq} lies on the boundary line of the region set by the inequality (1.145). All the points that satisfy (1.145) lie on the one and the same side of the hyperplane of support drawn via c^{eq}. The plane is set by the equation

$$\sum_j \left(c_j^0 - c_j^{\text{eq}}\right)\left[\frac{\upsilon_{\text{ent}} c_{j\text{ent}}}{c_j^{\text{eq}}} - \upsilon_{\text{out}}\left(\ln c_j^{\text{eq}} + m_j^0\left(T^0\right) + 1\right)\right] = 0. \tag{1.147}$$

This is the consequence of convexity of the region of possible c^0 values. Thus, at given T^0, c_{ent}, υ_{ent}, υ_{out} the stationary values of concentrations c_j^0 should satisfy the linear inequality

$$\sum_j \left(c_j^0 - c_j^{\text{eq}}\right)\left[\frac{\upsilon_{\text{ent}} c_{j\text{ent}}}{c_j^{\text{eq}}} - \upsilon_{\text{out}}\left(\ln c_j^{\text{eq}} + m_j^0\left(T^0\right) + 1\right)\right] \geq 0. \tag{1.148}$$

We can interpret (1.148) as follows: in the continuous stir flow reactor (CSFR), the steady state should lie on the same side of equilibrium as the input mixture. The stationary equilibrium detour in such a reactor is impossible. Input mixture composition here is by the vector $\frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{\text{ent}}$. It also belongs to the boundary line of the region given by the inequality (1.145), for $\upsilon_{\text{ent}} c_{j\text{ent}} - \upsilon_{\text{out}} c_j = 0$ at all j. We can write the analog of (1.148) having found the hyperplane of support at the point $\frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{\text{ent}}$. This hyperplane is set by the equation

$$\sum_j \left(c_j^0 - \frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}}\right)\left(\ln \frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}} - m_j^0\left(T^0\right)\right) = 0. \tag{1.149}$$

For any steady state of c^0 the linear inequality

$$\sum_j \left(c_j^0 - \frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}}\right)\left(\ln \frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}} - m_j^0\left(T^0\right)\right) \le 0. \tag{1.150}$$

is satisfied.

The preceding can be interpreted as follows: The steady state of the homogeneous CSFR lies on the same side of the input mixture as the equilibrium.

Summing up the analysis of the inequalities (1.138), (1.139), (1.145), (1.148) and (1.150), we note that at the given υ_{ent}, υ_{out} and T^0 the steady state of the homogeneous CSFR belongs to a set specified by the inequalities (1.138) and (1.139). Its special case (1.145) for chemically ideal systems is determined by the convex set. It contains the vector of equilibrium concentrations c^{eq} and the vector $\frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}}$. These vectors lie on the boundary line of the set and for them the inequalities (1.138) and (1.139) become equalities. The stationary state lies in the vicinity of c^{eq} at high rates of chemical reactions and near $\frac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}}$, at high flow rates.

Akramov and Yablonsky found that at the given functions of $w_s(c, T)$ and high enough flow rates the steady state of the homogeneous CSFR is unique and stable: At a place “very far” from the equilibrium the homogeneous system with ideal mixing behaves in the same manner as in the vicinity of it.

To analyze steady states of the heterogeneous CSFR we can use the equation (1.134) and write the inequality

$$\sum_j m_j^1\left(c^0, T^0\right)\left(\upsilon_{\text{ent}} c_{j\text{ent}}^1 - \upsilon_{\text{out}} c_j^{01}\right) \ge 0, \tag{1.151}$$

which, like similar inequalities for a homogeneous system, means that the entropy flow from the environment to the system is negative. The concentrations of substances of the second phase can enter into (1.151) only via dependence of m_j^1 on them. The existence of such dependence seems to be an extremely rare situation.

The relations of balances in the incoming flow and steady state are described in a way similar to (1.140):

$$\sum_j a_{ij}^1\left(\upsilon_{\text{ent}} c_{j\text{ent}}^1 - \upsilon_{\text{out}} c_j^{01}\right) = 0, \tag{1.152}$$

where c^{01} is a vector of stationary concentrations of the first phase.

Here, however, there is a distinction from homogeneous systems. The relations (1.152) contain the balance coefficients of substances of the first phase only and already are not as simple as (1.140). Indeed, the phases exchange the matter, and in the balance relations for a closed system the quantities of substances in different phases are summed up with relevant coefficients.

The boundary line of a set of concentrations that was given by the inequalities (1.151) contains an equilibrium point $c^{1\text{eq}}$ that is determined from the balance relations (1.152) and chemical equilibrium conditions. Note that the concentrations of substances of the second group enter into neither the inequality (1.151) nor the equation (1.152) nor the composition equilibrium condition. All the calculations can be performed as if there were no second phase. It is well known that at equilibrium between phases the composition of each phase is equilibrium. In heterogeneous catalytic reactions the catalysis does not shift the complete equilibrium point. As we see both equilibrium and thermodynamic estimations of steady states are not shifted by catalysis and, in the general case, by interaction of phases. For chemically ideal systems in the steady state of CSFR, the composition of the phase whose flow goes through the reactor cannot overcome the equilibrium, i.e., we can write the inequality of the form (1.148).

At first sight it seems strange that the composition cannot be assessed in a similar way for a phase that is neither input to reactor nor output from it. It seems that the possible changes of this composition are more arbitrary, at least from the viewpoint of thermodynamics. Indeed, if the exchange mechanism, i.e., the list of elementary reactions with participation of substances of both phases, is unknown, then it is difficult to assess the possible stationary values of c^2 by thermodynamics.

If the reaction mechanism is known, then it is possible for us to more accurately assess the region of steady states of an open system. In the assumption of a stage-by-stage coordination of the thermodynamic and kinetic laws, thermodynamics allows one to determine the directions of all the elementary stages at each point. A special part here is played by the surfaces of stage equilibria that are set by linear equations relative to the chemical potentials $(\gamma, \mu_x) = 0$.

Let us consider first the system of equations (1.135). At fixed c^1 and T or each σ, it is true that

$$\begin{aligned} w_\sigma^{12}\left(c^1, c^2, T\right) &> 0, \ \text{if}\left(\gamma_{\sigma 1}^{12}, \mu_{x1}\right) + \left(\gamma_{\sigma 2}^{12}, \mu_{x2}\right) < 0, \\ w_\sigma^{12}\left(c^1, c^2, T\right) &< 0, \ \text{if}\left(\gamma_{\sigma 1}^{12}, \mu_{x1}\right) + \left(\gamma_{\sigma 2}^{12}, \mu_{x2}\right) > 0, \end{aligned} \tag{1.153}$$

where μ_{x1}, μ_{x2} are vectors of chemical potentials of substances of the first and second groups, respectively. In the assumption that μ_{x1} is a function of c^1 and T, we have that the scalar product $\left(\gamma_{\sigma 1}^{12}, \mu_{x1}\right)$ at set c^1 and T is a constant value. Denote it by δ_σ.

Similarly to (1.153) the signs of rates $w_z^{12}\left(c^2, T\right)$ are determined. For each z

$$\begin{aligned} w_z^2\left(c^2, T\right) &> 0, \ \text{if}\left(\gamma_z^2, \mu_{x2}\right) < 0, \\ w_z^2\left(c^2, T\right) &< 0, \ \text{if}\left(\gamma_z^2, \mu_{x2}\right) > 0. \end{aligned} \tag{1.154}$$

The right-hand side of the equations (1.135) is a sum with nonnegative coefficients of the vectors $\gamma_{\sigma 2}^{12}\text{sign}(w_\sigma^{12})$, $\gamma_z^2\text{sign}(w_z^2)$ at all σ, z. The function $\text{sign}(w) = 1$ if $w > 0$; $\text{sign}(w) = -1$ if $w < 0$; $\text{sign}(w) = 0$ if $w = 0$. Therefore, the coefficient in (1.135) at γ can be rigorously positive when $w = 0$. Thus, the right-hand part of (1.135) can always be represented as a sum with positive coefficients of the vectors $\gamma_{\sigma 2}^{12}\text{sign}(w_\sigma^{12})$, $\gamma_z^2\text{sign}(w_z^2)$.

Consider c^{02} to be a stationary point of (1.135), then there is such a set of positive numbers $\lambda_\sigma > 0$, $\lambda_z > 0$ for which, in this point,

$$\sum_\sigma \lambda_\sigma \gamma^{12}_{\sigma 2}\mathrm{sign}(w^{12}_\sigma) + \sum_z \lambda_z \gamma^2_z \mathrm{sign}(w^2_z) = 0. \tag{1.155}$$

This statement allows inversion: if, for the given point c^{02} there are positive numbers λ_σ, λ_z such that conditions (1.155) are met, then there are such rate functions w_σ and w_z coordinated with thermodynamics for which c^{02} is a steady state. For the kinetic law of mass action, for example, a stationary character of c^{02} can be obtained by an appropriate rate constant change that does not affect the equilibrium constants.

The equality (1.155) contains only the signs of the function w. They can be determined if we know the stoichiometric vectors and chemical potentials (see (1.153) and (1.154)). The simplest way to determine them is to choose as the base coordinates the chemical potentials μ_{x2} rather than the concentrations of c^2. At fixed c^1 and T a set of hyperplanes (1.153), (1.154) is used to divide the space of chemical potentials into sets that have rates of stages with a constant sign. The number of these sets is finite and they are given by the systems of linear inequalities and equations of the form

$$\delta_\sigma + \left(\gamma^{12}_{\sigma 2}, \mu_{x2}\right) \geq\leq 0, \ \left(\gamma^2_z, \mu_{x2}\right) \geq\leq 0. \tag{1.156}$$

For each arrangement of signs in (1.156) we can answer the question if a set of positive numbers λ_σ, λ_z exists such that (1.155) is true at a given arrangement of signs. If such a set exists, then any point of the set determined by the inequalities and equations (1.156) can be a steady state; otherwise, no point of this set can be one.

The notion of *signature* is introduced to construct sets of stationary points. The signature is a set of numbers ε_σ, ε_z such that for any σ, z there will be $\varepsilon_\sigma, \varepsilon_z = 1, -1$, or 0. Each signature ε is bound to a set of those μ_{x2} for which at all σ, z

$$\mathrm{sign}\left(\delta_\sigma + \left(\gamma^{12}_{\sigma 2}, \mu_{x2}\right)\right) = -\varepsilon_\sigma, \ \ \mathrm{sign}\left(\gamma^2_z, \mu_{x2}\right) = -\varepsilon_z. \tag{1.157}$$

Denote this set as M_ε.

For each signature ε we can find out if there positive numbers λ_σ, λ_z such that

$$\sum_\sigma \lambda_\sigma \gamma_\sigma^{12} \varepsilon_\sigma + \sum_z \lambda_z \gamma_z^2 \varepsilon_z = 0. \tag{1.158}$$

Denote as E the set ε for which such combinations of λ_σ and λ_z exist. The set of all possible values of chemical potentials μ_{x2} in the stationary points is

$$M^0 = \bigcup_{\varepsilon \in E} M_\varepsilon. \tag{1.159}$$

The set M^0 can be considered an analog of the set of equilibrium points for the system (1.155). It is not always convex but it is a combination of a finite number of convex sets M_ε.

To refer the region of potential stationary states to the inequalities and equations that describe M it is necessary to add corresponding balance relationships. Here, unfortunately, the linearity is lost: inequalities and equations that describe M^0 are linear in coordinates μ_{x2}, and balance relationships are linear in coordinates c^2.

Let us pass to the analysis of the homogeneous reactor of ideal mixing (1.132), (1.133). For each stage the equilibrium surface is given by the equation $(\gamma, \mu_x) = 0$, a $\operatorname{sign}(w) = -\operatorname{sign}(\gamma, \mu_x)$. We let $\upsilon_{\text{ent}}, c_{\text{ent}}, T_{\text{ent}}, \upsilon_{\text{out}}$, and T be fixed, and we consider only the equations (1.132) for x. Assumeing $\upsilon_{\text{ent}} = \upsilon_{\text{out}} = \upsilon$, we do not lose generality as the equations contain only the product $\upsilon_{\text{ent}} c_{\text{out}}$. The value of concentrations c^0can be stationary only in the case of such numbers $\lambda_s > 0$ that in the point $c = c^0$:

$$\sum_s \lambda_s \gamma_s \operatorname{sign}(w_s) + \left(c_{\text{ent}} - c^0\right) = 0. \tag{1.160}$$

The set of all sums of vectors $\gamma_s \operatorname{sign}(w_s)$ with positive coefficients for each point c^0 forms a convex cone. The sets of the c^0, to which the same sets of vectors $\gamma_s \operatorname{sign}(w_s)$ correspond, are set by finite systems of equations and inequalities of the form

$$\sum_{j=1}^{n} (\gamma_s)_j \, \mu_{xj} = \left(\gamma_s, \mu_x\right) \geq\leq 0, \tag{1.161}$$

that are linear in the coordinates μ_x.

Compare with each signature ε_s a "compartment," the set M_ε specified in the coordinates μ_x by a linear system of equations and inequalities

$$\operatorname{sign}(\gamma_s, \mu_x) = -\varepsilon_s. \tag{1.162}$$

In the compartment M_ε we have $\operatorname{sign}(w_s) = \varepsilon_s$ for all s. For some ε the system (1.162) may turn out to be incompatible and the set M_ε may appear to be empty. Each signature ε is corresponds to a convex set Q_ε made up by all the sums of vectors $\gamma_s \varepsilon_s$ with positive coefficients: $q \in Q_\varepsilon$ if and only if there is a combination of positive numbers λ_s such that $q = \sum_s \lambda_s \gamma_s \varepsilon_s$. We describe Q_ε by linear equations and inequalities for all ε such that $M_\varepsilon \neq \emptyset$. If the point c^0 belongs to M_ε, it can be stationary only when $c^0 - c_{\text{ent}} \in Q_\varepsilon$, i.e., if vector $c^0 - c_{\text{ent}}$ satisfies the system of linear equations and inequalities that presets Q_ε.

At a given c_{ent} for each ε we consider the set of those $c \in M_\varepsilon$ for which $c^0 - c_{\text{ent}} \in Q_\varepsilon$. This set can be presented in the form $M_\varepsilon \cap (c_{\text{ent}} + Q_\varepsilon)$. It is given by two systems of equations and inequalities. The first system that describes M_ε is linear in coordinates μ_x; the second one that expresses the belonging of $c^0 - c_{\text{ent}}$ to the set Q_ε is linear in coordinates c. The aggregate of all possible stationary states is

$$\bigcup_\varepsilon [M_\varepsilon \cap (c_{\text{ent}} + Q_\varepsilon)]. \tag{1.163}$$

A detailed analysis of the example of constructing M^0 for the homogeneous CSFR is presented below.

The heterogeneous CSFR (1.134) is considered in a fashion similar to the preceding discussion. For each stage, the scalar product determines the sign of the stage's rate $\{\gamma, \mu_x\}$ and the possibilities of compensating the flow by chemical reactions are studied.

In *Equilibrium Encircling* the principle underlying the assessments of the set of stationary states is called a *principle of swan, crab and pike**—the SCP principle. The sense of this name is in the fact that points are found in which different processes "pull" into different sides in the way that the sum of directing vectors that have positive coefficients equals zero. This condition is necessary for "the carrige to stay there" for the stationary state of the composition. In [58] the SCP principle is extended to more complicated cases of open system behavior when, as $\tau \to \infty$, the stable auto-oscillations and other limiting modes occur.

An Example of Analysis of Possible Stationary States

We demonstrate the construction of the set M^0 for the CFSR (1.132), (1.133) on the elementary example of monomolecular reactions of isomerization.

We let the ideal system be under the isothermal conditions and consist of three substances A_1, A_2, A_3 obeying one balance relations

$$x_1 + x_2 + x_3 = \text{const}.$$

Suppose that the mechanism of reaction is $A_1 \rightleftarrows A_2 \rightleftarrows A_3 \rightleftarrows A_1$. For simplicity, the equilibrium constants for all stages will be taken to be equal to unity, i.e., the point $x_1 = x_2 = x_3 = x_j^{\text{eq}}$ is an equilibrium point. We write the kinetic equation

$$\dot{c} = \sum_{s=1}^{3} \gamma_s w_s + \frac{\upsilon\,(c_{\text{ent}} - c)}{V}, \tag{1.164}$$

where $\gamma_1 = (-1, 1, 0)^T$; $\gamma_2 = (0, -1, 1)^T$; $\gamma_3 = (1, 0, -1)^T$.

In time

$$b = \sum_{j=1}^{3} c_j \to \sum_{j=1}^{3} c_{j\text{ent}} = b_{\text{ent}}.$$

Therefore, we limit ourselves by the study of motion in $D\,(b_{\text{ent}})$, the triangle $c_j > 0, c_1 + c_2 + c_3 = b_{\text{ent}}$. For each three-valued signature $\varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3)$, $\varepsilon_j = 0, \pm 1$, the set M_ε can be determined in $D\,(b_{\text{ent}})$by the system of inequalities and equations $\text{sign}(w_j) = \varepsilon_j$. Of $3^3 = 27$ signatures, only 13 are determined by the nonempty sets M_ε. Among them 6 are two-dimensional, 6 are one-dimensional

---

*Transtator's note: In a classical Russian tale by I. Krylov the three creatures failed to move a carriage, pulling it in different directions.

and 1 consists of one point:

1) $\varepsilon = (1, 1, -1)$, $c_1 > c_2, c_2 > c_3, c_3 < c_1$;
2) $\varepsilon = (-1, 1, -1)$, $c_1 < c_2, c_2 > c_3, c_3 < c_1$;
3) $\varepsilon = (-1, 1, 1)$, $c_1 < c_2, c_2 > c_3, c_3 > c_1$;
4) $\varepsilon = (-1, -1, 1)$, $c_1 < c_2, c_2 < c_3, c_3 > c_1$;
5) $\varepsilon = (1, -1, 1)$, $c_1 > c_2, c_2 < c_3, c_3 > c_1$;
6) $\varepsilon = (1, -1, -1)$, $c_1 > c_2, c_2 < c_3, c_3 < c_1$;
7) $\varepsilon = (1, 0, -1)$, $c_1 > c_2, c_2 = c_3, c_3 < c_1$;
8) $\varepsilon = (0, 1, -1)$, $c_1 = c_2, c_2 > c_3, c_3 < c_1$;
9) $\varepsilon = (-1, 1, 0)$, $c_1 < c_2, c_2 > c_3, c_3 = c_1$;
10) $\varepsilon = (-1, 0, 1)$, $c_1 < c_2, c_2 = c_3, c_3 > c_1$;
11) $\varepsilon = (0, -1, 1)$, $c_1 = c_2, c_2 < c_3, c_3 > c_1$;
12) $\varepsilon = (1, -1, 0)$, $c_1 > c_2, c_2 < c_3, c_3 = c_1$;
13) $\varepsilon = (0, 0, 0)$, $c_1 = c_2 = c_3$.

The other signatures correspond to incompatible systems of inequalities. All the equations and inequalities are linear in coordinates c as the stages are monomolecular and the system is ideal.

Each of the 13 signatures ε corresponds to the set Q_ε, an aggregate of linear combination with positive coefficients of vectors $\gamma_s \varepsilon_s$. The compartments M_ε and sets Q_ε are shown in Fig. 1.3. For $\varepsilon = (0, 0, 0)$ obviously

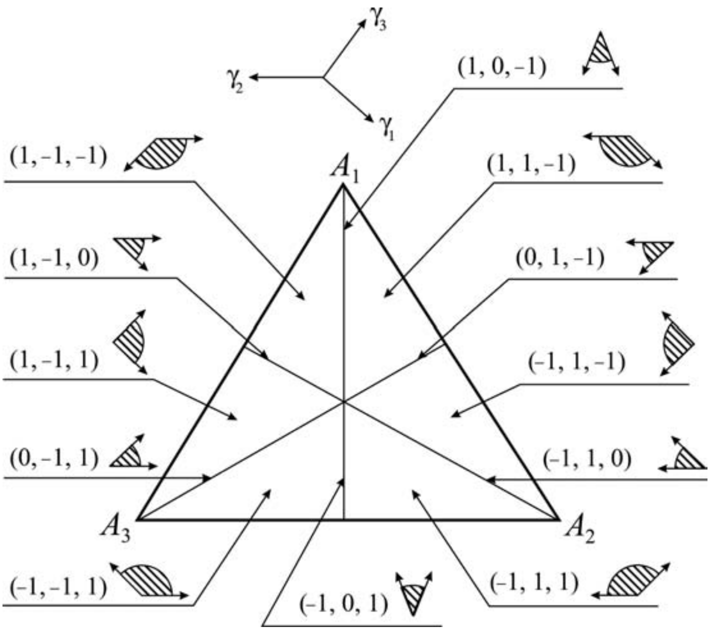

FIGURE 1.3. Compartments M_ε, sets Q_ε (inside the dashed angles).

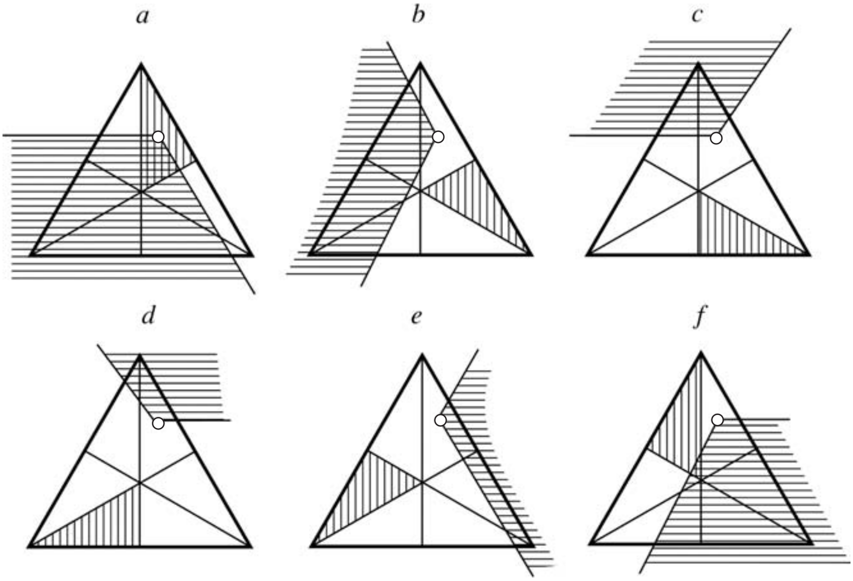

FIGURE 1.4. The sets $c_{\text{ent}} + Q_\varepsilon$ (horizontal dashing) and compartment M_ε (vertical dashing) for signatures. a. (1, 1, –1), b. (–1, 1, –1), c. (–1, 1, 1), d. (–1, –1, 1), e. (1, –1, 1), f. (1, –1, –1).

$Q_\varepsilon = \{0\}$. For the remaining ε the sets Q_ε are corners on the plane that do not include boundary axes. Let concentrations $c_{j\text{ent}}$ be bound by the inequality $c_{1\text{ent}} > c_{2\text{ent}} > c_{3\text{ent}}$. The case of another arrangement of inequalities implies the change in the numbers. The point c^0 of the compartment M_ε can be stationary at some relationship between the rate constants and flow velocity if $c^0 - c_{\text{ent}} \in Q_\varepsilon$. For each compartment M_ε consider the set $c_{\text{ent}} + Q_\varepsilon$. Combination for all ε intersections of $M_\varepsilon \cap (c_{\text{ent}} + Q_\varepsilon)$ is the set of all possible stationary states.

The sets $c_{\text{ent}} + Q_\varepsilon$ for signatures that do not contain zeros are presented in Fig. 1.4, and for signatures that contain zero they are shown in Fig. 1.5. If, as is supposed, $c_{1\text{ent}} > c_{2\text{ent}} > c_{3\text{ent}} \quad (c_{\text{ent}} \in M_\varepsilon, \varepsilon = (1, 1, -1))$, the set $c_{\text{ent}} + Q_\varepsilon$ does not intersect M_ε for $\varepsilon = (-1, 1, 1), (-1, -1, 1), (1, -1, 1)$ (Fig. 1.4*c*–*e*); and $\varepsilon = (-1, 1, 0), (-1, 0, 1), (0, -1, 1), (-1, 1, 0)$ (Fig. 1.5*c*–*f*). For $\varepsilon = (1, 1, -1)$ the intersection $M_\varepsilon \cap (c_{\text{ent}} + Q_\varepsilon)$ is not empty (Fig. 1.4*a*) at all c_{ent} that meet the assumption made: $c_{1\text{ent}} > c_{2\text{ent}} > c_{3\text{ent}}$. Depending on the relationship between $c_{2\text{ent}}$ and $c^{\text{eq}} = \dfrac{c_{1\text{ent}} + c_{2\text{ent}} + c_{3\text{ent}}}{3}$ the set $c_{\text{ent}} + Q_\varepsilon$ can intersect M_ε at four more different ε. Indeed, if $c_{2\text{ent}} < c^{\text{eq}}$, which corresponds to the case shown in Figs. 1.4, 1.5, then $M_\varepsilon \cap (c_{\text{ent}} + Q_\varepsilon) \neq \emptyset$ for $\varepsilon = (1, -1, -1)$ (Fig. 1.4e); and $\varepsilon = (1, 0, -1)$ (Fig.1.5*a*); if $c_{2\text{ent}} > c^{\text{eq}}$, then $M_\varepsilon \cap (c_{\text{ent}} + Q_\varepsilon) \neq \emptyset$ for $\varepsilon = (0, 1, -1)$. Finally, if $c_{2\text{ent}} = c^{\text{eq}}$, then $M_\varepsilon \cap (c_{\text{ent}} + Q_\varepsilon) = \emptyset$ for all ε except for the above $\varepsilon = (1, 1, -1)$. The regions of possible stationary states in the three described cases are shown in

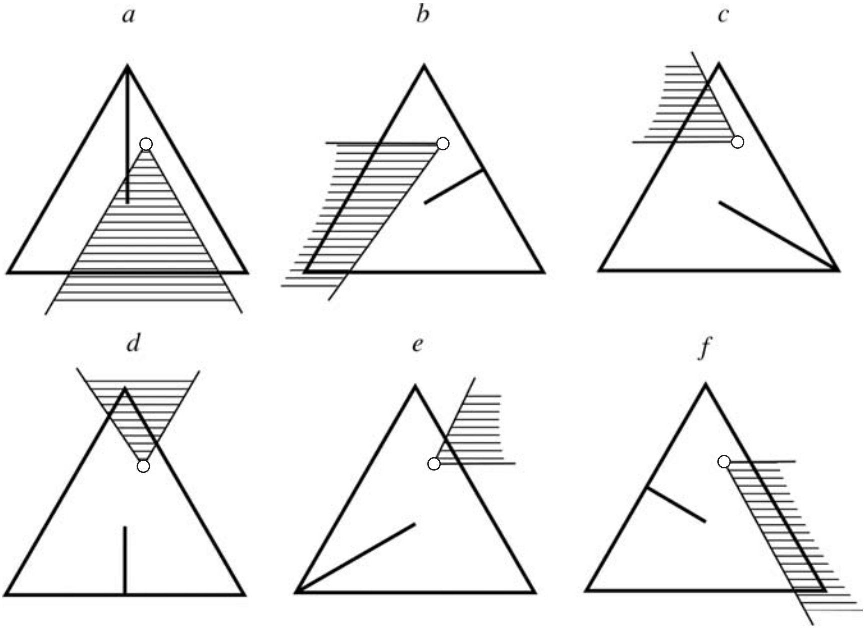

FIGURE 1.5. Sets $c_{\mathrm{ent}} + Q_{\varepsilon}$ (horizontal dashing) and compartments M_{ε} (bold sections) for signatures. *a.* (1, 0, –1), *b.* (0, 1, –1), *c.* (–1, 1, 0), *d.* (–1, 0, 1), *e.* (0, –1, 1), *f.* (1, –1, 0).

Figs. 1.6*a–c*. These regions are open and not always convex (Fig. 1.6*a*, *b*). The input mixture c_{ent} in all the figures is shown with a circle.

Certainly a search for the thermodynamic estimations of sets of stationary states for the systems of large dimensionality encounters severe computational difficulties. Construction of an SCP-set calls for the study of a great number of systems of linear inequalities relative to chemical potentials.

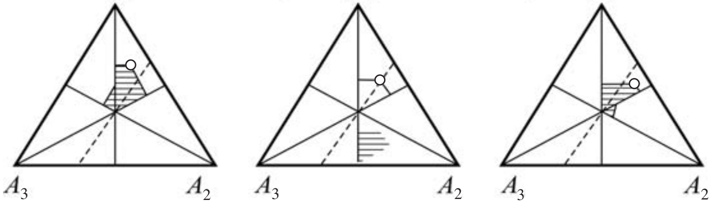

FIGURE 1.6. Sets of possible stationary states M^0 for the homogenous CSFR (dashed). *a.* $c_{2\mathrm{ent}} < c^{\mathrm{eq}}$; *b.* $c_{2\mathrm{ent}} = c^{\mathrm{eq}}$; *c.* $c_{2\mathrm{ent}} > c^{\mathrm{eq}}$; dashed line is set by the equality $c_2 = c^{\mathrm{eq}}\,(c_{1\mathrm{ent}} > c_{2\mathrm{ent}} > c_{3\mathrm{ent}})$.

To conclude this section we would like to note, that since the 1960s thermodynamic analysis of open system kinetics—with its main points briefly discussed in the sixth chapter of *Equilibrium Encircling*—has been developing in the works of a number of the authors: F. Horn [47, 71], M. Feinberg [44, 45, 46, 47], P. M. Bowen [24], B. D. Coleman [29], D. Glasser [57, 70], D. D. Hildebrant [46, 57, 70], J. C. Keck [98], and V. N. Parmon [136] et al.

2

Extreme Thermodynamic Models in Terms of Mathematical Programming

> Physicists are too bad at mathematics to deal with physics.
> Einstein discovered the general relativity theory owing to his poor knowledge of the non-Euclidean geometry.
>
> *D. Hilbert*

2.1. Brief Information from Mathematical Programming

Before discussing the extreme models of equilibrium thermodynamics let us address the general statements of problems in mathematical programming (MP) that are used for construction of these models. The theory and methods of MP are presented in detail in numerous publications, for example [19, 33, 94, 142]. In this chapter we present the minimum necessary information on linear, convex, and concave programming needed for understanding the further text of the book.

The general problem of mathematical programming is formulated as follows: Find maximum (minimum) of the objective function $f(x)$ provided that the vector $x = (x_1, \ldots, x_n)^T$ belongs to the admissible region $D \subset R^n$, where R^n is an n-dimensional Euclidean space. The vector $x^{\max}$ is called a global maximum point of an objective function if

$$f\left(x^{\max}\right) \geq f(x). \tag{2.1}$$

The vector $x^{\max}$ is called a local maximum point of the objective function if there is an ε-vicinity

$$U_\varepsilon = \left\{ x : \left[\left\| x^{\max} - x \right\| = \left(\sum_{j=1}^{n} \left(x_j^{\max} - x_j \right)^2 \right)^{0.5} \right] < \varepsilon \right\} \tag{2.2}$$

such that $f(x^{\max}) \geq f(x)$ for all $x \in U_\varepsilon$ Similarly the points of global and local minima are found.

According to the Weierstrass theorem the continuous function $f(x)$ determined on a closed limited admissible set D reaches the global maximum (minimum) on the internal or boundary point of D.

To analyze the MP problems the notions of convexity and concavity of sets and functions are rather important. The set $D \subset R^n$ is convex if from $x_1 \in D$ and $x_2 \in D$ at any λ ($0 \le \lambda \le 1$), it follows that

$$\lambda x_1 + (1 - \lambda) x_2 \in D. \tag{2.3}$$

This means that if any two points belong to a convex set the whole section connecting them belongs to this set.

The function $f(x)$ is called *convex* if at any x_1 and x_2 and $0 \le \lambda \le 1$.

$$f(\lambda x_1 + (1 - \lambda) x_2) \le \lambda f(x_1) + (1 - \lambda) f(x_2), \tag{2.4}$$

and *concave*, if

$$f(\lambda x_1 + (1 - \lambda) x_2) \ge \lambda f(x_1) + (1 - \lambda) f(x_2). \tag{2.5}$$

The sign of equality in (2.4) and (2.5) is true only for linear functions. At satisfied strict inequalities the functions are called *strictly convex* (2.4) and *strictly concave* (2.5).

The condition of strict convexity $f(x)$ is *positive definiteness* of the matrix of second derivatives (the Hessian matrix)

$$H(x) = \left\{ \frac{\partial^2 f}{\partial x_i \partial x_j} \right\}, \quad i = 1, \ldots, m, \quad j = 1, \ldots, n.$$

The symmetrical nonsingular (with a determinant distinct from zero) matrix is positive definite if it is subject to the condition

$$x^T H x > 0, \quad x \in R^n. \tag{2.6}$$

Nonnegative definiteness ($x^T H x \ge 0$) is indicative of function convexity.

If $f(x)$ is convex not on the whole space R^n but only on the polyhedron $Ax = b$, $x \ge 0$, the inequality (2.6) is supplemented by the condition $Ax = 0$.

When the determinant (Hessian) $H(x)$ equals zero, we have the most complicated situation for determining wheter a function is convex or concave. Here the property of nonnegative definite matrices can be used; the property consists of the fact that the eigenvalues and principal minors of the matrix are nonnegative numbers[1] (for nonpositive definite matrices these numbers are nonpositive). To be sure, in the present book we do not have the opportunity to present the main principles of matrix analysis in detail, and, therefore, give the references to the special literature [53, 72].

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[1] The number λ and nonzero vector x are called the eigenvalue and eigenvector of matrix A, respectively, if they satisfy the equation $Ax = \lambda x$, which is equivalent to the equation $(\lambda I - A)x = 0$. Where I is a singular matrix.

If the admissible region D is determined by the system of equations

$$\varphi_i(x) = b_i, \quad i = 1, \ldots, m, \tag{2.7}$$

the Lagrange function[2]

$$L(x, \lambda) = f(x) + \sum_{i=1}^{m} \lambda_i (b_i - \varphi_i(x)), \tag{2.8}$$

is used to find the local extremum in such a problem.

The problems of mathematical programming are divided into two classes: nonlinear and linear programming (LP).

In turn, in nonlinear programming there can be two types of problems. If the maximized function $f(x)$ is concave and the conditions that determine the admissible region $D(x)$, namely,

$$\varphi_i(x) \le b_i, \quad i = 1, \ldots, m, \tag{2.9}$$

represent constraints on the values of convex functions $\varphi_i(x)$, then the solved nonlinear problem is a convex programming problem (CP).

At minimization of $f(x)$ on a convex set of constraints the problem belongs to the convex programming problems still at convexity of an objective function. The problem of concave programming lies in the search for the convex function maximum and concave function minimum.

Fig. 2.1 shows that the convex programming problems have one extremum. Here the point of global maximum (minimum) can lie both on a boundary line and inside the region $D(x)$. In the case of linear objective function the point x^{ext} is located on the boundary line of $D(x)$. The problems of concave programming are of a multi-extrema character. The points of local extrema are located on a boundary line of $D(x)$ and at the linear polyhedron of constraints—on its vertices. Depending on dimensionality of the considered problem the number of maxima (minima) may become as large as desired. This indicates a principal complexity of solving concave programming problems.

If the Lagrange function of the nonlinear programming problem is differentiable the existence of the local maximum in the given point is determined by the

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$$\mathbf{I} = \begin{bmatrix} 1 & & & 0 \\ & \cdot & & \\ & & \cdot & \\ & & & \cdot \\ 0 & & & 1 \end{bmatrix}$$

The principal minor is called a *determinant* of the main submatrix of matrix A, i.e., of such a submatrix with a dimension $k \times k$ that has identical indices of lines and columns.

[2] As it was shown in Section 1.1, this function is obtained by integration of the equation suggested by Lagrange for the equilibrium of a mechanical system.

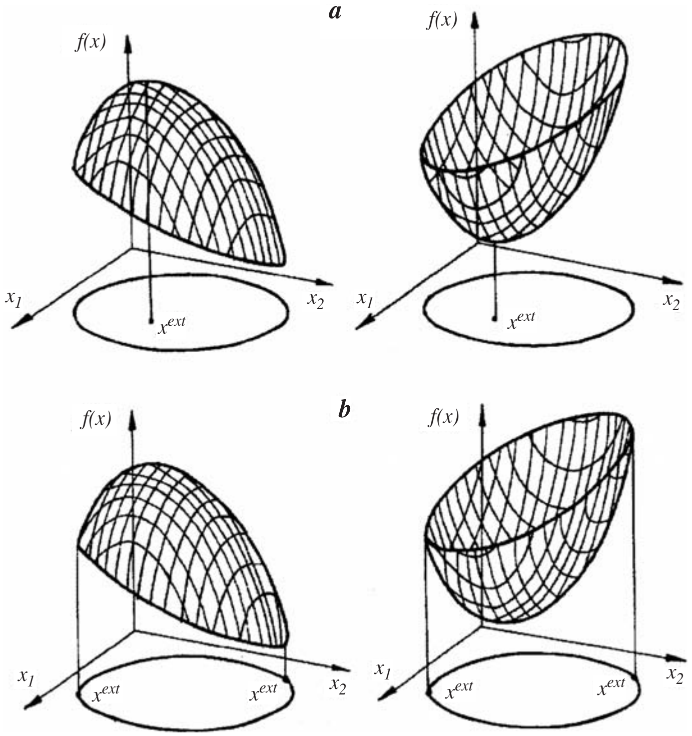


FIGURE 2.1. A graphical interpretation of the problems of convex (a) and concave (b) programming.

Kuhn–Tucker conditions:

$$\frac{\partial L(x,\lambda)}{\partial x_j} = \frac{\partial f(x)}{\partial x_j} - \sum_{i=1}^{m} \lambda_i \frac{\partial \varphi_i(x)}{\partial x_j} \leq 0; \tag{2.10}$$

$$\frac{\partial L(x,\lambda)}{\partial x_j} x_j = \left(\frac{\partial f(x)}{\partial x_j} - \sum_{i=1}^{m} \lambda_i \frac{\partial \varphi_i(x,\lambda)}{\partial x_j} \right) x_j = 0; \tag{2.11}$$

$$x_j \geq 0, \quad j = 1, \ldots, n; \tag{2.12}$$

$$\frac{\partial L(x,\lambda)}{\partial \lambda_j} = (b_i - \varphi_i(x)) \geq 0; \tag{2.13}$$

$$\lambda_i \frac{\partial L(x,\lambda)}{\partial \lambda_j} = \lambda_i (b_i - \varphi_i(x)) = 0; \tag{2.14}$$

$$\lambda_i \geq 0, \quad i = 1, \ldots, m. \tag{2.15}$$

The conditions (2.11) and (2.14) are called *conditions of complementary slackness*. They allow one to find a nonlinear programming problem solution that lies on a boundary line of the admissible region when the left-hand sides in conditions (2.10) and (2.13) can be distinct from zero.

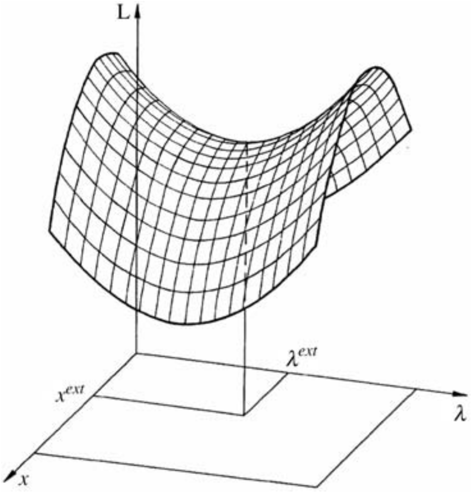


FIGURE 2.2. The Lagrange function of a nonlinear programming problem.

The Lagrange multipliers λ_i characterize the extent of the change in the optimal value of an objective function at small changes of b_i. The vector $\left(x^{\text{ext}}, \lambda^{\text{ext}}\right)$ is called a *saddle point* of the Lagrange function (Fig. 2.2), if, for all $x \geq 0, \lambda \geq 0$,

$$L(x, \lambda^{\text{ext}}) \leq L(x^{\text{ext}}, \lambda^{\text{ext}}) \leq L(x^{\text{ext}}, \lambda). \tag{2.16}$$

The theorem of a saddle point. *If* $(x^{\text{ext}}, \lambda^{\text{ext}})$ *is a saddle point of the Lagrange function, then* x^{ext} *is the solution to the nonlinear programming problem.*

The Kuhn–Tucker theorem. *If the function* $f(x)$ *is concave, the functions* $\varphi_i(x)$ *are convex, and there exists a vector x that belongs to the admissible region and satisfies the condition of regularity of constraints* $b_i - \varphi_i(x) > 0,\ i = 1, \ldots, m$, *then the vector* x^{ext} *is a solution to the nonlinear programming problem if and only if there is a vector* λ^{ext} *at which* $\left(x^{\text{ext}}, \lambda^{\text{ext}}\right)$ *is a saddle point of the Lagrange function.*

In the convex programming problem with functions $f(x)$ and $\varphi_i(x)$, $i = 1, \ldots, m$, that are differentiable, the Kuhn–Tucker conditions (2.10)–(2.15) are necessary and sufficient for the point x^{ext} satisfying them to be saddle and, hence, to be a solution of the nonlinear programming problem.

At solution of the minimization problem with the system of constraints

$$\varphi_i(x) \geq b_i, \quad i = 1, \ldots, m, \tag{2.17}$$

the Kuhn–Tucker conditions take the form

$$\frac{\partial f(x)}{\partial x} - \lambda \frac{\partial \varphi(x)}{\partial x} \geq 0; \tag{2.18}$$

$$\left(\frac{\partial f(x)}{\partial x} - \lambda \frac{\partial \varphi(x)}{\partial x}\right) x = 0, \quad x \geq 0; \tag{2.19}$$

$$b - \varphi(x) \leq 0; \tag{2.20}$$

$$\lambda(b - \varphi(x)) = 0, \lambda \geq 0. \tag{2.21}$$

The system (2.18)–(2.21) unlike (2.10)–(2.15) is presented in vector form.

The problem of linear programming is an important particular case of the convex programming problem. Mathematically, it is formulated as follows:

Find

$$\max f(x) = \sum_{j=1}^{n} c_j x_j \tag{2.22}$$

subject to

$$\sum_{j=1}^{n} a_{ij} x_j \le b_i, \quad i = 1, \dots, m. \tag{2.23}$$

This problem corresponds to the Lagrange function

$$L(x) = \sum_{j=1}^{n} c_j x_j + \sum_{i=1}^{m} \lambda \left(b_i - \sum_{j=1}^{n} a_{ij} x_j \right), \tag{2.24}$$

and the Kuhn–Tucker conditions take the form

$$c_j - \sum_{i=1}^{m} \lambda_i a_{ij} \le 0\,; \tag{2.25}$$

$$\left(c_j - \sum_{i=1}^{m} \lambda_i a_{ij} \right) x_j = 0, \quad x_j \ge 0, \quad j = 1, \dots, n\,; \tag{2.26}$$

$$b_j - \sum_{j=1}^{n} a_{ij} x_j \ge 0\,; \tag{2.27}$$

$$\lambda_i \left(b_i - \sum_{j=1}^{n} a_{ij} x_j \right) = 0, \quad \lambda_i \ge 0, \quad i = 1, \dots, m. \tag{2.28}$$

Along with (2.22), (2.23), the linear programming problem is often written in a matrix form as the following:

Find

$$\max f(x) = c^T x \tag{2.29}$$

subject to

$$Ax \le b, \quad x \ge 0, \tag{2.30}$$

where A is a matrix of $m \times n$ size.

The conditions (2.25)–(2.28) are also the Kuhn–Tucker conditions for the following problem:

Find

$$\min F(\lambda) = b^T \lambda \tag{2.31}$$

subject to

$$A^T \lambda \ge c, \quad \lambda \ge 0. \tag{2.32}$$

This minimization problem is called “dual” with respect to the direct maximization problem (2.22), (2.23) or (2.29), (2.30). The constraints (2.23) of the direct problem correspond to the variables λ_i (the Lagrange multipliers) of the dual problem and vice-versa.

Each constraint-inequality of the direct problem corresponds to part of the space R^n, and this part is limited by the plane

$$\sum_{j=1}^{n} a_{ij} x_j = b_j \tag{2.33}$$

or $x_j = 0$. Intersection of such half-spaces forms a convex admissible region $D(x)$, i.e., a polyhedron of constraints. Similarly the admissible region of solutions to a dual problem $D(\lambda)$ is formed. The vertices of the polyhedron are the interception points of the planes. The solution x^{ext} of the linear programming problem always coincides with one of the polyhedron vertices (in the case of degeneracy with an face) (Fig.2.3). This solution satisfies the duality theorem.

The duality theorem. *The admissible vector is a solution to the linear programming problem if and only if there exists such an admissible vector* λ *of the dual problem that the values of the objective functions on these vectors are equal* (i.e., $f(x) = F(\lambda)$). *Here the vector* λ *is the dual problem solution.*

When we set the constraints of the linear programming problem in the form of equalities the number of components of the vector x^{ext} always equals m, i.e., the number of constraints. If some of these components turn out to be equal to zero the solution of the direct problem is degenerate and the solution of the dual one is many-valued (a set of solutions is some face of the polyhedron of constraints).

To solve the linear programming problem a number of methods were developed including the most widely used simplex method [33] that was employed in numerous standard programs for computers.

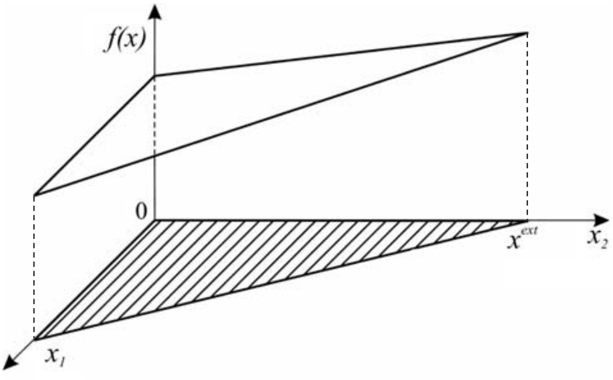


FIGURE 2.3. A graphical interpretation of the linear programming problem.

Along with convex, concave, and linear problems the book gives also consideration to the parametric programming problems. In the parametric programming the objective function value depends on both the variables x and parameter y. For the latter, a range of potential values is set. The extremum $f(x, y)$ is sought for each fixed value y among which we find y^{ext}.

2.2. The Model of Extreme Intermediate States (MEIS)

Description of Final Complete Equilibria

Let us analyze the models that represent the entire thermodynamic attainability region D_t of a physical-chemical system and start the analysis with the description of final (complete) equilibrium x^{eq} in terms of mathematical programming. First of all, the point x^{eq} corresponds to the global extremum of characteristic thermodynamic function on D_t and to a certain extent can serve as a reference point for locating the other equilibria in the attainability region. The model of x^{eq} is certainly much simpler than the descriptions of the other points in D_t, and consideration of its specific features must help one's understanding of the properties of the models of D_t, on the whole.

All the mathematical statements of the problems in this section are given as applied to constant T and P which is true for most of the technological and many natural processes. The other conditions of systems' interaction with the environment are considered in the next section.

For the conditions assumed here the problems of the search for x^{eq} in terms of MP takes the following form:

Find

$$\min\left[G(x) = \sum_j G_j(x)\, x_j\right] = G(x^{\mathrm{eq}}) \tag{2.34}$$

subject to

$$Ax = b, \tag{2.35}$$

$$G_j = f_j(x), \tag{2.36}$$

$$x_j \geq 0, \tag{2.37}$$

where G and G_j are Gibbs energy of the system and a mole of its jth component, respectively; $x = (x_1, \ldots, x_n)^T$ is a vector of mole quantities of components; $A = [a_{ij}]$ is the $m \times n$ matrix of element contents in the components of the system; $b = (b_1, \ldots, b_m)^T$ is a vector of mole quantities of elements; and the index i refers to the ith element.

The physical sense of the objective function (2.34) is obvious. The matrix equation (2.35) determines the condition of conservation of the element amounts. The form of the function (2.36) depends on the type of system under study (ideal gas, real gas, heterogeneous mixture, etc.).

To disclose the specific features of the model (2.34–2.37) important for further analysis of the models of complete thermodynamic attainability regions, we present two elementary examples of its construction.

The reaction of hydrogen burning in oxygen will be considered as the first of these. Suppose that the reaction mixture includes six components: H_2 (x_1), O_2 (x_2), $H(x_3)$, $O(x_4)$, water vapor $H_2O_{(g)}$ (x_5), and liquid water $H_2O_{(c)}$ (x_6). In the initial state the mixture contains two moles of H_2 and one mole of O_2, i.e., the vector $x = (2, 1, 0, 0, 0, 0)^T$. In this case, accounting for the substitution of expressions for the function (2.36) into (2.34), the model of x^{eq} is specified in the form:

Find

$$\min \left[G(x) = \sum_{j=1}^{5} \left(G_j^0 + RT \ln \left(P \frac{x_j}{\sigma} \right) \right) x_j + G_6^0 x_6 \right]$$

subject to

$$2x_1 + x_3 + 2x_5 + 2x_6 = 4,$$
$$2x_2 + x_4 + x_5 + x_6 = 2,$$
$$x_j \geq 0,$$

where σ is a total mole quantity of gaseous components; in the given case

$$\sigma = \sum_{j=1}^{5} x_j;$$

G_j^0 is standard mole Gibbs energy whose values are either found in the reference books (for example, [150, 160, 162, 170]), or calculated using the principles of statistical physics [125]. The present book does not consider the problems of determining the standard values of thermodynamic functions.

In the presented example the vector $b = (4, 2)^T$ and its components determine the mole quantities of elements H and O in the initial mixture, respectively. The results of x^{eq} calculations for the hydrogen burning process at $P = 0.1$ MPa and $T = 1500$ K are presented in Table 2.1.

In the second example of the model (2.34–2.37) we address the isomerization process discussed in Section 1.4. The process is very convenient for revealing the specific features of the models due to simplicity of material balances (the total number of moles in the system remains invariable). However, here, unlike the example

TABLE 2.1. Hydrogen burning in oxygen

Initial composition, mole		G_j^0, kJ/mole	x^{eq}, mole/kg
H_2	2	−231.80	$1.06 \cdot 10^{-2}$
O_2	1	−346.36	$5.30 \cdot 10^{-3}$
H	0	20.70	$1.34 \cdot 10^{-5}$
O	0	−18.25	$2.18 \cdot 10^{-6}$
$H_2O_{(g)}$	0	−569.51	55.50
$H_2O_{(c)}$	0	−467.79	0.00

TABLE 2.2. Hexane isomerization

Initial composition, mole		G_j^0, kJ/mole	x^{eq}, mole/kg	x^{ext}, mole/kg
Hexane	1	–421.034	3.28	0.95
2-methylpentane	0	–423.620	5.51	1.59
3-methylpentane	0	–420.255	2.81	9.07

in Section 1.4 we should consider a real substance, hexane (C_6H_{14}), and for graphical constructions (which will be necessary further) suppose that there are transformations of three isomers only: n-hexane(x_1), isohexane (2-methylpentane)(x_2) and 3-methylpentane (x_3). The material balance (2.35) for this example, namely

$$6x_1 + 6x_2 + 6x_3 = b_1$$

$$14x_1 + 14x_2 + 14x_3 = b_2,$$

is obviously transformed to the form

$$x_1 + x_2 + x_3 = \text{const.}$$

The results of the x^{eq} calculation for the initial composition $x = (1, 0, 0)^T$ at $P = 0.1$ MPa and $T = 600\,K$ are presented in Table 2.2. The implication of the column x^{ext} is explained below (the maximum of 3-methylpentane is found).

Based on the above mathematical description (2.34)–(2.37) and examples, we can point to some specific features of the extreme models presented in this book.

One of the specific features consists in the fact that the initial information for construction of the models is the list of substances (vector x) that can participate and form in chemical transformations. However, the LMA-based calculations require that a list of supposed reactions be set, i.e., some hypothesis on the mechanism of the studied process be assumed. From the computational viewpoint both approaches to the initial data choice are almost equivalent, since the employment of either necessitates the solution of the systems that include transcedent and linear algebraic equations and the dimensionality of systems appears comparable.

The advantages of setting the list of substances relate to the comparative simplicity of drawing up the list. Indeed, for well-studied processes it can be quite simple to put forward the hypothesis on the process mechanism and obtain the equations of equilibrium constants for all the components of its reaction; however, it can be hard to do this for processes studied for the first time. Yet it is precisely the little-studied processes that normally represent the main object of thermodynamic analysis.

However, even for studied processes, a not very successful replacement of a real mechanism that includes hundreds or thousands of elementary stages, by its approximate description based on the stoichiometric equations of complex reactions, results in a less accurate calculation of the complete equilibrium. Each specified list of reactions corresponds to its partial equilibrium satisfying the condition that the reactions absented from this list do not take place in the reacting system. This equilibrium does not coincide with the complete one.

To some extent the problem of the initial data preparation using LMA can be solved if, as in the case of applying the model (2.34)–(2.37), we make a list of supposed components of the reaction mixture and then write for each of them the reaction of its synthesis from elements. Such a replacement of the list of stages, that is, the actual mechanism of the process, by the synthesis reactions is admissible, since the state x^{eq} at a given vector b and conditions of interaction with the environment do not depend on the initial composition of reagents. However, here, in the case of modeling complex multicomponent and multiphase systems, difficulties in searching analytical solution to the problem may appear.

It should be emphasized that the extreme approach as compared to LMA does not impose strict limitations on the method of setting the initial information and allows its representation in the form of both the list of substances and the list of reactions. The model based on the latter method of initial data representation is considered at the end of this section.

Commenting on the model (2.34)–(2.37) let us focus once again on the fact (see Section I.17) that at its description (as in the later description of other extreme models) the notion of "component" has not been interpreted in the way that it has generally been in the thermodynamic literature, starting, apparently, with the book by Gibbs, *On Equilibrium of Heterogeneous Substances*. By "components" in thermodynamics, writers on the subject usually mean the substances of the reaction mixture, disregarding the number of phases in which they are present. In this book any single phase of a substance is considered to be an individual component. For instance, in the first of the above examples, water is represented by two components of the vector x: gaseous (x_5) and liquid (x_6). Such a break with the tradition makes easier the construction of mathematical models. Indeed, when calculating equilibria we always need to find the amount of each substance in each phase and, therefore, it is natural to consider these quantities as independent variables of the problem. Below, it will be shown that the assumed principle of forming the composition of variables allows one to overcome some computational difficulties in the search for equilibrium states.

The Model of Extreme Intermediate States (MEIS)

Now let us discuss the main thermodynamic model used by the authors, the *model of extreme intermediate states* (MEIS). For a fixed T, P, and initial composition of reagents y, MEIS has the following form:

Find

$$\max \left(F(x) = \sum_{j \in J^{\mathrm{ext}}} c_j x_j \right) = F(x^{\mathrm{ext}}) \tag{2.38}$$

subject to

$$Ax = b, \tag{2.39}$$

$$D_t(y) = \{x : x \le y\}, \tag{2.40}$$

$$G(x) = \sum_j G_j(x) x_j, \tag{2.41}$$

$$x_j \ge 0, \tag{2.42}$$

where c_j is a coefficient ranging either usefulness or harmfulness of the jth component of vector x, $c \ge 0$ or $c \le 0$; J^{ext} is a set of components indices whose formation is of interest; x^{ext} is a composition of the mixture in the point of partial equilibrium that meets the maximum of the objective function F; and $D_t(y)$ is a region (a set) of thermodynamic attainability from the initial state y (see Section I.22).

The form of the objective function (2.38) and system of constraints (2.39)–(2.42) shows that MEIS is intended to search for the thermodynamic attainability region of the partial equilibrium that corresponds to the extreme concentration of a set of substances given by a researcher.

Let us use the above isomerization reaction to exemplify the MEIS construction. Suppose that for the assumed condition the initial composition of the mixture is determined by the value of the vector $y = (1, 0, 0)$ and the extreme concentration of x_3 is found (3-methylpentane). Then MEIS take the following form:

Find

$$\max x_3$$

subject to

$$x_1 + x_2 + x_3 = y,$$

$$D_t(y) = \{x : x \le y\},$$

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

Table 2.2 presents the values of the components of the vector x at the point x^{ext} that corresponds to the given model.

A graphical interpretation of MEIS is presented in Fig. 2.4, which was constructed based on the hexane isomerization calculations described in the examples.

The equilateral triangle in Fig. 2.4*a* is a polyhedron of material balance $D(y)$ determined by equation (2.39) and inequalities (2.42). The vertices correspond to the states in which the mole content of one of the components equals an absolute value of y, i.e., unity (an index at the symbol of vertex A coincides with the index of this component) and of the remaining two, i.e., zero. The interior points of the edges represent reaction mixture compositions in which the concentration of only one reagent is zero and the total mole quantity of the remaining two makes up unity. On the area of the triangle you can see the points x^{eq} and x^{ext}, the lines $G = \text{const}$, as well as dashed zones of thermodynamic unattainability from y by the condition

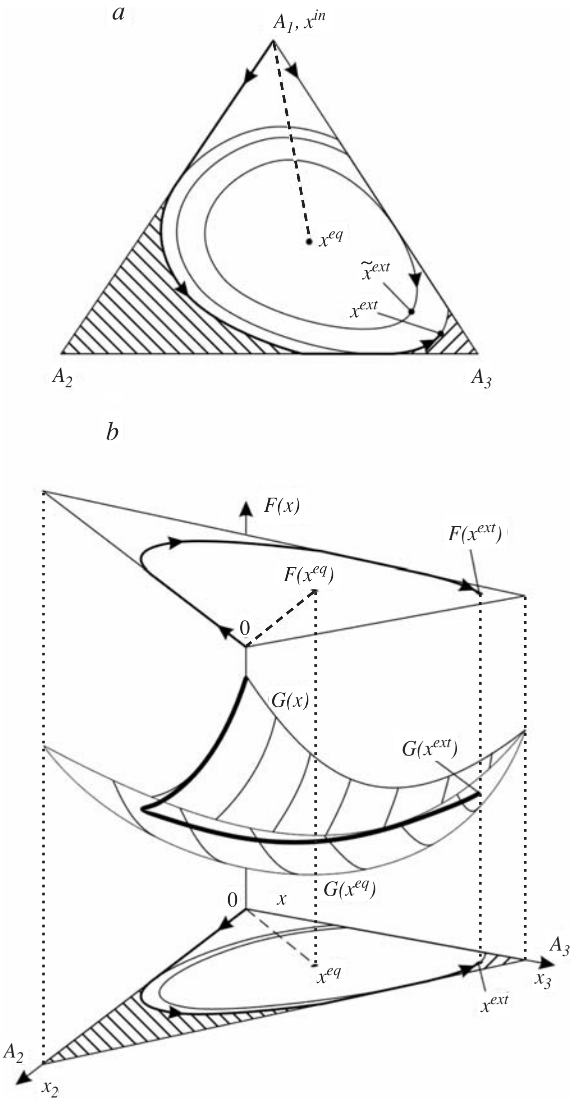


FIGURE 2.4. A graphical interpretation of the model of extreme intermediate states. (a) a polyhedron of material balance; (b) an objective function and a system of constraints.

(2.40) near the vertices A_2 and A_3. Correspondingly, the nondashed part of the triangle is thermodynamically attainable set $D_t\ (y)$. The two trajectories of motion from y to x^{ext} are shown: The one that meets the requirements of a monotonic nonincrease of Gibbs energy (a continuous line) and the one that that does not meet it (a dot-and-dash line).

In Fig. 2.4b, the MEIS is interpreted in three-dimensional space. Here the triangle $0A_2A_3$ is a projection of the polyhedron $A_1A_2A_3$ (Fig. 2.4a) to the horizontal plane

$x_2 0 x_3$ of a positive octant. Along the vertical axis the Gibbs energy values (in the middle of the figure) and the objective function $F(x)$ (on top) are plotted. The points x^{eq} and x^{ext}, the lines $G = \text{const}$, and the admissible and inadmissible trajectory of transition from y to x^{ext} are shown both on the plane of compositions ($x_2 0 x_3$), on the surface $G(x)$, and on the objective function plane.

Even based on the above short analysis, we can see the principal advantages of MEIS as compared to the traditional models of final equilibria [9, 32, 96, 97, 172].

First, instead of searching for the single point x^{eq}, the whole set $D_t(y)$ can be examined in the course of optimization. This allows many technological and natural processes in which final equilibria that are not attained by the conditions of kinetics to be included into the area of equilibrium thermodynamics applications.

Second, calculating the extreme values of the corresponding thermodynamic functions, we determine, depending on the purpose of the study, the extreme concentrations of useful or harmful substances formed in the studied process. This makes the thermodynamic analysis more substantial.

Third, the models of type (2.38)–(2.42) are easily supplemented by various constraints in the form of equalities and inequalities that can be employed in the thermodynamic analysis and make possible consideration for the impact of non-thermodynamic factors associated with the specific features of the system at issue: chemical kinetics; transfer processes (heat and mass transfer); and limiting values of parameters (if they are not fixed): temperature, pressure, concentrations of individual components, energy input and output, etc.

Description of Nonthermodynamic Constraints

Let us consider in more detail the last of the mentioned MEIS advantages. On one hand, this advantage is caused by the capabilities of the MP that allow the problem statements to be easily varied. On the other hand, it is due to the universal character of thermodynamics, whose principles rule diverse physical-chemical process. The examples of interpreting the stationary and nonstationary models of motion that differ in nature in terms of thermodynamics were already presented in Section 1.3. In all the considered cases it was difficult to replace the descriptions of change with time in the studied system's state by the description of the states of rest (equilibrium). Using as applied to MEIS the techniques of replacing the descriptions similar to those mentioned above, we should keep track of the transformation correctness in relation to both the final and the partial equilibria.

A natural way of taking into account the factors that are traditionally considered nonthermodynamic, for example, the specific features of the transfer processes, is to change the form of the functions entering into conditions (2.40) and (2.41), to include in them—along with the chemical—the electrical, gravitational, or other components related to the interactions that affect the transfer. Determination of the type of generalized functions to be formed is exemplified in the final two chapter of this book, which is devoted to applications of the extreme thermodynamic models. Here, we first consider the possibility of taking into account various processes running in a studied system by including additional constraints in the form of equalities and inequalities into the model (2.38)–(2.42).

The constraint on the rate of oxygen diffusion to the surface of a substance being oxidized can be presented in the form of inequality

$$x_{O_2} \geq x^b_{O_2},$$

where $x^b_{O_2}$ is the amount of O_2 that, subject to mass exchange, cannot participate in reaction.

The constraint on the endothermic process of nitrogen oxide formation at fuel burning in the system with fixed P and T is described by the inequality

$$H \leq H^b,$$

Where H is system enthalpy and H^b is fuel combustion heat. The latter inequality can be interpreted as a constraint on a potential range of technological regulation of the reaction mixture parameters. Meeting this constraint alone makes it possible to maintain the given T and P.

MEIS can also include essentially more complicated expressions than the above two inequalities. For example, if the mechanism of chemical transformations includes the isomerization reactions

$$x_1 \rightarrow x_2 \rightarrow x_3,$$

that meet the equation

$$\frac{dx_j}{d\tau} = -k_j x_j,$$

the integrals of kinetic equations

$$\begin{aligned}
x_1 &= e^{-k_1\tau}, \\
x_2 &= \frac{k_1}{k_2 - k_1}(e^{-k_1\tau} - e^{-k_2\tau}), \\
x_3 &= 1 - \frac{k_2}{k_2 - k_1}e^{-k_1\tau} + \frac{k_1}{k_2 - k_1}e^{-k_2\tau}
\end{aligned}$$

can be used to make up the system of MEIS constraints.

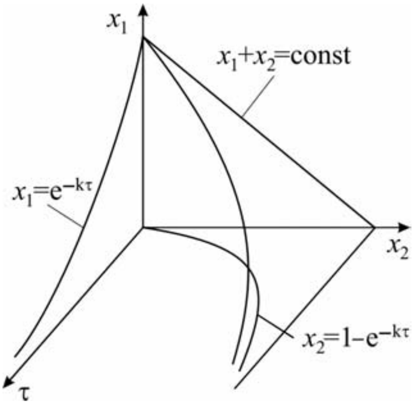
For example, we can write the constraint on the change in the amount of the second component

$$x_2 = \frac{k_1}{k_2 - k_1}(e^{-k_1\tau} - e^{-k_2\tau}), \quad \tau \leq \tau^b,$$

in which the main variable of kinetics, time, is used as a parameter of "rest" states.

Figure 2.5 shows that for the elementary system with only one isomerization reaction $x_1 \rightarrow x_2$ the curve of the kinetic equation $x = f(\tau)$ is projected on the polyhedron of material balance $x_1 + x_2 = \text{const}$, and, depending on the value of τ^b (a limiting time of the process), it limits the region of thermodynamic attainability from the initial state.

FIGURE 2.5. Kinetics and material balance constraints in chemical system.



Needless to say, consideration of the constraints on the mechanism of chemical transformations represents a most complicated problem of thermodynamic modeling of complex real systems, which will be touched upon many times below in the book. However, here we have only emphasized the principal possibility of its solution.

The Model of Systems With Variable Initial Composition of Reagents

This model is a generalization of the model (2.38–2.42) and has the form:

Find

$$\max \left[F(x, y) = \frac{\sum\limits_{j \in J^{\text{ext}}} c_j x_j}{\sum\limits_{j \in J^0} g_j y_j} \right] = F(x^{\text{ext}}, y^{\text{ext}}) \tag{2.43}$$

subject to

$$\sum_{j=1}^{l} M_j y_j = 1, \tag{2.44}$$

$$Ax = b(y), \tag{2.45}$$

$$Ay = b(y), \tag{2.46}$$

$$\alpha_k \sum_{j \in J_k} y_j \le y_k \le \beta_k \sum_{j \in J_k} y_j, \quad k \in K, \tag{2.47}$$

$$D_t(y) = \{x : x \le y\}, \tag{2.48}$$

$$G(x) = \sum_j G_j(x) x_j, \tag{2.49}$$

$$x_j \ge 0, \quad y_j \ge 0, \tag{2.50}$$

where $y = (y_1, \ldots, y_l)^T$ is a vector of mole quantities of the initial reagents, $y \subset x$; J^0 is a set of indices of initial components whose efficient (spare) use is of interest; g_j is a coefficient, ranging the value of the jth initial reagent, $g_j \geq 0$; M is a molar mass; α and β are coefficients; k is an index of inequality (equality); K is a set of indices of initial reagents on whose quantities the constraints are imposed; and J_k is a set of indices of initial reagents that are taken into account in the kth constraint.

The form of the objective function (2.43) is necessary because at a variable y we may often be interested in efficient use of separate components rather than in the initial mixture of reagents as a whole. For example, when we study the combustion processes, it is more important to assess the economic potential of an expensive fuel than of the air. When differences in values of initial components are not significant the denominator of the expression in the middle of (2.43) can be taken equal to unity, i.e., to use the linear objective function.

Using equations (2.44) the amounts of the initial reagents are normed in relation to a unit of their mass. The matrix equations (2.45) and (2.46) express the condition of conservation the amounts of the elements for each of the varied values of y. The inequalities (equalities) (2.47) determine the admissible relations between the values of different components of the vector y. The expression (2.48) describes the region of thermodynamic attainability for each varied value of y.

We will show the construction of the model (2.43–2.50) for specific systems using the hexane isomerization that is a somewhat standard example for this book. Similar to the example given for the model (2.38–2.42) suppose that the maximum of x_3 is sought. Next assume that the initial mixture contains only components y_1 and y_2 (the coinciding indices of components of vectors x and y relate to the same substances) and their values are equal. Then the model (2.43–2.50) will take the form:

Find

$$\max x_3 (x, y)$$

subject to

$$My_1 + My_2 = 1,$$

$$\sum_{j=1}^{3} x_j = b(y) = 1/M,$$

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

$$G(x) = \sum_{j=1}^{3} G_j(x) x_j,$$

$$x_j \geq 0, \quad y_1 \geq 0, \quad y_2 \geq 0.$$

Here, unlike the example illustrating the model (2.38–2.42) the total amount of matter in the system is assumed equal not to unity but to $1/M$. Equations (2.46) and (2.47) in this case turn out to be unnecessary, due to their linear dependence on the equations of norming. (For the relationships between y_1 and y_2, no additional conditions were introduced except for equality of their sum to $1/M$).

The results of calculations for two values are presented in Table 2.3.

TABLE 2.3. Hexane isomerization at different compositions of the initial mixture ($T = 600$ K, $P = 0.1$ MPa).

	Initial composition, mole			
	$y = (1/\mathrm{M}, 0, 0)$		$y = (0, 1/\mathrm{M}, 0)$	
Substance	x^{eq}, mole/kg	x^{ext}, mole/kg	x^{eq}, mole/kg	x^{ext}, mole/kg
x_1	3.28	0.95	3.28	1.62
x_2	5.51	1.59	5.51	2.71
x_3	2.81	9.07	2.81	7.28

Representation in the model (2.43)–(2.50) of the composition of its variables using two vectors x and $y \subset x$ is rather important in terms of application: It allows one, because of the thermodynamic analysis, to strictly formalize the solution of the problem on the optimal composition of the initial reagents. The search for such a composition using the variant calculations may appear to be rather laborious. Besides, compared to variant calculations, strict optimization gives a clearer idea of how y^{ext} depends on the main factors than that affect it.

Thus, the possibility of varying the composition of the initial reagents is, along with the above mentioned, another, the fourth principal advantage of MEIS as compared to the traditional models of equilibrium thermodynamics.

Model of Systems With Variable Extents of Reactions Completeness

In the beginning of the present section we discussed the advantages of setting the list of substances over the list (a mechanism) of reactions in the initial information for extreme models. However, in a number of cases the use of the notion "mechanism" may appear necessary to more completely reveal the specific features of the studied process. The authors constructed the MEIS with variable extents of reaction completeness based on setting the mechanism with the help of L. I. Rozonoer. For fixed T and P it has the following form:

Find

$$\max \left[F\left(x\left(\xi\right)\right) = \sum_{j \in J^{\mathrm{ext}}} c_j x_j\left(\xi\right) \right] = F(x(\xi^{\mathrm{ext}})) \tag{2.51}$$

subject to

$$x_j = y_j + \sum_i \nu_{ij} \xi_i, \quad j = 1, \ldots, n, \quad i = 1, \ldots, m, \tag{2.52}$$

$$D_t\left(y\right) = \left\{\xi : x\left(\xi\right) \le y\right\}, \tag{2.53}$$

$$G\left(x\left(\xi\right)\right) = \sum_j G_j\left(x\left(\xi\right)\right) x_j, \tag{2.54}$$

$$x_j \ge 0, \quad {}_1 \ge \xi_i \ge 0, \tag{2.55}$$

where $\xi = (\xi_1, \ldots, \xi_m)^T$ is an ξ_i extent of completeness (a coordinate) of the ith reaction.

The equation (2.52) represents a material balance of transformations of the jth component of the system. It is obvious that by linear transformations we can pass from the system of such equations to the form of material balance representation in the main variants of MEIS: (2.38)–(2.42) and (2.43)–(2.50).

Let us illustrate the construction of MEIS with the variable ξ on the example of hydrogen burning in oxygen that was used above in the discussion of the final equilibria model. In this case we compose vector x of four components only: H_2 (x_1), O_2 (x_2), $H_2O_{(g)}$ (x_3) and $H_2O_{(c)}$ (x_4) and by two reactions:

$$2H_2 + O_2 = 2H_2O_{(g)};$$
$$2H_2O_{(g)} = 2H_2O_{(c)}.$$

The second reaction is a phase transition. Thus, the vector ξ turns out to have two components. Assume the initial value of the vector y to be equal to $(2, 1, 0, 0)^T$ and suppose that the purpose of the process is production of the maximum quantity of gaseous water. With the assumptions made the model (2.51)–(2.55) takes the following form:

Find

$$\max x_3(\xi)$$

subject to

$$\begin{aligned} x_1 &= 2 - 2\xi_1, \\ x_2 &= 1 - \xi_1, \\ x_3 &= 2\xi_1 - 2\xi_2, \\ x_4 &= 2\xi_2, \\ D_t(y) &= \{\xi : x(\xi) \le y\}, \\ G(x(\xi)) &= \sum_{j=1}^{4} G_j(x(\xi))\, x_j, \\ x_j &\ge 0, \quad 1 \ge \xi_i \ge 0. \end{aligned}$$

The results of calculations by the model are given in Table 2.4. The equilibrium state in this case under a set accuracy of calculations coincides with the extreme one.

TABLE 2.4. Calculated hydrogen burning in oxygen at a set list of reactions ($T = 2500$ K, $P = 0.1$ MPa).

	y, mole	G_j^0, kJ/mole	Equilibrium composition, mole				Extreme composition, mole			
			x^{eq}		ξ_i^{eq}		x^{ext}		ξ_i^{ext}	
H_2	2	−419.860	x_1	0.08	ξ_1	0.96	x_1	0.08	ξ_1	0.96
O_2	1	−614.612	x_2	0.04	ξ_2	0.00	x_2	0.04	ξ_2	0.00
$H_2O_{(g)}$	—	−833.984	x_3	1.92	—	—	x_3	1.92	—	—
$H_2O_{(c)}$	—	−732.262	x_4	0.00	—	—	x_4	0.00	—	—

The hopes placed on the model (2.51)–(2.55) are associated with its application to the studies of mechanisms of chemical processes. The mechanism optimal in terms of maximizing the yield of a given set of substances is determined by making up the abundant list of reactions and automatically excluding unnecessary stages in the course of searching for ξ^{ext}. It is possible to set the mechanisms that correspond to different catalysts and compare the efficiency of the latter by the attained x^{ext}. Studies of such kind may certainly call for different modifications of the model (2.51)–(2.55), for example, inclusion of additional constraints (on the change in parameters of system, energy and mass exchange, etc.) or change in the kind of constraints on the admissible values of x_j and ξ_i $(\overline{x}_j \geq \underline{x}_j \geq x_j; \overline{\xi}_i \geq \xi_i \geq \underline{\xi}_j$ and so on). Doing this, as in the case of using the models (2.38)–(2.42) and (2.43)–(2.50), has nothing to do with the principal difficulties, since it does not change essentially the character of the mathematical programming problems solved.

2.3. Description of Different Types of Thermodynamic Systems

Introductory Notes

In thermodynamics it is assumed that systems are divided into open, closed, and isolated; homogeneous and heterogeneous. The open systems can and the closed systems cannot exchange matter with the environment. The isolated system exchanges neither matter nor energy with other systems. The homogeneous systems consist of a single and heterogeneous consist of several phases divided by surfaces.

The properties of open and closed systems depend on the conditions of their interaction with the environment. The classical conditions of interaction and related equilibrium criteria are shown in Table I.1:

Further the systems can differ by the nature of forces in whose fields they are located. Finally, a distinct feature of the system can be a character of spatial inhomogeneity, namely, changes along the coordinates of intensive parameters. The latter feature is often due to the specific nature of a field affecting the system.

Certainly, it is impossible to describe the whole variety of thermodynamic systems, though the subject of thermodynamics encompasses the most general regularities of the macroworld. Here we will try to give only a preliminary set of models that, on the one hand, will explain the technique of extreme descriptions accounting for a specific nature of the systems to be modeled and, on the other hand, will reveal the advantages of the extreme thermodynamic approach on the whole.

First, let us consider the problems of modeling systems under different conditions of their interaction with the environment; next we will describe seperate phases of heterogeneous systems, and then give the models of spatially inhomogeneous structures.

Description of the Conditions for the System Interaction with the Environment

Since the above equilibrium conditions affect only the type of characteristic function (that takes an extreme value), let us discuss only the impact these conditions have on the model of x^{eq}, which is a block of MEIS.

The most general model of the final equilibria is an isolated system model that includes a reaction mixture and thermal reservoir with which the reagents exchange energy. This model is written in terms of MP as follows:

Find

$$\max \left[\begin{array}{l} S(x, T, P) = \sum_j S_j \left(T, P_j\right) x_j \\ \quad + T^{-1} \left(\sum_j H_j^y y_j - \sum_j H_j \left(T, P_j\right) x_j \right) \end{array} \right] = S\left(x^{\text{eq}}\right) \tag{2.56}$$

subject to

$$Ax = b, \tag{2.57}$$

$$\sum_j H_j^y y_j + H_{\text{hr}}^y - H = 0, \tag{2.58}$$

$$H = \sum_j H_j(T, P) x_j + H_{\text{hr}}, \tag{2.59}$$

$$f_1(T, P, V) = 0, \tag{2.60}$$

$$P_j = f_{2j}(P, x), \tag{2.61}$$

$$S_j = f_{3j}(T, P_j), H_j = f_{4j}(T, P_j), \tag{2.62}$$

$$x_j \geq 0, \tag{2.63}$$

where H_j^y is mole enthalpy of the jth initial reagent; H_{hr}^y is enthalpy of the thermal reservoir in the initial state; H is total enthalpy of the system (a reaction mixture and thermal reservoir).

The first term in the right-hand side of the expression in the square brackets for the objective function (2.56) is total entropy of the reagents, and the second is entropy transferred to the thermal reservoir. It is clear that the assumed equation of determining the latter is strictly satisfied only at a constant temperature of the reaction mixture. Otherwise, the integrals should be used in accordance with the entropy determination. The equation (2.58) describes the condition of energy conservation. Certainly it can be simplified by excluding the term H_{hr}^y, i.e., by assuming the initial enthalpy value of the thermal reservoir equal to zero. The expression (2.60) is the equation of the reaction mixture state.

From an extremality criterion for the isolated system (max S) we can pass to the extremality criteria for its parts at fixed conditions of interaction among them, i.e., we can derive the criteria given in the beginning of the section. Thus, if T and P are maintained constant in the parts of the system, by substituting

$$S_j = \frac{(H_j - G_j)}{T}$$

into (2.56) and by multiplying (2.56) by T, we can obtain a transformed criterion

$$\max\left[TS = \sum_j H_j x_j - \sum_j G_j x_j + \sum_j H_j^y y_j - \sum_j H_j x_j\right].$$

Taking into account that $\sum\limits_j H_j^y y_j$ is a constant value we find that max S of the system in this case corresponds to the max $(-G)$ of its parts, and, hence, to min G. This explains the form of the objective function in the model (2.34)–(2.37).

Let us present the extreme models of x^{eq} for two more important cases:

1) $T = \text{const}$, $V = \text{const}$:
Find

$$\left.\begin{array}{ll} & \min\left[F(x) = \sum\limits_j F_j(x) x_j\right] = F(x^{\text{eq}}) \\ \text{subject to} & \\ & Ax = b, \quad x_j \geq 0\,; \end{array}\right\} \quad (2.64)$$

2) $H = \text{const}$, $P = \text{const}$:
Find

$$\left.\begin{array}{ll} & \max\left[S(x,T) = \sum\limits_j S_j(x,T) x_j\right] = S(x^{\text{eq}}) \\ \text{subject to} & \\ & Ax = b, \quad \sum\limits_j H_j(x,T) x_j - \sum\limits_j H_j^y y_j = 0\,; \\ & H_j = f_{1j}(T,x), \quad S_j = f_{2j}(T,x), \quad x_j \geq 0 \end{array}\right\} \quad (2.65)$$

Description of Multiphase Systems

This book addresses the systems that may include:

- an ideal gas phase;
- real gases;
- a plasma consisting of a neutral active species (radicals), ions, and electronic gas;
- pure condensed substances;
- ideal solutions of electrically neutral substances and solutions of electrolytes;
- ideal surface gas (ideal two-dimensional gas of the adsorbed substances on the adsorbent surface);
- substances in the colloidal (fine-disperse) state, the surfaces of whose particles are subjected to surface tension forces.

The description of the ideal phases (gas, plasma, solution, surface gas) and pure condensed substances is based on the assumption that the thermodynamic functions are additive, i.e., for each phase,

$$U = \sum_j U_j x_j; \quad H = \sum_j H_j x_j; \quad F = \sum_j F_j x_j;$$
$$G = \sum_j G_j x_j; \quad S = \sum_j S_j x_j \tag{2.66}$$

and the values of these functions for the system as a whole are determined as sums of values for different phases. For example,

$$G = \sum_r \sum_j G_{rj} x_{rj}, \tag{2.67}$$

where r is an index of phase.

The functions of real phases, when possible, are represented in the form of a sum of the "ideal" component and the correction for nonideality.

When determining the correction of ΔG for real gas (the correction takes into account the pressure deviation from a standard one), E. G. Antsiferov used transformation of the integral

$$\int_{P^0}^{P_j} V_j dP_j = \int_{V^0}^{V_j} P_j dV_j + P_j V_j - P^0 V_j^0, \tag{2.68}$$

which has a clear physical sense. The work of the open thermodynamic system $\int VdP$ (an area *abcda* in Fig. 2.6.) is represented by three terms: the work of compression (expansion) of the closed system $\int PdV$ (the area of *ebcfe*); the work of transfer from the space with pressure $P = P^0$ to the space in which the volume of the system ($abe0a = P^0V^0$) changes; the work of ejection to the space where $P = P_j$ ($0dcf0 = P_jV_j$).

The equations of ΔG that were obtained based on (2.68) have the form:

a) for the van der Waals gas that meets the equation of state

$$P = \frac{RT}{V - b_\upsilon} - \frac{a_\upsilon}{V^2}, \tag{2.69}$$

$$\Delta G = RT \ln \frac{V^0 - b_\upsilon}{V - b_\upsilon} - \frac{a_\upsilon (V^0 - V)}{V^0 V} + (PV - P^0V^0); \tag{2.70}$$

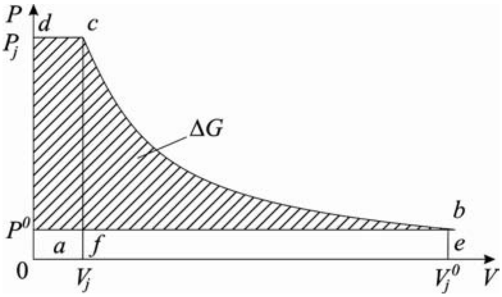


FIGURE 2.6. Derivation of the relationship $\Delta G = f(P)$.

b) for the Redlich–Kwong gas that meets the equation of state,

$$P = \frac{RT}{V - b_r} - \frac{a_r}{T^{0.5} V(V + b_r)}, \tag{2.71}$$

$$\Delta G = RT \ln \frac{V^0 - b_r}{V - b_r} - \frac{a_r}{T^{0.5} b_r} \ln \frac{V^0 (V + b_r)}{V(V^0 + b_r)} + (PV - P^0 V^0), \tag{2.72}$$

where the indices of υ and r relate to the van der Waals and Redlich–Kwong gas, respectively. The equations (2.70) and (2.72) are named the *Antsiferov equations* in memory of our colleague who passed away untimely.

The widely spread reference book [144] where integration of the expression $V_j dP_j$ was substituted by an artificial splitting of the integral into two parts—one describing the behavior of ideal gas and the other, the behavior of a real one, presented the equation obtained for the Redlich–Kwong gas

$$\begin{aligned} \Delta G = {} & \frac{b_r RT}{V - b_r} - \frac{a_r}{T^{0.5}(V + b_r)} - RT \ln \frac{V - b_r}{V} \\ & - \frac{a_r}{b_r T^{0.5}} \ln \frac{V + b_r}{V} - RT \ln \frac{V}{V^0}. \end{aligned} \tag{2.73}$$

The analysis of the expressions (2.70) and (2.72) shows that, at $V = V^0$ and $P = P^0$, they turns out equal to zero, which is as it should be in a standard state ($G = G^0$). The equation (2.73) gives some error in this case. The advantage of the Antsiferov equations over (2.73) is a possibility of physical interpretation of individual terms in their right-hand sides. The last term shows the change in the potential energy PV and the sum of two first ones, the change in the Helmholtz free energy. The first term at $V \gg b$ (which is satisfied in the region of low pressures) is a correction ΔG for ideal gas, since in this case

$$RT \ln \frac{V^0 - b}{V - b} \approx RT \ln \frac{P}{P^0}.$$

Obviously the two last terms in (2.70) and (2.72) at low pressures are close to zero.

The Gibbs energy of a multicomponent real gas phase (G_{rg}) can be divided into two constituents: ideal and nonideal ("surplus" energy):

$$G_{\text{rg}} = \sum_j \left(G_j^0 + RT \ln P \frac{x_j}{\sigma_{\text{rg}}} \right) x_j + \left(\int_P^{P_m} V_m dP \right) \sigma_{\text{rg}}, \tag{2.74}$$

where σ_{rg} is a total amount of the gas phase; P is a pressure assumed as the largest at which the gas phase still has the ideality property (can be taken, for example, equal to the atmospheric one); and P_m and V_m are an actual pressure of a mixture and a volume its moles, respectively.

When calculating the integral in the right-hand side of (2.74) by the Antsiferov equations and determining V_m from the equations (2.69) or (2.71), the coefficients

a and b can be found by the rules of mixing [170]:

$$a = \sum_i \sum_j \frac{x_i x_j}{\sigma_{\text{rg}}^2} a_{ij}, \tag{2.75}$$

$$a_{ij} = (a_i a_j)^{0.5}, \tag{2.76}$$

$$b = \sum_j \frac{x_j}{\sigma_{\text{rg}}} b_j. \tag{2.77}$$

For plasma the equations determining ΔG remain the same as for the molecular gas, but the electric neutrality equation

$$\sum_j a_{ij} x_j^+ + \sum_j a_{ij} x_j^- = 0 \tag{2.78}$$

is added to the material balance constraints. Here x_j^+ and x_j^- are the amounts of positively and negatively charged components of the reaction mixture, respectively; a_{ij} is the charge of a mole of the jth component; and i in this case is an index of the electric neutrality equation.

Description of a condensed phase (more exactly, phases) of pure substances turns out simplest, as for it, the linear dependence

$$G_j = G_j^0 x_j. \tag{2.79}$$

is satisfied.

Among the solutions the present book considered only the dilute aqueous solutions of electrically neutral substances and electrolytes that are often dealt with when studying the processes of nature pollution (the atmosphere, water reservoirs and soil) and many technologies of cleaning harmful anthropogenic emissions.

The Gibbs energy of one mole of the jth component of the solution can be presented in the form

$$G_j = G_j^0 + RT \ln \frac{x_j}{\sigma_s} + RT \ln \gamma_j, \tag{2.80}$$

where σ_s is the total mole amount of a solvent and soluted substances; γ_j is a rational (referred to a mole fraction) coefficient of activity of the jth component.

The last term in the right part is deviation from ideality (a surplus Gibbs energy). The activity coefficients γ and activities a make it possible to describe real solutions in a way similar to ideal ones. This similarity is seen from the following equations:

a) for an ideal phase,

$$G_j = G_j^0 + RT \ln \frac{x_j}{\sigma_s}; \tag{2.81}$$

b) for a real phase,

$$G_j = G_j^0 + RT \ln a_j. \tag{2.82}$$

Comparison of (2.81) and (2.82) shows that the activity coefficient is determined by the relation

$$\gamma_j = a_j \sigma_s / x_j . \tag{2.83}$$

The main problem of modeling the solutions consists in finding the form of the function

$$\gamma_j = f(x).$$

When using the Debey–Hückel statistical theory of dilute solutions of strong electrolytes [53, 73, 113, 145], we find γ_j from the equations:

$$\lg \gamma_{\pm j} = -\frac{\varphi \left| Z_{1j} Z_{2j} \right| I\left(x_e\right)^{0.5}}{1 + I\left(x_e\right)^{0.5}} + \Psi\left(x_e\right), \tag{2.84}$$

$$\varphi = \frac{1.823 \cdot 10^6}{\varepsilon\left(T\right)^{1.5} T^{1.5}}, \tag{2.85}$$

$$I \approx \frac{27.778}{x_{\mathrm{H_2O}}} \sum_{j \in J_\pm} x_j \left(Z_{1j}^2 \nu_{1j} + Z_{2j}^2 \nu_{2j} \right), \tag{2.86}$$

$$\Psi = 0.1 \left| Z_{1j} Z_{2j} \right|, \tag{2.87}$$

$$\gamma_{\pm j}^{\nu_j} = \gamma_{+j}^{\nu_{1j}} \cdot \gamma_{-j}^{\nu_{2j}}, \tag{2.88}$$

$$\nu_j = \nu_{1j} + \nu_{2j}, \tag{2.89}$$

where $\gamma_{\pm j}$ is an average rational activity coefficient of the jth electrolyte; ν_{1j} and ν_{2j} are stoichiometric coefficients of cations and anions in the dissociation reaction of the jth electrolyte; φ and Ψ are coefficients; Z_{1j} and Z_{2j} are charges of cations and anions, respectively, into which the jth electrolyte dissociate; I is an ionic strength of solution; x_e is a vector of mole amounts of electrolytes; ε is water permitivity; and $J_\pm$ is a set of ions in solution. The form of the function $\varepsilon = f(T)$ can be obtained by approximating the tabulated data, for example, from [145]. The equation (2.86) was obtained from a generally accepted equation for ionic strength,

$$I = 0.5 \sum_{j \in J_\pm} Z_j^2 c_j \tag{2.90}$$

by representation of molar concentrations (c_j, mole/l) through mole amounts x_j.

Using (2.84)–(2.89) it is easy to transform (2.80):

$$\begin{aligned} G_j &= \nu_{1j} G_{+j}^0 + \nu_{2j} G_{-j}^0 + \nu_{1j} RT \ln \frac{\gamma_{+j} \nu_{1j} x_j}{\sigma_s} + \nu_{2j} RT \ln \frac{\gamma_{-j} \nu_{2j} x_j}{\sigma_s} \\ &= G_j^0 + RT \ln \left[\nu_{1j}^{\nu_{1j}} \nu_{2j}^{\nu_{2j}} \left(\frac{\gamma_{\pm j} x_j}{\sigma_s} \right)^{\nu_j} \right] = G_j^0 + RT \ln \left[\theta \left(\frac{\gamma_{\pm j} x_j}{\sigma_s} \right)^{\nu_j} \right], \end{aligned} \tag{2.91}$$

where θ is a coefficient.

The antilog is interpreted as activity of the jth electrolyte

$$a_{ij} = \theta \left(\frac{\gamma_{\pm} x_j}{\sigma_s} \right)^{\nu_j}. \tag{2.92}$$

Taking into account (2.91), the total Gibbs energy of the phase which is a mixed aqueous solution of neutral substances and electrolytes will be written in the form

$$\begin{aligned} G_s = G^0_{\mathrm{H_2O}} x_{\mathrm{H_2O}} + \sum_{J_n} \left(G^0_{nj} + RT \ln \tfrac{x_j}{\sigma_s} \right) x_j \\ + \sum_{J_e} \left[G^0_{ej} + RT \ln \left[\theta \left(\frac{\gamma_{\pm j} x_j}{\sigma_s} \right)^{\nu_j} \right] \right] x_j . \end{aligned} \tag{2.93}$$

The Gibbs energy of substances adsorbed on the surface of a solid phase in the first closure can be determined based on the idea of ideal surface gas:

$$G_{sg} = \sum_{j \in J_{sg}} \left(G^0_j + RT \ln \frac{x_j}{f} \right) x_j + \sum_{J_n} \left(G^0_z + RT \ln \frac{Z}{f} \right) Z, \tag{2.94}$$

where x_j is an amount of the adsorbed jth component: Z is a quantity of empty active centers on the surface of adsorbent (the mole amount of emptiness); f is the adsorbent surface measured in the total number of active centers; and G^0_z is assumed equal to zero.

For the ideal surface gas, we describe the balance of surfaces

$$\sum_{j \in J_{sg}} a_{ij} x_j + Z = f, \tag{2.95}$$

which is included in the system of material balances where a_{ij} is the adsorbent mole amount bound by one mole of the jth component (the number of active centers covered by one molecule of an adsorbed substance).

It is clear that the amounts of the surface gas components with the corresponding coefficients a_{ij} are included into the balances of conservation of the element amounts.

Equations (2.94)–(2.95) undoubtedly represent a maximum idealization of the surface thermodynamics and can serve for the initial studies of equilibria in a heterogeneous system.

The description of the substances in the colloid (fine-dispersed) state contains the Gibbs energy component associated with formation of the phase separation surface

$$\Delta G^d = \frac{2\alpha (T) \upsilon_d}{r} x_d, \tag{2.96}$$

where α is surface tension; υ_d and x_d are molar volume and mole amount of the dispersed phase, respectively; and r is radius of a spherical particle.

Modeling of Spatially Inhomogeneous Structures

The need to present the studied system in the form of an inhomogeneous structure may appear, for example, when we study the processes of atmospheric pollution or fuel burning in the furnaces of powerful boilers. In the atmosphere the air density as well as the concentrations of both its main components and pollutants change with altitude. In large furnaces whose cross-sections may reach several hundreds of square meters and height, several tens of meters, the individual zones often strongly differ from each other in gaseous phase composition, temperature, and conditions of heat and mass transfer. Figure 2.7 shows the elementary graph of a spatially inhomogeneous open system. At different levels of the system there can be inflows and sinks of a substance (shown by arrows). As was mentioned in the beginning of the section, the character of inhomogeneity is determined by the nature of the forces acting on the system.

The possible MEIS version of spatially inhomogeneous systems is written in the following form:

Find

$$\max \sum_{k,j\in J^{\text{ext}}} c_{kj}x_{kj} \tag{2.97}$$

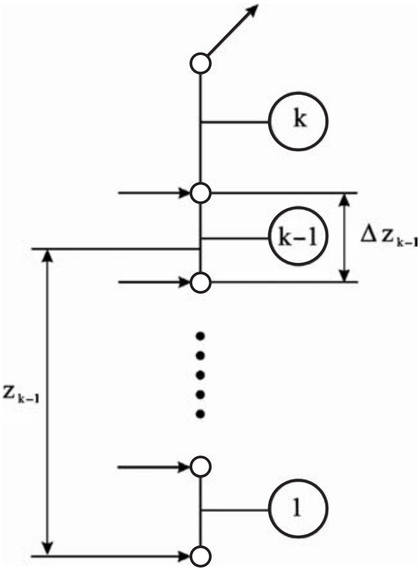


FIGURE 2.7. A graph of a spatially inhomogeneous system.

subject to

$$Ax = b, \tag{2.98}$$

$$A^{\text{in}}\sigma = Q, \tag{2.99}$$

$$\Delta z_1 P_1 \sigma_k T_k - \Delta z_k P_k \sigma_1 T_1 = 0, \quad k = 1, \ldots, K \tag{2.100}$$

$$D_t(y) = \{x : x \leq y\}, \tag{2.101}$$

$$\Phi(x) = \sum_{kj} \Phi_{kj}(x) x_{kj}, \quad j = 1, \ldots, n, \tag{2.102}$$

$$\Phi_{kj(g)} = G^0_{kj}(T_k) + RT \ln\left(P_k \frac{x_k}{\sigma_k}\right) + M_j g z_k, \tag{2.103}$$

$$\Phi_{kj(c)} = G^0_{kj(c)}(T_k) + \frac{2\alpha_j V_j}{r_{kj}}, \tag{2.104}$$

$$x_{kj} \geq 0, \tag{2.105}$$

where x and x_{kj} are a vector of substance amounts and its *kj*th component, respectively; A^{in} is a matrix of incidences (connections) of independent nodes and arcs of the graph mapping the system structure; $\sigma = (\sigma_1, \ldots, \sigma_k)^T$ is a vector of total substance amounts in the regions (on the graph arcs); Q is a vector of external inflows and sinks; z_k and Δz_k are a vertical coordinate in the middle of the *k*th zone and a thickness of the gas layer modeled by it, respectively; Φ and Φ_{kj} are generalized Gibbs energy of the system and a potential of the *kj*th component, respectively; g is free fall acceleration; and index “1” relates to the zone with the minimum z_k.

The model (2.97)–(2.105) includes two material balances: the first of them (2.98) represents the condition for mass conservation of elements in chemical reactions and phase transitions; the second balance (2.100) is the expression of the first Kirchhoff law (mass conservation at matter transfer along the branches of the system graph). Equation (2.100) is based on the assumption that the gas phase in each zone is ideal and describes the bond between the substance quantities in individual zones.

The generalized Gibbs energy in the model (2.97)–(2.105) represents the sum of chemical, gravity, and surface (associated with formation of phase interfaces) components. The form of the function Φ can be found by the technique of transforming the thermodynamic equilibrium equation. The technique was illustrated by a number of examples in Section 1.3. In the given case for the gaseous phase such an equation will be written in the form

$$V dp + M g dz + \sum_j \mu_j dx_j - S dT = 0, \tag{2.106}$$

where the terms on the left-hand side represent the works of the forces of pressure, gravity, chemical interactions, and elementary thermal impact, respectively. Since

$$V dp + \sum_j \mu_j dx_j - S dT = dG$$

(see equation 1.21), the equation (2.106) is transformed to the form

$$dG + mgdz = 0. \tag{2.107}$$

Thus the form of the function to be minimized becomes clear

$$\Phi = \sum_j \left(G_j + M_j g dz\right) x_j. \tag{2.108}$$

From (2.106) we can derive the equation of distribution of pressure and density throughout the height of the gas column:

$$\int_{P^0}^{P} V dp = RT \int_{P^0}^{P} \frac{dp}{P} = -Mg \int_{0}^{z} dz - \sum_j \mu_j dx_j + S \int_{T^0}^{T} dT,$$

$$P = P^0 \exp\left[-\frac{Mgz + \sum_j \mu_j dx_j - S(T - T^0)}{RT}\right], \tag{2.109}$$

where index "0" refers to the zero level of z. The equation (2.109) represents the Boltzmann distribution that takes into account gravitational, chemical, and thermal effects in the gas phase.

The form of the correction for the Gibbs energy of the condensed phase associated with the action of the surface tension force (the second term in the right-hand side of (2.104)) has already been discussed above. Equation (2.104), unlike expression (2.103) for Φ of the gas phase, does not include the components $M_j g z_k$ because the action of gravitantional forces on condensed particles is balanced by resistance forces whose field is not a potential. Therefore, it is impossible (or very difficult) to associate the solution to the equilibrium problem of these two types of forces with the solution to the extreme problem. At the same time their equilibrium does not affect the remaining equilibria that take place in the heterogeneous system and can be excluded from consideration.

Let us make an additional comment to explain the model (2.97)–(2.105). Inhomogeneity of the modeled system is represented in a "discreet" form in it. It is distributed among the final number of zones, each supposed to be homogeneous. Location of these zones in space can be presented in the form of a graph and the laws of conservation in the processes of substance and energy exchanges between the zones are presented in a network form. This explains the interpretation of (2.99) as a form of the first Kirchhoff law for the flows of the matter moving along a hydraulic circuit. It is clear that, according to the thermodynamic approach, the description of such a motion is reduced to the description of states of rest.

The use of the model (2.97)–(2.105) for the analysis of real objects can be illustrated by the calculation of substance distribution in the vertical air column of the isothermic atmosphere 5 km high. We divide this column into five zones, per convention, each one kilometer high, and suppose that on the system graph there is one node with the substance's inflow (0) and one with its sink (k). The assumed scheme can be understood if we imagine that up to some time instant there is no air above the earth's surface, and then it is gradually supplied to node 0 and from the node k with the sink, as a result of this motion, the air is distributed throughout the height of the vertical column.

The chosen initial set of reagents (y) and the results of calculations of states x^{eq} and $x^{\text{ext}}_{H_2O(g)}$ are presented in Table 2.5. The values in the columns x^{ext} are obtained by a number of calculations. Each calculation is the supposed search for the maximum concentration of one of the four components: NO_2, CO, HNO_3, and O_3. For the remaining components of the system the extreme concentrations are not calculated. Similar calculations are discussed in detail in Section 5.1, which is specially dedicated to the thermodynamic analysis of atmospheric pollution processes. In this section we only note that at highly idealized assumption (the atmosphere is isothermal; there is no condensed phase) the calculations performed confirm at least to some extent the correctness of the model (2.97)–(2.105) suggested by the authors. Thus, altitudinal distribution of each component x_j turned out to satisfy the Boltzmann distribution

$$x_{kj} = x_{1j} \exp\left(-\frac{M_j g z_k}{RT}\right), \tag{2.110}$$

and the impact of chemical reactions on the exponent index almost did not manifest itself. The results of these calculations correspond to the experimental data in [25].

We should also comment on the numerical values of x_{kj} presented in Table 2.5. Certainly, there is no physical sense in determining the concentrations of atmospheric components of less than 10^{-20}–10^{-25}. At such low densities of the matter, thermodynamics laws cease to obtain. The aim of including such extremely accurate results into Table 2.5 is only to demonstrate the reliability of the computation algorithm that allows solution of the problem with a great scatter in values of variables. The computational aspect of the thermodynamic analysis is considered in Chapter 4.

2.4. Mathematical Features of the Extreme Thermodynamic Models

Introductory Remarks

It is necessary to understand the mathematical features of the extreme models discussed both for development of effective methods and computational algorithms and for correct physical interpretation of the problems studied with these models. Indeed, there is a strong tie between the mathematical and physical nature of scientific problems. Below, as applied to the presented mathematical programming models, consider the specific features of the objective functions $F(x, y)$, systems of constraints and extreme solutions: x^{eq}, x^{ext}, and (x^{ext}, y^{ext}). The main problem of the analysis is, undoubtedly, the estimation of whether it is possible to reduce these extreme problems to the CP problems. The CP are subject to formalized

TABLE 2.5. Substances distribution in the vertical air column of the isothermal atmosphere (T = 273 K), (in moles).

Pressure, bar		0.985		0.869		0.766		0.676		0.526	
Height, m		0		1000		2000		3000		5000	
Substance	y	x^{eq}, mole	x^{ext}, mole	x^{eq}, mole	x^{ext}, mole	x^{eq}, mole	x^{ext}, mole	x^{eq}, mole	x^{ext}, mole	x^{eq}, mole	x^{ext}, mole
N_2	78.80	20.25	—	17.93	—	15.90	—	13.67	—	11.05	—
O_2	20.95	5.55	—	4.84	—	4.22	—	3.56	—	2.78	—
Ar	0.930	0.262	—	0.220	—	0.186	—	0.152	—	0.111	—
CO_2	$3.0\cdot10^{-2}$	$8.71\cdot10^{-3}$	—	$7.20\cdot10^{-3}$	—	$5.96\cdot10^{-3}$	—	$4.78\cdot10^{-3}$	—	$3.36\cdot10^{-3}$	—
He	$5.0\cdot10^{-4}$	$1.04\cdot10^{-4}$	—	$1.03\cdot10^{-4}$	—	$1.01\cdot10^{-4}$	—	$9.63\cdot10^{-4}$	—	$9.56\cdot10^{-5}$	—
H_2	$5.0\cdot10^{-5}$	$2.8\cdot10^{-49}$	—	$2.8\cdot10^{-49}$	—	$2.8\cdot10^{-49}$	—	$2.7\cdot10^{-49}$	—	$2.8\cdot10^{-49}$	—
NO	0	$1.6\cdot10^{-16}$	—	$1.4\cdot10^{-16}$	—	$1.3\cdot10^{-16}$	—	$1.1\cdot10^{-16}$	—	$8.5\cdot10^{-17}$	—
NO_2	0	$9.3\cdot10^{-10}$	$1.15\cdot10^{-4}$	$7.6\cdot10^{-10}$	$1.05\cdot10^{-4}$	$6.3\cdot10^{-10}$	$8.99\cdot10^{-5}$	$4.9\cdot10^{-10}$	$7.60\cdot10^{-5}$	$3.4\cdot10^{-10}$	$6.54\cdot10^{-6}$
N_2O	0	$3.0\cdot10^{-19}$	—	$2.5\cdot10^{-19}$	—	$2.1\cdot10^{-19}$	—	$1.7\cdot10^{-19}$	—	$1.2\cdot10^{-19}$	—
N_3	0	$7.7\cdot10^{-87}$	—	$7.7\cdot10^{-87}$	—	$7.7\cdot10^{-87}$	—	$7.7\cdot10^{-87}$	—	$7.7\cdot10^{-87}$	—
CO	0	$4.4\cdot10^{-52}$	$1.19\cdot10^{-5}$	$4.4\cdot10^{-52}$	$1.06\cdot10^{-5}$	$4.4\cdot10^{-52}$	$9.40\cdot10^{-6}$	$4.4\cdot10^{-52}$	$8.13\cdot10^{-6}$	$4.4\cdot10^{-52}$	$6.20\cdot10^{-5}$
H	0	$2.0\cdot10^{-63}$	—	$2.0\cdot10^{-63}$	—	$2.0\cdot10^{-63}$	—	$2.0\cdot10^{-63}$	—	$2.0\cdot10^{-63}$	—
H_2O	0	$1.18\cdot10^{-5}$	—	$1.09\cdot10^{-5}$	—	$1.01\cdot10^{-5}$	—	$9.09\cdot10^{-6}$	—	$8.01\cdot10^{-6}$	—
HN_3	0	$1.2\cdot10^{-86}$	—	$1.0\cdot10^{-86}$	—	$8.5\cdot10^{-87}$	—	$6.5\cdot10^{-87}$	—	$4.5\cdot10^{-87}$	—
HNO_2	0	$7.2\cdot10^{-16}$	—	$5.9\cdot10^{-16}$	—	$4.8\cdot10^{-16}$	—	$3.8\cdot10^{-16}$	—	$2.6\cdot10^{-16}$	—
HNO_3	0	$2.8\cdot10^{-10}$	$2.56\cdot10^{-5}$	$2.1\cdot10^{-10}$	$1.06\cdot10^{-5}$	$1.6\cdot10^{-10}$	$2.01\cdot10^{-5}$	$1.2\cdot10^{-10}$	$1.75\cdot10^{-5}$	$7.1\cdot10^{-11}$	$1.41\cdot10^{-5}$
N	0	$8.3\cdot10^{-87}$	—	$8.3\cdot10^{-87}$	–	$8.3\cdot10^{-87}$	—	$8.3\cdot10^{-87}$	—	$8.3\cdot10^{-87}$	—
N_2H_2	0	$2.4\cdot10^{-95}$	—	$2.4\cdot10^{-95}$	—	$2.4\cdot10^{-95}$	—	$2.4\cdot10^{-95}$	—	$2.4\cdot10^{-95}$	—
O	0	$2.9\cdot10^{-44}$	—	$2.9\cdot10^{-44}$	—	$2.9\cdot10^{-44}$	—	$2.9\cdot10^{-44}$	—	$2.9\cdot10^{-44}$	—
O_3	0	$4.8\cdot10^{-31}$	$2.14\cdot10^{-5}$	$3.9\cdot10^{-31}$	$1.87\cdot10^{-5}$	$3.2\cdot10^{-31}$	$1.68\cdot10^{-5}$	$2.5\cdot10^{-31}$	$1.48\cdot10^{-5}$	$1.7\cdot10^{-31}$	$8.82\cdot10^{-6}$
OH	0	$2.5\cdot10^{-31}$	—	$2.3\cdot10^{-31}$	—	$1.2\cdot10^{-31}$	—	$1.9\cdot10^{-31}$	—	$1.7\cdot10^{-31}$	—

interpretations and their numerical solutions are much easier than the multicriteria problems of concave programming (see Section 2.1).

To prove that the applied model belongs to the CP models it is necessary to reveal the concave or linear character of the maximized function (convexity or linearity of the minimized one) and convexity of $D_t(y)$. The latter is to a large extent determined by the character of the thermodynamic functions: U, H, F, G, and S. Like V, these functions are known to be extensive thermodynamic parameters and are homogeneous functions of the first power, that is, they satisfy the relationship

$$f(kx_1, \ldots, kx_n) = kf(x_1, \ldots, x_n). \tag{2.111}$$

The intensive thermodynamic parameters T, P, μ, mole energy, and mole entropy are homogeneous functions of the zero power for which

$$f(kx_1, \ldots, kx_n) = k^0 f(x_1, \ldots, x_n) = f(x_1, \ldots, x_n). \tag{2.112}$$

For homogeneous functions the Euler equation

$$\sum_{j=1}^{n} \frac{\partial f(x_1, \ldots, x_n)}{\partial x_j} x_j = \lambda f(x_1, \ldots, x_n), \tag{2.113}$$

is true where λ is a power of the homogeneous function. For ideal systems, U, H, F, G, S have the additivity property, which was explained in previous sections. However, for our analysis, it is most important to confirm the convexity property in these functions (for S, concavity), which is caused by the uniqueness of the point x^{eq} (see below). A strict convexity analysis of the thermodynamic functions in ideal systems is presented in a number of works (see [58, 167, 177]). As applied to real systems, the authors here consider these points in [81, 83]. As the convexity problem is very important, the whole section will be dedicated to it below, but here the MEIS features will be analyzed assuming convexity of thermodynamic functions.

Specific Features of the Block x^{eq}

In the block (2.34)–(2.37) of the general MEIS, the Gibbs energy is the objective function. At its convexity the region of the thermodynamic attainability $D_t(y)$ that represents part of the material balance polyhedron also becomes convex. Indeed, assume that there are two points $x' \in D_t(y)$ and $x'' \in D_t(y)$, i.e., such points that each of them can be reached from the initial state y by continuous trajectories that entirely belong to $D_t(y)$ and, along the what trajectories the Gibbs energy does not increase. However, then meeting the thermodynamic constraints, it is possible, iw we start the motion from y, to attain any point z of the section $[x', x'']$ either along the path $y - x' - z$ or along the path $y - x'' - z$, as the convex function $G(x)$ on either of the sections $[x', z]$ and $[x'', z]$ does not necessarily increase. Hence, along with the points x' and x'' that belong to $D_t(y)$, any point x of the section connecting them belongs to the same set. Therefore, the set $D_t(y)$ is convex. Thus, the search for x^{eq} belongs to CP problems.

Here, if the studied system is ideal or reduceable to the ideal—for example, by introducing the notion of activity, that is,

$$G_j = G_j^0 + f\left(\ln x_j\right), \tag{2.114}$$

the point x^{eq} is an interior point of $D_t(y)$ and all the components of vector x are contained in it, even if in negligibly small quantities.

Suppose the opposite, namely, that in the equilibrium state the amount of the jth component equals zero. Consider the behavior of the function $G(x)$ on the section $[x^{\mathrm{eq}}, x^{\rho}]$, where x^{ρ} is the point in which $x_j > 0$. Obviously, on the balance polyhedron (2.35) denoted below by $D(y)$, such a point can be found. By virtue of the fact that the derivative of $G(x)$ with respect to x_j at $x_j = 0$ goes to $-\infty$ in a rather small vicinity of x^{eq} on the section $[x^{\mathrm{eq}}, x^{\rho}]$, there will be a point whose jth coordinate will be strictly positive (since $x_j^{\rho} > 0$) and the value of $G(x)$ will be less than the value at the point $G(x^{\mathrm{eq}})$, a situation that is impossible. It is clear that with the presence of condensed substances in the mixture, the point x^{eq} by the corresponding coordinates can be located on the boundary line of $D_t(y)$.

Certainly the presented property of the point x^{eq} is satisfied only within applicability of the equilibrium thermodynamics itself. When the concentration of some component of x_j^{eq} is so insignificant that statistical rules cannot be applied to it, the strict inequality

$$x_j^{\mathrm{eq}} > 0 \quad \text{for all } j = 1, \ldots, n,$$

can be employed to analyze the behavior of mathematical models of type (2.34)–(2.37), but it cannot be extensively interpreted as applied to real objects.

There is another specific feature of the systems that obey equation (2.114). This feature is very important for the development of computational algorithms and analysis of solutions. It consists of this: If the line of the constant level $D(y)$ passing via some vertex of $G(x)$ does not contain any other point of the material balance polyhedron, then there is a region of thermodynamic unattainability near this vertex and it is impossible to get to this region from any other point of the polyhedron. The vertex itself in this case is the point of local maximum of the Gibbs energy. The presence of condensed phases in the system may lead to the absence of unattainability regions at some vertices (the minimum of $G_j(x)$ of liquid and solid substances is located at the points $x_j = 0$). In the case where the line $G(x) = \text{const}$ passing through a vertex crosses the interior region of $D(y)$, several vertices at once can belong to the thermodynamic unattainability region.

In concluding the discussion of the specific features of the model x^{eq} we note that the possibility of its reduction to the CP problem is not affected by the presence of condensed phases in the modeled system. Here the mathematical characteristics of the model are essentially improved owing to the above (see Section 2.2) description of individual phases of one and the same substance by different variables (components of vector x). This fact is illustrated by Fig. 2.8.

Suppose that some substance A is formed in the course of chemical relaxation. In the initial period of formation, A is contained only in the gas phase, and its Gibbs energy with the increasing amount x_A changes along the curve 1, which

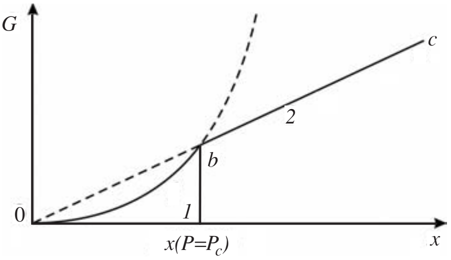


FIGURE 2.8. The Gibbs energy of the substance versus its mole quantity in the mixture.

corresponds to the equation

$$G_A = \left(G_A^0 + RT \ln P_A\right) x_A.$$

When reaching the point $x\,(P = P_c)$ in which the partial pressure P_A becomes equal to the saturation pressure, the condensed phase formation starts and the change of G_A is shown by straight line 2. At the point b the bold line $0bc$ has a disrupted derivative and the function G_A in the vicinity of this point loses the convexity property. In multicomponent and multiphase systems, the form of the function G_A can get additionally complicated due to dependence of P_A on the total composition of the mixture. However, since the condensed and gas phases of A are described by different variables, the problem of convexity and, moreover, of multi-extremality of G_A does not arise. Along the axes corresponding to the gas phases there is convexity of G, and along the axes on which the values of G_{jc} are plotted there is linearity.

Specific Features of the Problem of the Search for x^{ext}

The described properties of the model (2.34)–(2.37) are due entirely for $D_t\,(y)$, which is set by the expression (2.40) in the model of x^{ext} (2.38)–(2.42). However, transition to a more general and complicated mathematical description naturally generates the new principal features in the mathematical nature of the problem solved.

First of all, let us show the possibility of degeneracy of extreme states. For this purpose we address once again the elementary example, the isomerization reaction. Let the maximum of the function

$$F\,(x) = x_2 + x_3$$

be sought on the material balance triangle (see Fig. 2.4*a*) and $y = (1, 0, 0)^T$. Then all the points of the edge 2–3 that belong to $D_t\,(y)$ are the maximum points of $F\,(x)$, i.e., are solutions of the problem stated. The function $F\,(x)$ under these conditions turns out to be parallel to the edge A_2A_3. In a general case, at degeneracy of the solutions $F\,(x)$ is parallel to one of the $D\,(y)$ edges.

Nondegenerate solutions are located on the boundary line of $D\,(y)$ due to linearity of the objective function and convexity of the set of its definition. Here there can be three situations, as pointed out by E. G. Antsiferov and graphically presented

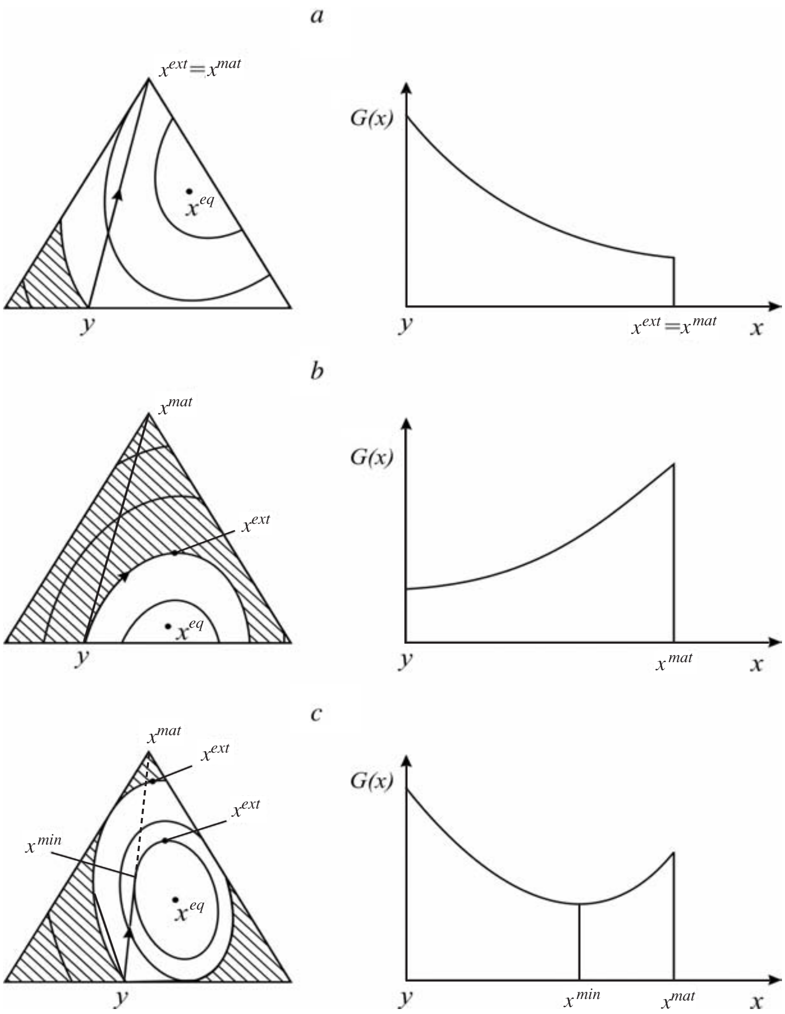


FIGURE 2.9. Possible locations of the extreme point (x^{ext}) of the objective function.

in Fig. 2.9. Their analysis is based on the preliminary solution of the auxiliary LP problem (2.22)–(2.23).

The first situation (Fig. 2.9*a*) is characterized by the fact that the Gibbs energy monotonically decreases on the section $[y, x^{\text{mat}}]$ between the initial state (y) and the solution to the LP problem x^{mat}—the solution that corresponds to the maximum of the objective function (2.38) on $D(y)$. In this case the point x^{mat} is a solution to the problem of the search for x^{ext}. The physical interpretation of the situation is in the fact that thermodynamics does not affect the extreme concentration of the process products, a concentration that is determined solely by the material balance.

From the mathematical viewpoint the problem is transformed into the canonic LP problem coinciding with the mentioned auxiliary one:

Find

$$\left.\begin{array}{ll} & \max\left(F\left(x\right)=\sum\limits_{j}c_{j}x_{j}\right)=F(x^{\text{ext}}) \\ \text{subject to} & \\ & \sum\limits_{j}a_{ij}x_{j}=b_{i},\quad x_{j}\geq 0,\quad i=1,\ldots,m,\;\; j=1,\ldots,n\;; \end{array}\right\} \qquad (2.115)$$

It follows that the extremum point is located in one of the $D\left(y\right)$ vertices and the number of nonzero components $x^{\text{ext}}=x^{\text{mat}}$ does not exceed m—the number of material balance equations. As is clear from the analysis of the problem of the search for x^{eq}, the first situation may appear either in the absence of unattainability regions in the vicinity of some vertices or in the case when these regions are negligibly small.

In the second situation (Fig. 2.9*b*) in the direction from y to x^{mat} the Gibbs energy increases continuously and, hence, motion along the section $[y, x^{\text{mat}}]$ turns out to be impossible. The search for maximum concentrations is reduced to the following CP problem:

Find

$$\left.\begin{array}{ll} & \max\left(F\left(x\right)=\sum\limits_{j}c_{j}x_{j}\right)=F(x^{\text{ext}}) \\ \text{subject to} & \\ & \sum\limits_{j}a_{ij}x_{j}=b_{i},\quad x_{j}\geq 0,\quad i=1,\ldots,m,\quad j=1,\ldots,n, \\ & G\left(x\right)\leq G\left(y\right). \end{array}\right\} \qquad (2.116)$$

The point x^{ext} is located on the initial surface of the Gibbs energy $G=G\left(y\right)$. The value of the objective function in this case meets the condition

$$F(y)\leq F(x^{\text{ext}})\leq F(x^{\text{mat}}). \qquad (2.117)$$

The third situation (Fig. 2.9*c*) consists in the fact that on the section $[y, x^{\text{mat}}]$ there is a minimum of G (point x^{min}). The point x^{ext} turns out to be located on the boundary line of $D_t\left(y\right)$. The problem of determining its location is considered in Chapter 3. The CP problem solved takes the following form:

Find

$$\left.\begin{array}{ll} & \max\left(F\left(x\right)=\sum\limits_{j}c_{j}x_{j}\right)=F(x^{\text{ext}}) \\ \text{subject to} & \\ & \sum\limits_{j}a_{ij}x_{j}=b_{i},\quad x_{j}\geq 0,\quad i=1,\ldots,m,\quad j=1,\ldots,n, \\ & G\left(x\right)\leq G(x^{\text{ext}}). \end{array}\right\} \qquad (2.118)$$

Solution of the problem (2.118) as well as that of (2.116), meets the condition of (2.117). Further, this third situation will be called "a thermodynamic pothole."

The mathematical nature of the problem of searching for x^{ext} gets essentially more complicated in the cases where the system of constraints includes nonlinear energy balances (at fixing H and P, or U and V) or nonlinear entropy balances (at fixing S and P, or S and V).

Thus, at constant H and P, on the way from y to x^{mat} we should observe the nonlinear enthalpy balance and, hence, the section $[y, x^{\text{mat}}]$ becomes curvilinear. Under these circumstances it is sensible to replace the point x^{mat} by $x^{\text{m.h}}$ in which the objective function extreme is attained and simultaneously the material and enthalpy balances are met.

However, the difficulties that arise can be overcome by the transition from the space (x, T) to the space x, at which, as will be shown in Section 2.5, the concavity of entropy and convexity of $D_t(y)$ are maintained. Such a transition makes the studies of the systems with given U and V, S and P, or S and V mathematically similar to the study of systems with fixed T and P, or T and V.

Perhaps the last specific feature of the model x^{ext} worth mentioning is the implicitly set constraints on the change in thermodynamic functions (the expression (2.40)), which, to an essential extent, complicates the construction of computational algorithms for solution of the problem of type (2.38)–(2.42).

Analysis of the Problem of the Search for the Point $(x^{\text{ext}}, y^{\text{ext}})$

The general problem (2.43)–(2.50) of the search for the point $(x^{\text{ext}}, y^{\text{ext}})$ differs from the blocks of x^{eq} and x^{ext}, first of all, by nonlinearity and fractional character of the objective function. To represent objective function form on the linear polyhedron (2.45), (2.46), (2.50) at a varying initial composition of reagents, we suppose that the mole number of the jth component whose extremum is sought for is determined by the expression

$$x_j = y_\rho - \varepsilon_\rho , \tag{2.119}$$

where y_ρ is an initial reagent involved in the reaction of x_j formation and the only initial reagent whose economical use is of interest to us; ε_ρ is an unreacted part of y_ρ .

With the taken assumptions, which simplify the problem significantly, the objective function and the Lagrange function of the system (2.43)–(2.46) takes the form

$$F(x, y) = x_j / y_\rho = \left(y_\rho - \varepsilon_\rho\right) / y_\rho \tag{2.120}$$

and

$$L = \frac{y_\rho - \varepsilon_\rho}{y_\rho} + \lambda_1 \left(1 - \sum_{j=1}^{l} M_j y_j\right) + \sum_{i=2}^{m+1} \lambda_i \left(b_i - \sum_j a_{ij} x_j\right) + \sum_{i=m+2}^{2m+1} \lambda_i \left(b_i - \sum_j a_{ij} y_j\right), \tag{2.121}$$

and two first derivatives of the Lagrange function turn out to be equal to

$$\frac{\partial L}{\partial y_\rho} = \frac{\varepsilon_\rho}{y_\rho^2} - \lambda_1 M_\rho - \sum_{i=m+2}^{2m+1} \lambda_i a_{i\rho}, \tag{2.122}$$

$$\frac{\partial^2 L}{\partial y_\rho^2} = -\frac{2\varepsilon_\rho}{y_\rho^3} \leq 0. \tag{2.123}$$

From this follows the concavity of the function (2.43) by y for the considered case. Obviously, a similar proof can be given for the somewhat less strict constraints than those assumed above, for example, for the situation where we are interested in the economical use of several reagents, and in which the relationship between x_j and y_ρ gets more complicated as compared to equality (2.119). In all the previous studies on the model (2.43)–(2.50) there were no deviations from concavity of $F(x, y)$. Hence, at least in many cases, the problem (2.43)–(2.50) at maximization of $F(x, y)$ is reduced to a CP problem. However, in the future the character of the objective function of MEIS should be analyzed more strictly.

The problem of finding the value of y, optimal in terms of minimization of $F(x)$ relates to concave mathematical programming, and it is of a multi-extreme character. Practically, the solution of this problem is very important in creating environmentally friendly technologies (the search for the most environmentally benign composition of reagents) and, therefore, is worth further scrutiny.

Another important distinction of the model (2.43)–(2.50) from the models (2.34)–(2.37), and (2.38)–(2.42) is that it does not contain explicit relationships between the values of vectors x and y and, therefore, it is not possible to find the analytical expressions for the derivatives

$$\frac{\partial F(x, y)}{\partial y}.$$

A feature that imposes constraints on the choice of computational algorithms.

In conclusion of this section we would like to make a comment on MEIS concerning the variables ξ. Transition from the space x to the space ξ is due to replacement of the material balance polyhedron

$$Ax = b, \quad x \geq 0,$$

by the polyhedron

$$\nu\xi = x^e - y, \quad \xi \geq 0, \tag{2.124}$$

with the edges of unit length along the coordinate axes (see condition (2.55)). In (2.124) ν is a vector of stoichiometric coefficients: x^e is a value of the vector x provided that all the reactions are completed ($\xi = 1$ for all $i = 1, \ldots, m$). Such a linear transformation of balance equations seems not to affect noticeably the mathematical nature of the problem stated.

2.5. Convex Analysis of the Thermodynamics Problems

Preliminary Considerations

After a brief analysis of the main mathematical features of MEIS, which is made assuming the convexity of thermodynamic functions, let us discuss in more detail the problem of determining this convexity, as this problem is a key point in both the estimation of the $D_t(y)$ convexity and the estimation of the possibility itself of reducing the extreme thermodynamic problems to CP problems.

Ya. B. Zeldovich [177] proved free energy convexity on the material balance polyhedron only for the ideal gas. One of the difficulties of proving the convexity (nonconcavity) or concavity of U, H, F, G, and S consists in the fact that their Hessians are identically equal to zero when the variables x_j are chosen as independent ones.

Indeed, for homogeneous functions of the first power that include all the above extensive quantities, according to the Euler equation it is true that

$$f(x) = \sum_{j=1}^{n} x_j \frac{\partial f(x)}{\partial x_j}. \tag{2.125}$$

Hence,

$$\frac{\partial f(x)}{\partial x_k} = \sum_{j=1}^{n} \frac{\partial x_j}{\partial x_k} \frac{\partial f(x)}{\partial x_j} + \sum_{j=1}^{n} x_j \frac{\partial^2 f(x)}{\partial x_j \partial x_k}.$$

Since only at $k = j$

$$\frac{\partial x_j}{\partial x_k} \neq 0, \ \frac{\partial f(x)}{\partial x_k} = \frac{\partial f(x)}{\partial x_k} + \sum_{j=1}^{n} x_j \frac{\partial^2 f(x)}{\partial x_j \partial x_k}$$

and

$$\sum_{j=1}^{n} x_j \frac{\partial^2 f(x)}{\partial x_j \partial x_k} = 0,$$

then for any nonzero vector x

$$H(x) = \left| \frac{\partial^2 f}{\partial x_j \partial x_k} \right| \equiv 0. \tag{2.126}$$

Satisfaction of equality (2.126) can be explained in another way, without employing the Euler equation. For homogeneous functions of the first power for any vector $y = kx$, the following equations are obtain:

$$\frac{df}{dy} = \text{const and } \frac{d^2 f}{dy^2} = 0.$$

This, certainly, relates to the regions of intersections of the above vectors with the polyhedron $Ax = b$, $x \geq 0$. Hence, the equality of Hessians of thermodynamic functions to zero becomes clear.

We illustrate the validity of (2.126) by finding the value of the Gibbs energy Hessian

$$H(x) = \begin{vmatrix} \dfrac{\partial^2 G}{\partial x_1^2} & \dfrac{\partial^2 G}{\partial x_1 \partial x_2} \\ \dfrac{\partial^2 G}{\partial x_2 \partial x_1} & \dfrac{\partial^2 G}{\partial x_2^2} \end{vmatrix} \tag{2.126a}$$

for a two-component mixture of ideal gas that satisfies the equation

$$G_j = \left(G_j^0 + RT \ln\left(\frac{x_j}{\sigma}\right)\right) x_j. \tag{2.127}$$

In (2.127) the multiplier P whose value does not affect the Hessian property is excluded from the logarithmic expression. For such a mixture, the following relations are true:

$$\frac{\partial G}{\partial x_j} = G_j^0 + RT \ln\left(\frac{x_j}{\sigma}\right), \tag{2.128}$$

$$\frac{\partial^2 G}{\partial x_j^2} = RT\left(\frac{1}{x_j} - \frac{1}{\sigma}\right), \quad \frac{1}{x_j} > \frac{1}{\sigma}, \quad \frac{\partial^2 G}{\partial x_j^2} > 0, \tag{2.129}$$

$$\frac{\partial^2 G}{\partial x_j \partial x_k} = -\frac{RT}{\sigma}, \tag{2.130}$$

$$H = (RT)^2 \left[\left(\frac{1}{x_1} - \frac{1}{\sigma}\right)\left(\frac{1}{x_2} - \frac{1}{\sigma}\right) - \frac{1}{\sigma^2}\right] = 0. \tag{2.131}$$

The inequalities (2.129) are rigorous since all the components of the ideal gas mixture are rigorously more than zero.

The circumstance forces us to determine the signs of either eigenvalues or principal minors of the Hessian matrix when proving the convexity or concavity of thermodynamic functions. However, these signs allow one to strictly determine the character of the studied problem only for the two-component systems; for homogeneous functions, however, the conclusions obtained for a two-dimensional problem are easily applied to multicomponent systems.

We will begin the analysis of thermodynamic function convexity with a proof of the last statement. The analysis will then follow the plan:

1) substantiation of the possibility to extend the proof of convexity of the homogeneous functions of two variables to similar functions of a larger number of variables;
2) determination of conditions for the convexity of functions for gas mixtures subject to Dalton's law;
3) derivation of convexity conditions for real gases;
4) analysis of convexity of additive functions in systems with nonlinear balances;
5) analysis of convexity of nonadditive functions.

We hope this short plan will guide the reader through the discussion.

Determination of Convexity of Functions in Multidimensional Systems

Suppose we have found the Gibbs energy G convexity at dimensionality of the vector x, $n = 2$. Then the function of change in this energy due to deviation of the mixture components from the standard states will also be convex:

$$\Delta G = \Delta G_1 (P_1) x_1 + \Delta G_2 (P_2) x_2$$

(G_j^0 does not affect the form of the second derivatives that determine the convexity).

Now consider the function

$$\sum_{j=1}^{n} \Delta G_j \left(P \frac{x_j}{\sigma (x)} \right) x_j$$

of a multicomponent system. To determine the convexity of $\Delta G (x)$ it is necessary to prove the inequality

$$\begin{aligned} \sum_{j=1}^{n} \Bigg[& x_j \Delta G_j \left(P \frac{x_j}{\sigma (x)} \right) + y_j \Delta G_j \left(P \frac{y_j}{\sigma (y)} \right) \\ & - (x_j + y_j) \Delta G_j \left(P \frac{x_j + y_j}{\sigma (x) + \sigma (y)} \right) \Bigg] \geq 0 \end{aligned} \tag{2.132}$$

for any pairs of points x_j and y_j from the set of reaction mixture compositions. It is easy to see that (2.132) is reduced to a general determination of convexity of the functions (2.4). Introduce the notation:

$$u_j = \sigma (x) - x_j; \quad t_j = \sigma (y) - y_j.$$

It is obvious that $u_j \geq 0$ and $t_j \geq 0$ (the equalities may take place in the presence of condensed phases in the system). Now the equation in the square brackets on the left-hand side of (2.132) can be written in the form

$$\begin{aligned} \Delta j = {} & x_j \Delta G_j \left(P \frac{x_j}{x_j + u_j} \right) + y_j \Delta G_j \left(P \frac{y_j}{y_j + t_j} \right) \\ & - (x_j + y_j) \Delta G_j \left(P \frac{x_j + y_j}{x_j + y_j + u_j + t_j} \right), \end{aligned} \tag{2.133}$$

i.e., using the homogeneity property, we represent the function of many variables as a function of two variables and, hence, prove for the assumed convexity of the latter the convexity of the former. There was only one assumption made for the proof: that the partial pressure of the component depends on its mole fraction and, apparently, it should not at all essentially affect the generality of the obtained conclusion.

Convexity of Functions for the Systems that Satisfy Dalton's Law

For a two-component mixture it is easy to show that from the condition of positiveness of eigenvalues of the Hessian matrix follows the positiveness of its diagonal elements

$$\left|\frac{\partial^2 G}{\partial x_1^2}\right| \quad \text{and} \quad \left|\frac{\partial^2 G}{\partial x_2^2}\right|,$$

a result that turns out to be sufficient to prove convexity of the function G.

We write with the assumption of observing Dalton's law ($P = P_1 + P_2$) the variable part of G in the form

$$\tilde{G} = \tilde{G}_1\,(P_1)\,x_1 + \tilde{G}_2\,(P_2)\,x_2, \tag{2.134}$$

and we find the statement of the condition of the Gibbs energy convexity:

$$2\frac{\partial G_j}{\partial P_j} + P_j\frac{\partial^2 G_j}{\partial P_j^2} > 0. \tag{2.135}$$

Derivation of (2.135) from (2.134) is presented in [81, 83].

Since $\partial G/\partial P = V$, expression (2.135) can be transformed as applied to the variables P and V:

$$2V_j + P_j\frac{\partial V_j}{\partial P_j} \geq 0 \quad \text{for all} \quad j = 1, \ldots, n. \tag{2.136}$$

We write the condition (2.136) taking into account that the conclusion obtained on the example of the two-component mixture can be applied to a mixture of as large a number of components as we desire. In the case of ideal gas for which $V_j = \frac{RT}{P_j}$, (2.136) passes to the relations

$$\frac{2RT}{P_j} - \frac{RT}{P_j} = \frac{RT}{P_j} \geq 0,$$

which is, apparently, true for any T.

Real Systems

To specify the criteria (2.135) and (2.136) as applied to the systems that meet different equations of state it is convenient to use the reduced parameters:

$$\tau = \frac{T}{T_c}, \quad \pi = \frac{P}{P_c} \quad \text{and} \quad \varphi = \frac{V}{V_c}, \tag{2.137}$$

where index c relates to the critical state of the substance. The convenience of this is due to the dependence of the thermodynamic function behavior on the location of the studied process trajectory relative to a critical point. The condition (2.136) in the given coordinates takes the form

$$2\varphi_j(\pi_j) + \pi_j \frac{\partial \varphi_j}{\partial \pi_j} \geq 0. \tag{2.138}$$

The algorithm for determination of the convexity conditions of G at a set equation of state is reduced to the following procedures:

- Using a number of transformations the criterion (2.138) is replaced by the inequality

  $$\Psi(\varphi_j, \tau_j) \geq 0,$$

  where Ψ is monotonically increasing function τ.
- The values φ_j and τ_j are found for the case where the equality

  $$\Psi(\varphi_j, \tau_j) = 0$$

  corresponds to the minimum of Ψ, and for this purpose the system of equations

  $$\frac{\partial \Psi}{\partial \tau} = 0, \quad \Psi(\varphi_j, \tau_j) = 0 \tag{2.139}$$

  is solved.

At values τ equal to or larger than the obtained solution of (2.139), G of the system turns out to be a strictly convex function due to monotonicity of Ψ. The condition (2.139) is sufficient but not necessary. Indeed, the convexity region may appear to be somewhat larger than what follows from the condition.

For the gas mixture obeying the equation of van der Waals that, in the given coordinates, has the form

$$\pi = 8\tau\big/(3\varphi - 1) - 3\varphi^{-2}, \tag{2.140}$$

the function Ψ is determined by the expression[1]

$$\Psi(\varphi_j, \tau_j) = \frac{8}{3}\varphi_j^2(3\varphi_j + 1) - 3(3\varphi_j - 1)^2, \tag{2.141}$$

---

[1] We present the derivation of the equation that determines the value $\Psi_j\left(\varphi_j, \tau_j\right)$, for the van der Waals gas. First, find the set of values τ for which $\varphi_j\left(\pi_j\right)$ satisfies the condition (2.138). It is obvious that

$$\frac{d\pi_j}{d\varphi_j} \cdot \frac{d\varphi_j}{d\pi_j} = 1 \quad \text{and} \quad \varphi'_j(\pi_j) = \frac{1}{\pi'_j(\varphi_j)}.$$

Substituting the expression for $\varphi'_j(\pi_j)$ into (2.138) we obtain

$$2\varphi_j + \pi_j/\pi'_j(\varphi_j) \geq 0.$$

Since the derivative of the reduced pressure with respect to the reduced volume for the van der Waals gas

$$\pi'_j(\varphi_j) = -24\tau_j(3\varphi_j - 1)^{-2} + 6\varphi_j^{-3} \tag{2.140a}$$

at $\tau > 1$ is always negative, the condition of convexity (2.136) can be rewritten in the form

$$2\varphi_j(\pi_j)\pi'_{j\varphi}(\varphi, \tau) + \pi_j(\varphi, \tau) \leq 0.$$

Substituting the values π_j and π'_j from (2.140) and (2.140a) into this expression and making elementary transformations, we find that $\Psi(\varphi_j, \tau_j)$ is determined by the equation (2.141).

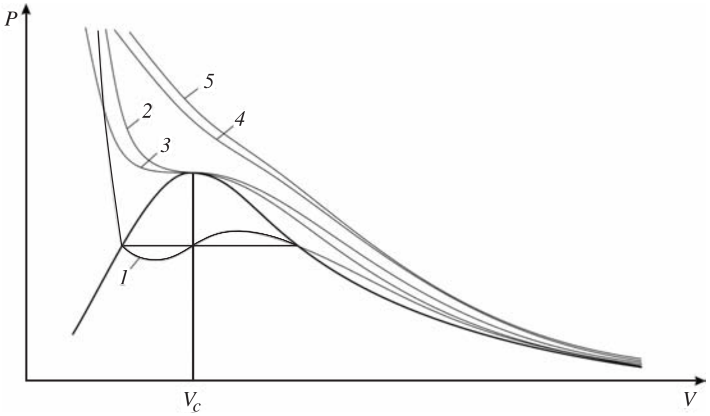


FIGURE 2.10. Isotherms and regions of convexity: P, V - diagram of ideal and real gases. *1, 2, 4*: the van der Waals gas ($1 - T < T_c$; $2 - T = T_c$; $4 - T = 1.148T_c$); *3, 5*: the Redlich–Kwong gas ($3 - T = T_c$; $5 - T = 1.111T_c$).

and conditions (2.139) are described by the equalities

$$\frac{8}{3}\varphi_j\tau_j\left(9\varphi_j+2\right)=18(3\varphi_j-1);\quad \frac{8}{3}\varphi_j^2\tau_j(3\varphi_j+1)=3(3\varphi_j-1)^2. \tag{2.142}$$

The solution to (2.142) is the point with coordinates $\varphi = 1.187$ and $\tau \approx 1.148$. Hence, G turns out to be a strictly convex function at

$$T \geq 1.148T_{cj} \quad \text{for all} \quad j = 1, \ldots, n.$$

Application of such transformations for gases that meet the Redlich–Kwong equation (2.71) showed that for them the condition of the Gibbs energy convexity is determined by the inequality

$$T \geq 1.111T_{cj} \quad \text{for all} \quad j = 1, \ldots, n.$$

Isotherms and regions of convexity of G for the van der Waals and Redlich–Kwong gases are shown in Fig. 2.10.

Additive Models with Nonlinear Balances

Nonlinear energy balances can be included in the system of constraints in the models of isolated systems (see (2.56)–(2.63)) and systems with fixed U and V or H and P (see (2.65)). When we set the constant S and P or S and V, the mathematical description of a system should contain nonlinear entropy balances.

Along the axes of x_j the objective functions of the models with nonlinear constraints retain all the above specific features. For example, using the transformations similar to those made when analyzing the convexity of G it is possible to show that the condition of entropy convexity on the polyhedron $D(y)$ at constant H, P and T has the form:

$$2\frac{\partial S_j}{\partial P_j} + P_j \frac{\partial^2 S_j}{\partial P_j^2} \le 0 \tag{2.143}$$

or

$$-\frac{1}{T}\left(2V\left(P_j\right) + P_j \frac{\partial V_j}{\partial P_j}\right) \le 0. \tag{2.144}$$

To study the extreme properties of the model (2.65) in coordinates x, T we construct the Lagrange function, supposing that the reagents represent a mixture of ideal gases and $P = 1$ (the latter supposition, obviously, does not affect the results of analysis):

$$\begin{aligned} L &= \sum_{j=1}^{n}\left(S_j^0(T) - R\ln\left(\frac{x_j}{\sigma}\right)\right)x_j + \sum_{i=1}^{m}\lambda_i\left(b_i - \sum_{j=1}^{n}a_{ij}x_j\right) \\ &\quad + \lambda_{m+1}\left[H^y - \sum_{j=1}^{n}H_j\left(x_j, T\right)x_j\right]. \end{aligned} \tag{2.145}$$

To get the equations of derivatives of L with respect to x and T let us make another simplifying assumption: that the relationship between the isobaric heat capacity and the temperature is expressed by the equation

$$c_p = \alpha + \beta T. \tag{2.146}$$

Such a binomial approximation of the function $c_p(T)$ in this case is quite sufficient, since at $\alpha \ge 0$ and $\beta \ge 0$ it correctly shows the monotonically nondecreasing character of this function and, hence, the convexity of $H(T)$.

With satisfaction of (2.146) and assumption that $S_j(0) = 0$ and $c_{pj}(0) = 0$,

$$S_j^0(T) = \int_0^T \frac{\left(\alpha_j + \beta_j T\right)}{T}dT = \alpha_j \ln T + \beta_j T, \tag{2.147}$$

$$H_j(T) = \int_0^T (\alpha_j + \beta_j T)dT + \Delta H_j(0) = \alpha_j T + 0.5\beta_j T^2 + \Delta H_j(0), \tag{2.148}$$

where $\Delta H_j(0)$ is the enthalpy of the jth component formation at 0 K.

Taking into account (2.147) and (2.148), we find the first and second derivatives of L with respect to x_j and T:

$$\frac{\partial L}{\partial x_j} = S_j^0(T) - R \ln\left(x_j/\sigma\right) - \sum_{i=1}^{m} \lambda_i a_{ij} - \lambda_{m+1} H_j(T), \tag{2.149}$$

$$\frac{\partial^2 L}{\partial x_j^2} = -R\left(\frac{1}{x_j} - \frac{1}{\sigma}\right), \tag{2.150}$$

$$\frac{\partial L}{\partial T} = \frac{1}{T} \sum_j \left(\alpha_j + \beta_j T\right) x_j - \lambda_{m+1} \sum_j \left(\alpha_j + \beta_j T\right) x_j, \tag{2.151}$$

$$\frac{\partial^2 L}{\partial T^2} = -\frac{1}{T^2} \sum_j \alpha_j x_j - \lambda_{m+1} \sum_j \beta_j x_j.$$

Since at the derivative (2.151) equal to zero (which is true at equilibrium)

$$\lambda_{m+1} = 1/T, \tag{2.152}$$

then

$$\frac{\partial^2 L}{\partial T^2} = -\frac{1}{T^2} \sum_j \alpha_j x_j - \frac{1}{T} \sum_j \beta_j x_j. \tag{2.153}$$

From the equality of (2.150) we can conclude that

$$-R\left(\frac{1}{x_j} - \frac{1}{\sigma}\right) < 0 \tag{2.154}$$

is the condition of the entropy concavity along the axes x_j. This inequality is strict since for ideal mixtures $x_j > 0$ for all $j = 1, \ldots, n$. The mathematical relation between (2.154) and the condition (2.144) can easily be found.

From (2.153) it follows that concavity of L with respect to T is determined by the equation

$$-\frac{1}{T^2} \sum_j \alpha_j x_j - \frac{1}{T} \sum_j \beta_j x_j \le 0,$$

which is equivalent to the condition

$$-\frac{1}{T^2} \sum_j c_{pj} x_j \le 0, \tag{2.155}$$

Which, in turn, is always satisfied due to positiveness of c_P.

Thus, the conditions of interaction with the environment and related nonlinear balances practically do not affect the convexity of the thermodynamic functions. It even appears possible, maintaining the convexity of the functions, to simplify the problem by passing from the space x, T to the space x and get rid of the nonlinear constraint

$$\sum_{j=1}^{n} H_j(T) x_j - H^y = 0, \tag{2.156}$$

an approach that is convenient in terms of calculations.

Indeed, due to monotonicity of the function

$$\sum_{j=1}^{n} H_j x_j = H(T)$$

temperature can be presented as a single-valued function x:

$$T = T(x).$$

To find the extreme properties of the transformed model for the systems with $H = \text{const}$ and $P = \text{const}$, note that we have already proved the concavity

$$\sum_j \Delta S_j \left(P_j\right) \neq f(T)$$

and so we determine the character of the function

$$\tilde{S}(x, T(x)) = \sum_{j=1}^{n} S_j^0 (T(x)) x_j. \tag{2.157}$$

For this purpose we find the first and second derivatives of $\tilde{S}(x, T(x))$ with respect to some coordinate x_k.

The first derivative is

$$\frac{\partial \tilde{S}(x, T(x))}{\partial x_k} = \sum_j \frac{\partial S_j^0 (T)}{\partial T} \frac{\partial T(x)}{\partial x_k} x_j + S_k^0 (T(x)). \tag{2.158}$$

To obtain the equation for $\frac{\partial T(x)}{\partial x_k}$ we use the derivative

$$\frac{\partial}{\partial x_k} \left(\sum_{j=1}^{n} H_j (T(x)) x_j - H^y \right) = \sum_{j=1}^{n} \frac{\partial H_j (T)}{\partial T} \frac{\partial T}{\partial x_k} x_j + H_k (T).$$

Taking into account that this derivative equals zero, we find

$$\frac{\partial T(x)}{\partial x_k} = -\frac{H_k (T)}{\sum\limits_{j=1}^{n} x_j c_{pj}}$$

since $\frac{\partial H_j(T)}{\partial T} = c_{pj}$.

Bearing in mind that

$$\frac{\partial S_j^0 (T)}{\partial T} = \frac{c_{pj}}{T},$$

we have that

$$\frac{\partial \tilde{S}(x, T(x))}{\partial x_k} = -\frac{H_k (T)}{T} + S_k^0 (T(x)) = -\frac{G_k^0 (T)}{T}. \tag{2.159}$$

The second derivative

$$\frac{\partial^2 \tilde{S}(x, T(X))}{\partial x_k^2} = -\frac{\partial}{\partial x_k} \left(\frac{G_k^0 (T)}{T} \right) = -\frac{H_k^2 (T)}{T^2} \left(\sum_{j=1}^{n} x_j c_{pj} \right)^{-1}. \tag{2.160}$$

It is obvious that this is always less than zero and at transition from the space x, T to the space x, the problem discussed still belongs to CP problems.

Nonadditive Heterogeneous Models

Nonadditive systems comprise practically all the real systems, since there is always interaction to some or another extent between particles of different types and, hence, the expressions for entropy and energy should contain the terms that reflect this interaction.

First of all, we point out that the nonadditive models have a very important property in terms of mathematical analysis: It consists in the fact that the mole thermodynamic functions of the jth component are not derivatives of the corresponding functions of the system with respect to x_j, i.e.,

$$G_j \neq \frac{\partial G}{\partial x_j}, \quad F_j \neq \frac{\partial F}{\partial x_j}, \quad H_j \neq \frac{\partial H}{\partial x_j}, \quad U_j \neq \frac{\partial U}{\partial x_j}, \quad S_j \neq \frac{\partial S}{\partial x_j}. \tag{2.161}$$

We write the Gibbs energy of the nonadditive system in the form similar to that assumed for description of the ideal mixtures,

$$G = \sum_{j=1}^{n} \left[G_j^0 + RT \ln \left(\gamma_j \left(x \right) \frac{x_j}{\sigma} \right) \right] x_j, \tag{2.162}$$

where γ is an activity coefficient.

The simplest transformations show that

$$\frac{\partial G}{\partial x_k} = G_k^0 + RT \ln \gamma_k \left(x \right) \frac{x_k}{\sigma} + RT \sum_{j=1}^{n} \frac{x_j}{\gamma_j \left(x \right)} \frac{\partial \gamma_j \left(x \right)}{\partial x_k}, \tag{2.163}$$

and the molar Gibbs energy

$$G_k = G_k^0 + RT \ln \left[\gamma_k \left(x \right) \frac{x_k}{\sigma} \right]$$

does not equal $\partial G / \partial x_k$ and, hence, is not a potential. Thus, the conditions of phase equilibrium of nonadditive systems do not consist in the equality of molar Gibbs energies of one and the same substance in different phases, but in the equality of derivatives $\partial G / \partial x_k$. This is seen from the expression for the derivative of the Lagrange function:

$$L = \sum_{j=1}^{n} G_j x_j + \sum_{i=1}^{m} \lambda_i \left(b_i - \sum_{j=1}^{n} a_{ij} x_j \right), \tag{2.164}$$

$$\frac{\partial L}{\partial x_j} = \frac{\partial G}{\partial x_j} + \sum_{i=1}^{m} \lambda_i a_{ij} = 0 \tag{2.165}$$

(the derivative equality to zero corresponds to the equilibrium state).

Since, for the components of vector x that meet different phases of some substance, the coefficients of a_{ij} are equal and the derivatives of $\partial G / \partial x_k$ are equal, too.

Note that according to the Euler equation, for homogeneous functions,

$$\sum_{k=1}^{n} x_k \sum_{j=1}^{n} \frac{x_j}{\partial \gamma_j(x)} \frac{\partial \gamma_j(x)}{\partial x_k} \equiv 0, \tag{2.166}$$

i.e., the total value of the latter terms on the right-hand sides of the equations of type (2.163) equals zero and the Gibbs energy of a nonadditive mole mixture as a whole retains the property of the potential, which is natural.

The conditions for convexity of the Gibbs energy function of nonadditive models were analyzed on the example of the van der Waals gas for which we obtained comparatively simple dependences that can be quantitatively analyzed.

When using the equations (2.70) and (2.75)–(2.77) the convexity criterion takes the form

$$\begin{aligned}\frac{\partial^2 G}{\partial x_j^2} &= RT\left(\frac{1}{x_j} - \frac{1}{\sigma}\right) + RT\frac{\left(b_j - b\right)^2}{\sigma}\left(\frac{1}{(V-b)^2} - \frac{1}{(V^0-b)^2}\right) \\ &\quad - \frac{2(V^0-b)}{V^0 V}\frac{a_j^{0.5}}{\sigma}(a_j^{0.5} - a) \geq 0, \quad j = 1, \ldots, n.\end{aligned} \tag{2.167}$$

In (2.167), the first term is the second derivative of the Gibbs function of ideal gas, the second one takes into account the impact of repulsion forces, and the third term takes into account the attraction forces between particles. The analysis of equation (2.167) shows that the convexity condition can be violated in the cases when the third term being negative sign exceeds in absolute value the sum of the first two terms in the absolute value. A preliminary consideration shows that this can take place only at very high pressures and is unlikely under real conditions.

Thus, the discussions of different types of models in this section make it clear that though the convexity of thermodynamic functions can be strictly determined only under a number of simplifying assumptions on the physics of the studied processes, the assumption on the convexity turns out acceptable for solution of a wide range of practical problems. This, certainly, does not deny the need to develop the convex analysis of thermodynamic models.

3
Thermodynamic Modeling on Graphs

> Formulas are written figures.
> Figures are drawn formulas.
> *D. Hilbert*

3.1. Problem Statement and History

The question on the effectiveness of geometrical methods for development and interpretation of extreme thermodynamic models is evidently subject to essential subjectivism and partiality. So, whereas Newton in his *Principles* started to solve each of more than 200 considered problems with graphical explanations, and only then passed to formulas, Lagrange in *Mechanique Analytique* did not present any drawings, demonstrating thus the possibility of constructing the "building" of mechanics without graphical representation.

Though in thermodynamics, geometrical methods have been applied starting with Gibbs's classical works, in the works known to the authors on computer modeling of thermodynamic systems, such methods have not been practically used. Our reference to graphical construction is based on the assumption that graphs should provide an insight into mathematical peculiarities of the problems solved, on the one hand, and contribute to expansion of the sphere for applications of extreme models, on the other.

Yet Kirchhoff had shown the possibility of reducing problems dealing with the study on multidimensional systems to problems on graphs. In [111] he tested the revealed theoretical relationships for current and potential distribution in the flat round plate by comparison with the experimental results on the electric circuit, i.e., on the object with the scheme in a graph form. Thus, he established the correspondence between electric fields in the continuous two-dimensional space and on the one-dimensional continuum, i.e., the "graph." Kirchhoff deduced his known laws of current distribution for graphs and showed in [112] how to derive an independent system of equations by using these laws, choosing the calculated loops corresponding to chords, that is, edges that remain after separation of the spanning tree from the closed graph.

In later works on the theory of electric circuits [108–110] Kirchhoff factually constructed a complete system of models to study these circuits. In [108] he showed the possibility of a transition from solving a closed system of equations (of Kirchhoff's laws) to the extreme problem – the search for the minimum heat generation in a passive circuit (one without sources of electromotive forces). To put it differently, he suggested an extreme model of current distribution. In [109, 110] the motion equation (the Ohm law) is derived in terms of the equilibrium of forces acting on "electric liquids," and the considered equilibrium in this case can be interpreted as the thermodynamic one.

Kirchhoff's works make clear the possibility of equivalent mutual transformations of models that are based on different physical principles (conservation, equilibrium, extremality); Kirchhoff's analysis alse substantiates the transition from such models, including extreme thermodynamic multidimensional systems, to graphical models.

Maxwell suggested the *method of potentials* [129] for calculation of electrical circuits as graphs, which is equivalent to the method of loop currents based on Kirchhoff's circuit laws of conservation. At about the same time Gibbs introduced in the thermodynamics the method of potentials for multidimensional continua [53].

Geometrical methods were developed by A. N. Gorban in *Equilibrium Encircling* for thermodynamic analysis of chemical system kinetics. These methods made it possible for one to pass from searching the extremum of the Lyapunov thermodynamic function on the material balance polyhedron to searching for it on the graph called a *thermodynamic tree*. This tree vividly and simply represents an aggregate of paths along which the Lyapunov function changes monotonically and the sets of compositions attainable from the initial state of a system (*the thermodynamic attainability region*). It is constructed by the relations of thermodynamic equivalence of x_1 and x_2: That is, $x_1 \sim x_2$ if there exists a continuous curve running 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 enables transformation of the domain of definition of the studied function to one-dimensional space, namely the tree, which facilitates substantially the analysis of processes in chemical systems.

Studies similar to those performed by A.N. Gorban, but belonging to pure mathematics were conducted by A.S. Kronrod [116] and V.I. Arnold [10]. Their works were aimed at solving the thirteenth Hilbert problem, i.e., representation of the continuous function of many variables as a superposition of continuous functions of a lesser number of variables [69]. A.S. Kronrod suggested a method to transform a multidimensional domain of definition of functions into a one-dimensional continuum, the *tree of functions* (which can be handled as the mathematical generalization of the notion of the thermodynamic tree); V.I. Arnold applied such a tree to obtain exact and approximate representations of some specific functions.

In our opinion the idea of a tree is interesting from the general principles of mathematical programming (MP)—the principles for solving extreme problems. Actually each MP method is characterized by the rule that determines at each step of the computational process a direction of motion and a path length over the function surface whose extremum is sought for. If we use the tree with set initial state and convexity of considered function, our choice of trajectory becomes unambiguous.

Note also the paper by A.I. Volpert [168], in which *bichromatic* graphs are applied to the qualitative analysis of solutions to differential equations of definite form for the problems of chemical kinetics. The work [28] presents a rather wide view of the application of topology and theory of graphs to quantum chemistry.

B.M. Kaganovich employed extreme thermodynamic models to study hydraulic circuits [77–79], i.e., objects whose structure is naturally represented as graphs. In so doing, he proceeded from the concepts of the *hydraulic circuit theory* (HCT), which was founded by V.Ya. Khasilev and A.P. Merenkov [104–107, 132, 130].

Creation of extreme thermodynamic models of flow distribution in circuits and physical interpretation of HCT on their basis provided a deeper insight into this theory, facilitated correct comparison of its methods, and enhanced potential of its applications. Thus, the low sensitivity of extreme methods to change in the space of variables made a wide variation of problem statements possible, e.g., inclusion of diverse constraints on parameter regulation in the models of post-emergency regimes of pipeline networks. The ideas of thermodynamic modeling of hydraulic systems may turn out to be useful in studying electric networks as well.

As a result of the thermodynamic analysis of HCT the problem of modeling heterogeneous hydraulic circuits (i.e., circuits with multiphase chemically reacting flows in the branches, or graph arcs was formulated in [91]. Studies of this problem substantially extended an area of HCT applications.

B.M. Kaganovich also made attempts to employ jointly thermodynamics and the hydraulic circuit theory to analyze multidimensional continua. The works [81, 83, 85] interpret *model of extreme intermediate states* (MEIS) with the variable ξ in the graphical form and represent some other extreme models of chemical systems with the specified mechanism of reactions in the form of hydraulic systems. In [91] MEIS of spatially inhomogeneous structures, which is somewhat different than the model of (2.97)–(2.105), is interpreted as a hydraulic circuit to study atmospheric pollution processes.

Descriptions of continua in the form of circuits certainly make sense, if for no other reason than the joint analysis of several possible mathematical models of one and the same object contributes to deeper understanding of it's the object's physical properties. On the whole, graphical models are useful in substantiating applicability of thermodynamics concepts to different types of physicochemical systems. If we manage to represent the studied function as a function of no more than two variables for each graph branch, then because of the holonomy of the corresponding Pfaffian forms it becomes possible to prove its possible representation as a differentiable potential function, which determines applicability of thermodynamics techniques.

Below we discuss just two, seemingly most topical, "graphical" ideas: a thermodynamic tree proposed by A.N. Gorban and thermodynamic modeling of multiloop hydraulic systems.

3.2. Thermodynamic Tree

The effectiveness of the idea of a thermodynamic tree, which was called in [58] an "entropy tree," will be illustrated at first by our "through" example of hexane isomerization. Fig. 3.1*a* presents the same triangle of the material balance as Fig. 2.4*a*, but with some additional details. Different kinds of hatching are used to denote five components of the *arcwise connectedness*. These are regions in each

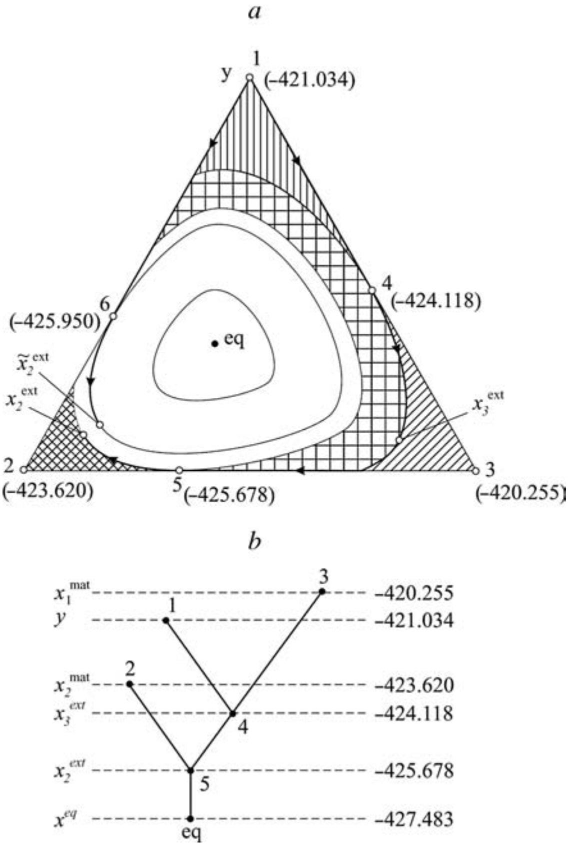


FIGURE 3.1. Polyhedron of material balance (*a*) and the thermodynamic tree (*b*) for the hexane isomerization reaction, $T = 600$ K, $P = 0.1$ MPa.

of which any two points can be connected by a thermodynamically admissible path.

Fig. 3.1*b* shows the thermodynamic tree whose branches have a one-to-one correspondence with the regions hatched in Fig. 3.1*a*. Every point of the tree represents an intercept of a line $G = \text{const}$ belonging to the corresponding component of connectedness. The points on this intercept satisfy the linear balance:

$$\sum_j G_j x_j = G = \text{const}. \tag{3.1}$$

The constructed tree that replaces the polyhedron $D(y)$ allows the study on the behavior of the Gibbs energy (a thermodynamic Lyapunov function in this case) and the objective function (2.38). Suppose that the initial state y is represented by the vertex 1 ($y = (1, 0, 0)^T$) and the process objective is to obtain a maximum possible quantity of the isomer x_3 (the objective function (2.38) takes the form $F(x) = x_3$). The desired maximum point on $D(y)$ is obviously vertex 3. We can move to it from y along tree branch 1–4, monotonically decreasing the function $G(x)$. However, after point 4 is reached, further movement to 3 becomes impossible because the Gibbs energy monotonically increases on branch 3–4 from 4 towards 3. Point 4 determines a level of G (the isopotential surface of $G = -424.118$ kJ/mole), at which the extreme composition x_3^{ext} (the linear function maximum is achieved at the convex set boundary) should lie.

With the choice of vertex 2 as an initial state y and the new maximization of x_3, the solution will be on the surface $G_5 = -425.678$ kJ/mole. When we maximize x_2 the same Gibbs energy level is attained from the initial states 1 and 3.

Note that when we solve all the mentioned problems:

$$\begin{aligned}
y &= (1,0,0)^T, && \max x_3,\\
y &= (0,1,0)^T, && \max x_3,\\
y &= (1,0,0)^T, && \max x_2,\\
y &= (0,0,1)^T, && \max x_2,
\end{aligned}$$

there is a situation of the "thermodynamic pothole," for which we cannot indicate the exact Gibbs energy levels $G\left(x^{\text{ext}}\right)$ (see Section 2.4). Application of the tree overcomes the difficulty that arises. Fig. 3.1*a* illustrates a potential benefit thanks to improvement of the obtained problem solution by the thermodynamic tree. If we moved from vertex 1 to vertex 2 (tending to max x_2), reached the point min G on the intercept 1–2 (point 6) and then continued to move along the curve $G = G_6$, we would be able to reach the point $\tilde{x}_2^{\text{ext}}$, which contains the component $x_2$in a somewhat lesser amount than at the point of exact solution x_2^{ext} (the errors of different algorithms are discussed in Chapter 4).

The tree can be applied to the analysis of situations, when the stated problem's solution proves to be degenerate. For hexane isomerization such a situation occurs at maximization of the total amount of any two components and at equality of each coefficient c_j in (2.38) to unity (see Section 2.4). If we find, for example, $\max(x_2 + x_3)$ and $y = (1, 0, 0)^T$, all the points of edge 2–3 (Fig. 3.1*a*) belonging to $D_t(y)$ are the points of the objective function maximum. This situation can be analyzed using the tree on the natural assumption that we are equally satisfied with two extreme cases: 1) $x_2 = 1$, $x_3 = 0$; and 2) $x_2 = 0$, $x_3 = 1$, and hence we may try to reach vertices 2 and 3. In the first case the sought Gibbs energy level will be $G = G_5$ and in the second, $G = G_4$. In Fig. 3.1*a* the region of extreme solutions that is part of edge 2–3 and lies between the point of its intersection with the curve $G = G_4$ and the point of contact with the curve $G = G_5$ corresponds to the determined range of levels $G_4 - G_5$. In Fig. 3.1*b* the range of possible solutions is represented by branch 4–5 of the tree.

When some arbitrary point of the triangle edge or the internal region rather than its vertex corresponds to the initial composition, we start moving on the tree not from one of the vertices, but from the internal point of a branch corresponding to the initial Gibbs energy level and the initial component of arcwise connectedness.

The idea of the thermodynamic tree is further discussed based on Fig. 3.2*a* and *b*, taken from *Equilibrium Encircling*. There, this idea was illustrated on the example of hydrogen combustion in oxygen. The vector x comprised in that case six components: H_2, O_2, H_2O, H, O, OH, and two components of the vector y are taken as: $y_{H_2} = 2$ and $y_{O_2} = 1$. Fig. 3.2*a* presents the graph $\tilde{D}$ of the balance polyhedron $D(y)$ and Fig. 3.2*b* presents the thermodynamic tree.

Assume that we maximize the amount of water (x_{H_2O}) achievable from the vertex H_2, O_2 as the initial state. According to the material balance conditions, the maximum admissible concentration of water corresponds to the vertex H_2O. From Fig. 3.2 it is easy to see that for the analysis of the properties of the problem we require not the whole tree (13 branches and 14 vertices), but only a smaller part of it (4 branches and 5 vertices). This smaller part is indicated in Fig. 3.2 by bold lines. Hence, in some cases it is possible in principle to reduce graphical constructions to solve specific problems. One should certainly remember that the

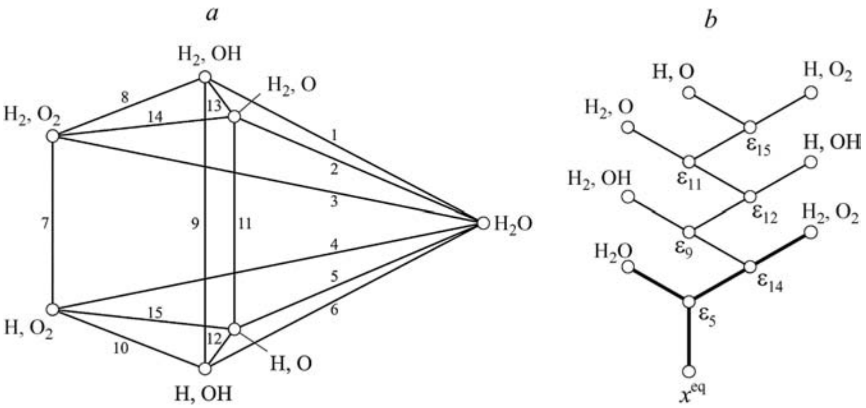


FIGURE 3.2. A graph of the polyhedron of material balance (a) and thermodynamic tree (b) for the reaction of hydrogen burning.

TABLE 3.1. Combinations of C_m^n

	n			
m	20	50	100	200
3	1140	$1.96 \cdot 10^4$	$1.62 \cdot 10^5$	$1.31 \cdot 10^6$
5	$1.55 \cdot 10^4$	$2.12 \cdot 10^6$	$7.53 \cdot 10^7$	$2.54 \cdot 10^9$
10	$1.89 \cdot 10^5$	$1.03 \cdot 10^{10}$	$1.73 \cdot 10^{13}$	$2.25 \cdot 10^{16}$
20	1	$4.71 \cdot 10^{13}$	$5.36 \cdot 10^{20}$	$1.61 \cdot 10^{27}$

only thing left to do is to develop algorithms that would allow the researcher to construct a needed part of the tree.

The algorithm described in [58] supposes that the graph $\tilde{D}$ of the whole polyhedron is known. However, in studies of real systems the polyhedron (and, thus, the graph) can reach astronomical sizes because the maximum possible number of vertices of $D(y)$ corresponding to the system of m linear equalities with n unknowns is determined by the formula

$$C_m^n = \frac{n!}{m!\,(n-m)!}.$$

The swift growth of this number with increasing dimensionality of the problem is illustrated in Table 3.1.

The above two examples show that it is possible for the number of elements (vertices or branches) of the tree to exceed considerably the number of elements in $\tilde{D}\,(y)$.

We can reduce the dimensionality of thermodynamic trees by two approaches. In the first we decrease dimensionality of the vector x. Its application is admissible in cases where several macrocomponents, whose concentrations are by many orders of magnitude higher than the concentrations of other components in the reacting mixture, can be isolated in chemical systems. It is clear that these components determine, with an inessential error, a surface shape of the thermodynamic function corresponding to the problem solved. If x is chosen properly, inclusion of a small number of the sought microcomponents in the list of the components of x can lead to addition of the admissible (in terms of calculations) number of "microbranches" to the "macrotree." System components are divided into micro and macro rather easily when the thermodynamic analysis is applied to environmental problems involving the search for quantities of substances that can be dangerous, for example, at concentrations of 10^{-10}–10^{-12} of the total system.

The second approach consists in construction of the tree equivalent not to the whole balance polyhedron but to only one face of special interest for the researcher. In the analysis of environmental characteristics of combustion processes it may be interesting to reveal interrelations between formations of nitrogen oxides and carbon monoxide. This problem can be properly analyzed if we use the face whose vertices correspond to the maximum concentrations of NO_x and CO in terms of the material balance, and the point y. Mathematically this approach is equivalent to the first one, since the polyhedron face can be treated as a polyhedron corresponding to the reduced dimensionality of the space of variables. When we construct flat two-dimensional faces, an approach that is convenient from the standpoint of graphical interpretation of the problem solved, in order to choose a list of the vector x components, we should apparently apply the relation

$$n = m + 2,$$

where n is the dimensionality of x, and m is the number of linear material balances.

With the efficient application of both approaches the algorithm presented in [58] may also be admissible in terms of calculation time. Of course, it does not mean that the search for new effective algorithms for constructing thermodynamic trees is not advisable. Irrespective of the success in these efforts the theoretical value of the "idea of tree" is unquestioned. A sketch variant of the algorithm of tree construction on the basis of the second approach is discussed in Section 4.4.

3.3. Thermodynamic Interpretations of Hydraulic Circuit Theory

Historical Background

Relations between thermodynamics and hydrodynamics, and hence hydraulic circuit theory, since the latter can be handled as part of the hydrodynamics from the standpoint of physics, were considered in Section 1.3.

The methods of *loop flows* (currents) and *nodal pressures* (potentials) are known to be basic in describing flow (current) distribution. In so far as they are analogs of the methods of cycles and potentials in the thermodynamics, they emerged almost simultaneously with the latter (the methods of cycles and loop currents are suggested by Clausius and Kirchhoff; the methods of potentials in the thermodynamics and the circuit theory are suggested by Gibbs and Maxwell). Kirchhoff [108] and Maxwell [129] who are the founders of the theory of electric circuits, showed the possibility for transition from their methods to extreme models. In [129] Maxwell also established mathematical equivalence of the methods of potentials and loop currents.

Both the method of loop currents, whose mathematical prerequisite is the equality to zero of the integral over a closed loop, and the method of potentials are only applicable to studying equilibrium systems that can be defined as "conservative" ($\oint df = 0$) and as "potential" (see Chapter 1). Note that Euler was the first to introduce, in 1765, the potential function into hydrodynamics and physics as a whole.

Section 1.3 of the book has already presented equilibrium interpretations of the laws of motion of electric charges (Ohm's law) and viscous liquid (the Darcy–Weisbach law). In addition we recall here an equilibrium nature of the classical system of hydrodynamics equations:

$$\tfrac{\partial \rho}{\partial \tau} + \operatorname{div}(\rho w) = 0, \tag{3.2}$$

$$\rho \tfrac{dw}{dt} = \rho F - \nabla P + (\eta + \zeta)\nabla \operatorname{div} w + \eta \Delta w, \tag{3.3}$$

$$\begin{aligned} c_p \rho \frac{dT}{d\tau} - \frac{dP}{d\tau} &= q + \operatorname{div}(\chi \nabla T) \\ &+ \left\{ \zeta\, (\operatorname{div} w)^2 + 2\eta \left[\left(\frac{\partial w_x}{\partial x}\right)^2 + \left(\frac{\partial w_y}{\partial y}\right)^2 + \left(\frac{\partial w_z}{\partial z}\right)^2 \right] \right. \\ &\left. + \eta \left[\left(\frac{\partial w_x}{\partial y} + \frac{\partial w_y}{\partial x}\right)^2 + \left(\frac{\partial w_x}{\partial z} + \frac{\partial w_z}{\partial x}\right)^2 + \left(\frac{\partial w_y}{\partial z} + \frac{\partial w_z}{\partial y}\right)^2 \right] \right\}, \end{aligned} \tag{3.4}$$

$$P = f_1(\rho, T)\,, S = f_2(\rho, T)\,, \tag{3.5}$$

where ρ is density; τ is time; w is velocity; F is volumetric force; η, ζ are coefficients of dynamic and volumetric viscosity; c_p is specific heat capacity at constant pressure; q is the heat quantity supplied to a unit volume in a unit time due to nonmechanical reasons; and χ is a coefficient of thermal conductivity.

Equation (3.2) describes a flow continuity condition. The Navier-Stokes equation (3.3) is an extension of Newton's second law to moving liquid. Equation (3.4) formulates the energy conservation law. Relations (3.5) are the thermal and caloric state equations, respectively. Inclusion of the state equations into system (3.2)–(3.5) implies application of the assumption on the equilibrium thermodynamic nature of liquids dynamics.

In the 1960s V.Ya. Khasilev extended the main statements of electric circuits theory developed in late 19th century, applying them to multiloop hydraulic circuits. The equilibrium nature of the liquid flow equations proves the validity of such an extension. In the basic works on hydraulic circuit theory [104–107, 132, 130] V.Ya. Khasilev made a comparative analysis of computational properties for the methods of loop flow rates and nodal pressures, and he suggested extreme methods (MP) for solving HCT problems. He outlined thereby two directions in MP application: 1) calculations of flow distribution and 2) technical and economic optimization of hydraulic networks. In the first case the objective function form was determined from the Kirchhoff-Maxwell heat theorem on least heat production in a passive circuit [130].

V.Ya. Khasilev showed the impact of *closing relations* (relations between the pressure losses and the flow rates in circuit branches) on mathematical features of the optimization problems of circuit schemes and parameters (namely, convexity or concavity of the objective function and its slight slope near the extremum point) [104, 106]. In their book, A.P. Merenkov and V.Ya. Khasilev [130] studied these relations mainly in terms of the accuracy of flow distribution calculations.

A.P. Merenkov and N.N. Novitsky performed a rather detailed analysis of the inverse flow distribution problems [132, 130, 134].

O.A. Balyshev extended the HCT principles to the analysis of nonstationary flow distribution in networks [16–18]. From the joint solution of the equations of continuity, Navier–Stokes, and state, he obtained formulas of closing relations for motion of media with constant density and media subject to the equation of state for the ideal gas (or real gas with constant compressibility).

B.M. Kaganovich formulated the problems of thermodynamic interpretation of HCT and study of heterogeneous hydraulic circuits, i.e., circuits with a complex phase and chemical composition of flows [85, 91].

Fundamentals of Hydraulic Circuit Theory

The cited work [130] presents two definitions of hydraulic circuits (HCs). According to the first definition, HCs represent an aggregate of conductors intended for transportation of liquids. The second defines HC as a mathematical model consisting of two constituents: a calculated scheme in the form of the directed graph [180]; and algebraic relations describing flow of liquids (gases) along graph's arcs. The present book applies only the second definition as the most adequate to its purposes.

HCT studies direct and inverse problems of flow distribution in hydraulic circuits and problems of the *optimal synthesis* (choice of the schemes and parameters) of circuits. The latter are usually related to the technical and economic optimization of pipeline networks (water, heat, oil and gas supply, etc.).

For real objects HCT has studied three key types of models up to now:

1) circuits with lumped parameters, in which the resistances of branches (graph arcs) and effective heads are independent of flow distribution;
2) circuits with variable (regulated) parameters, in which at least part of the branch characteristics (effective heads, heads and sinks (sources) at nodes, etc.) are the functions of sought quantities, and determined ("regulated") by the flow distribution itself;
3) circuits with distributed parameters, in which the characteristics of branches (resistances, effective heads) alter depending on distances to the nodes adjacent to the corresponding branch.

If all relationships for the branches of a distributed or regulated circuit are represented as a differentiable function of no more than two variables (for example, length and time or length and temperature), then the closing relations for them may be written in a "lumped" integral form, at least theoretically. At the same time the holonomy of the Pfaffian forms makes the thermodynamic representation of hydrodynamic relationships feasible.

For each mentioned model, the circuit branches are divided into active (with sources of effective heads: pumps, compressors, gravity, wind pressure, etc.) and *passive* (without such sources). By the graph theory the circuit scheme (part of the scheme) without closed loops is called a *tree* and the branches supplementing the tree to the closed (cyclic) scheme are called *chords*.

Application of the thermodynamics concepts in HCT calls for expansion of the accepted classifications of models and the system of notions. Open and closed, homogeneous and heterogeneous circuits naturally supplement the classification. The open circuits have sources and sinks: As do any other open thermodynamic systems, they exchange substance with the environment. In the closed circuits sources and sinks are absent.

There are two approaches to division of hydraulic circuits into *homogeneous* (uniform) and *heterogeneous* (nonuniform) types. In thermodynamics the heterogeneous systems include those in which a substance is present in different phases. Based on thermodynamic terminology we can assume conditionally that the flows in different circuit branches subject to different closing relations (e.g., flows corresponding to turbulent and laminar flow modes) belong to different phases. Therefore, the circuits with the distinct relationships between head losses and flows in the branches can be considered heterogeneous. This classification of circuits was suggested in [81].

In this context, the book addresses basically heterogeneous circuits, ones in which flows in separate branches contain several phases. In general, such flows are the vectors whose components are the flows of different chemical substances in different phase states on the branch.

For circuits with lumped parameters the problems of stationary flow distribution calculation are described in [130] in three ways: a) on the basis of the loop system of equations; b) using nodal potentials; c) in the extreme statement on the basis of the minimum heat production theorem.

The loop system of equations has the form:

$$Ax = Q, \tag{3.6}$$

$$Bh = BH, \tag{3.7}$$

$$h_i = f_i\left(x_i\right), i = 1, \ldots, n, \tag{3.8}$$

where x and x_i are a vector of flows in the circuit branches and its ith component, respectively; $A = [a_{ij}]$ is an $(m-1) \times n$-matrix of connections of independent nodes to branches; $a_{ij} = 1$, if the flow in the ith branch runs to the jth node in accordance with the specified direction; $a_{ij} = -1$, if the ith flow runs from the jth node and $a_{ij} = 0$ if j does not belong to branch i; Q is a vector of external sources and sinks at the nodes

$$\sum_{i=1}^{m} Q_j = 0;$$

m is the number of nodes; n is the number of branches; h and h_i are a vector of head losses and its ith component, respectively; H is a vector of effective heads; $B = [b_{ki}]$ is an $c \times n$-matrix of the coincidences of loops and branches; $b_{ij} = 1$ if the initially specified direction of flow in the branch coincides with the specified direction of loop encircling; $b_{ij} = -1$ when these directions are opposite; $b_{ij} = 0$ when the ith branch is not included in loop k.

The matrix equation (3.6) describes the first Kirchhoff law, which expresses the requirement of mass conservation in the flows of liquid for hydraulic circuits. Equation (3.7) formulates the second Kirchhoff law, which may be interpreted as the extension of the general energy conservation principle to separate circuit loops. Expression (3.8) is a closing relation.

For the method of nodal potentials equation (3.7) in system (3.6)–(3.8) is substituted by the equation

$$h - H = \bar{A}^T \bar{P}, \tag{3.9}$$

where $\bar{A}^T - [a_{ij}]$ is an $m \times n$ complete transposed matrix of connections of nodes to branches; $\bar{P}$ is a vector of nodal pressures.

The extreme principle of flow distribution in circuits as based on the works by Kirchhoff and Maxwell is formulated in [130] as the *heat theorem*. It means that flows in the open passive circuit are distributed so that they produce a minimum amount of heat. The corresponding mathematical problem is formulated in this case as the following:

Find

$$\min \sum_i h_i x_i \tag{3.10}$$

subject to

$$\begin{aligned} Ax &= Q, \\ h_i &= f_i\left(x_i\right), i = 1, \ldots, n. \end{aligned}$$

The authors of [130] also studied the possible extension of the theorem about least thermal effect on active circuits, in particular with different exponents β in the closing relations (see below). This was done by such variation of the objective function type that the solution to the extreme problem coincided with the solution to the system of equations (3.6)–(3.8). As a result the following function was determined:

$$F(x) = \sum_{i=1}^{n} \left(\frac{f_i\left(x_i\right) x_i}{1+\beta} - H_i x_i \right). \tag{3.11}$$

In [78] it is shown that this formula can be derived directly from the Lagrange principle of virtual work. Actually for hydraulic circuits this principle is interpreted as follows. If the flow distribution in the circuit is equilibrium, i.e., the equilibrium of all forces exerted on a moving medium (pressure, friction, gravity, etc.) is observed in every section of every branch, the work done on any infinitesimal deviation of flows in the branches from their equilibrium values equals zero. Mathematically, this principle is interpreted as follows:

$$dL = z_i x_i^{\beta} dx_i - H_i dx_i = 0, i = 1, \ldots, n, \tag{3.12}$$

where z_i is the resistance of the ith branch.

Obviously equation (3.12) represents an extremum condition of the objective function (3.11) and reveals its physical sense. $F(x)$ is the variation of energy of the total flow in the circuit at its deviation from the optimal (equilibrium) value (the Lagrange function). It is clear that the principle of virtual work allows an easy determination of the extremality criterion for passive circuits ($H = 0$).

The closing relations $f_i(x_i)$ for incompressible liquids for the HCT problems in [92] are represented in two forms:

$$h_i = f_i(x_i) = z_i x_i^{\beta}, \tag{3.13}$$

$$h_i = z_{i1} x_i + z_{i2} x_i^2. \tag{3.14}$$

These relations can be applied to model characteristics of the sources of effective heads by the equation

$$H = H^0 - z_{\text{in}} x_{\text{in}}^{\beta}, \tag{3.15}$$

in which the second term on the right-hand side is a head loss in an imaginary branch simulating the internal resistance of a pump.

The formulas to determine z from the Darcy–Weisbach equation and experimental relations for the friction coefficient λ were studied in [132] from the computational standpoint.

V.Ya. Khasilev [104, 106] and, later, B.M. Kaganovich [76] examined the effect of type of closing relations on the mathematical properties of problems pertaining to technical and economic optimization of hydraulic circuits. V.Ya. Khasilev performed the analysis on the basis of the following formula of pipeline diameter that was derived from the elementary transformation of the Darcy–Weisbach equation

$$d = a x^{\psi} \ h^{-\varphi},$$

Where a, ψ and φ are coefficients. For turbulent flow ($\beta = 2$) $\psi \approx 0.38$ and $\varphi \approx 0.19$.

Assume, for an objective function that indicates some cost characteristic of the network, that the function's term are proportional to d_i in the problem of technical and economic optimization; in the case of $1 \le \beta \le 2$ this function proves to be convex by the axes h_i and concave by x_i. In the extremum point h here it will be characterized by the exceptionally slight slope (the small curvature). The doubling of head loss in comparison to optimal value increases the liquid transportation cost by 4.6%, and a twofold decrease in the loss leads to just a 3.8% cost increase. Some adjustments in the results of analysis made by V.Ya. Khasilev were performed in [76] in terms of constraints on the conditions of network development and upgrading.

The methods of network optimization and solutions to direct and inverse problems of flow distribution that were developed in HCT are presented in detail in [130]. On the whole, hydraulic circuit theory has been applied extensively for several decades to solve engineering problems of development and operation of pipeline, and of other hydraulic networks with flows homogeneous in their chemical and phase compositions.

Models of Nonstationary Flow Distribution

O.A. Balyshev extended HCT principles to the analysis of nonstationary flow distribution in multiloop hydraulic systems using the premises of the "equilibrium dynamics" [16–18]. In the context of our discussion his results are of interest as the basis for thermodynamic studies on nonstationary processes in complex hydraulic networks. Application of the thermodynamic analysis to the hydraulic shock in a separate pipe was demonstrated in Section 1.3.

The laws of mass and energy conservation, as is customary in HCT, were written by O.A. Balyshev in the circuit (Kirchhoff) form, and closing relation type was determined by transforming the Navier–Stokes and state equations.

For the circuits with lumped parameters, O.A. Balyshev's model has the form

$$Ax(\tau) = Q(\tau), \tag{3.17}$$

$$Bh(\tau) = BH(\tau), \tag{3.18}$$

$$h_i = f_i(x_i(\tau)), \quad i = 1, \dots, n. \tag{3.19}$$

In the simplest case, when each ith flow of incompressible liquid experiences only forces of inertia, pressure and friction, the form of the functions f_i is determined from the initial Navier–Stokes equation

$$\rho\frac{dw}{d\tau} = -\frac{dP}{dl} - \lambda\frac{\rho w^2}{2d}, \tag{3.20}$$

or from

$$\frac{dx(\tau)}{d\tau} = -\frac{\pi d^2}{4}\frac{dP}{dl} - \frac{2\lambda x^2(\tau)}{\pi d^3 \rho} \tag{3.21}$$

when we pass from velocity w to mass flow x.

From here we have the differential closing relation

$$-dP = \frac{8\lambda x^2(\tau)}{\pi^2 d^5 \rho}dl + \frac{4}{\pi d^2}\frac{dx(\tau)}{d\tau}dl. \tag{3.22}$$

Introduction of the notion of instantaneous head (pressure) drop

$$h_i = P_i(0, \tau) - P_i(l_i, \tau), \tag{3.23}$$

will lead to

$$h_i = \frac{8\lambda x_i^2(\tau)}{\pi^2 d^5 \rho}l + \frac{4}{\pi d^2}\frac{dx_i(\tau)}{d\tau}l \tag{3.24}$$

or

$$h_i(\tau) = f_i(x_i(\tau)) = z_{i1}x_i^2(\tau) + z_{i2}\frac{dx_i(\tau)}{d\tau}. \tag{3.25}$$

Model (3.17)–(3.19) enriched the hydraulic circuit theory in terms of opportunities it afforded to analysis of network stability to variations in the vectors H, Q and Z, and to optimization of operation conditions.

Thermodynamic Models

We seek to determine a type of the objective function for an extreme thermodynamic flow distribution model for a closed active circuit with lumped parameters and isothermal liquid flow. In such a function the entropy production in the ith branch will be represented by the relation

$$\Delta S_i = \Delta q_i T^{-1} = h_i x_i T^{-1}, \tag{3.26}$$

which is based on the assumption on the equalities

$$T_i = T_{\text{env}} = T, i = 1, \ldots, n,$$

where the index "env" refers to the environment. Entropy production in the circuit as a whole is

$$\Delta S_{\text{cir}} = \frac{1}{T} \sum_i h_i x_i. \tag{3.27}$$

The same amount of entropy is transferred to the environment and its accumulation there leads to the increase in entropy of an isolated system (the circuit plus the environment), given as

$$\Delta S_{\text{is}} = \frac{1}{T} \sum_i h_i x_i. \tag{3.28}$$

Hence, for the considered system the function value

$$\sum_i h_i x_i.$$

should be maximal. Then the following model becomes obvious:

Find

$$\max \sum_i h_i x_i \tag{3.29}$$

subject to

$$Ax = 0, \tag{3.30}$$

$$\sum_i H_i x_i - \sum_i h_i x_i = 0, \tag{3.31}$$

$$h_i = f_i(x_i), i = 1, \ldots, n. \tag{3.32}$$

The right-hand side of the first Kirhchhoff law equation (3.30) is equal to zero due to the absence of sources and sinks ($Q = 0$) in the closed system. Equation (3.31) is the balance of produced and consumed energy in the circuit. The signs are chosen from the condition of thermodynamics that the removed heat ($\sum_i h_i x_i$) be negative.

If the closing relation is determined by expression (3.13), model (3.29)–(3.32) takes the following form:

Find

$$\max \sum_i z_i x_i^{\beta+1} \tag{3.33}$$

subject to

$$Ax = 0, \tag{3.34}$$

$$\sum_i H_i x_i - \sum_i z_i x_i^{\beta+1} = 0, \tag{3.35}$$

$$h_i = z_i x_i^{\beta}, \quad i = 1, \ldots, n. \tag{3.36}$$

Comparison between (3.33) and (3.35) reveals the possibility of replacing the objective function (3.31) by the expression

$$\max \sum_i H_i x_i \tag{3.37}$$

and then formulating the following statement: The flows in a closed active hydraulic circuit are distributed so that the energy produced by sources of effective heads and, correspondingly, the energy consumed is maximal. This statement provides information about the physical regularities of flow distribution in circuits, in addition to information of the theorem concerning the least thermal action.

To analyze mathematical properties of model (3.33)–(3.36) we will write the Lagrange function of the circuit, representing preliminarily condition (3.34) in the form

$$\sum_{i \in I_j} a_{ij} x_i = 0, \quad j = 1, \ldots, m-1, \tag{3.38}$$

where I_j is a subset of branches incident to node j.

Then the Lagrange function will be

$$L = \sum_{i=1}^{n} z_i x_i^{\beta+1} - \sum_{j=1}^{m-1} \lambda_j \sum_{i \in I_j} a_{ji} x_i + \lambda_m \left(\sum_{i=1}^{n} z_i x_i^{\beta+1} - \sum_{i=1}^{n} H_i x_i \right), \tag{3.39}$$

where λ_j and λ_m are Lagrange multipliers.

Let us take the derivative of (3.39) with respect to x_i and equate it to zero:

$$(\beta + 1)(\lambda_m + 1) z_i x_i^{\beta} + \lambda_{bi} - \lambda_{ei} - \lambda_m H_i = 0, \tag{3.40}$$

where λ_{bi} and λ_{ei} are multipliers for the initial and final nodes of branch I, respectively.

Since, at $H_i = 0$,

$$\lambda_{bi} - \lambda_{ei} = (\beta + 1)(\lambda_m + 1) z_i x_i^{\beta} = (\beta + 1)(\lambda_m + 1) h_i, \tag{3.41}$$

the difference of the Lagrange multipliers for nodes incident to the ith branch is proportional to the head loss in it.

The analytical expression for λ_m is obtained by addition of the derivatives $\partial L / \partial x_i$ for all i belonging to any closed loop k with effective heads. The sum will have the form

$$(\beta{+}1)\,(\lambda_m + 1)\sum_{i\in k} h_i - \lambda_m \sum_{i\in k} H_i = (\beta + 1)\,(\lambda_m + 1)\sum_{i\in k} H_i - \lambda_m \sum_{i\in k} H_i = 0. \tag{3.42}$$

(Equality to zero is explained by the equilibrium character of flow distribution). Expression (3.42) does not contain λ_j, since "$+\lambda_j$" and "$-\lambda_j$" vanish for each node j. From (3.42) it follows that

$$\lambda_m = -\frac{(\beta + 1)}{\beta}. \tag{3.43}$$

As $\beta > 0$, then $|\lambda_m| > 1$. For the linear closing relation ($\beta = 2$), $\lambda_m = -2$, and for the quadratic relation ($\beta = 2$), $\lambda_m = -1.5$. Since the multiplier λ_m is a derivative of the entropy with respect to the energy imbalance, its negativity is quite clear. If we could increase the energy of flows $\sum_i H_i x_i$ without an increase of its consumption $\sum_i z_i x_i^{\beta+1}$ and entropy production, then with respect to the equilibrium state

$$\sum_i H_i x_i = \sum_i z_i x_i^{\beta+1} \quad \text{and} \quad S = \max S$$

S of the system should have decreased.

Substituting (3.43) into (3.40) we will find that in a general case

$$\lambda_{bi} - \lambda_{ei} = \Delta\lambda_i = \lambda_m\,(H_i - h_i)\,. \tag{3.44}$$

Depending on the choice of the $m - 1$ independent nodes the absolute values of λ_j ($j \neq m$) will vary, but the $\Delta\lambda_i$ will remain unchanged.

The second partial derivatives of L with respect to x_i are

$$\frac{\partial^2 L}{\partial x_i^2} = \beta\,(\beta + 1)\,(\lambda_m + 1)\,z_i x_i^{\beta-1} \leq 0,$$

since $\lambda_m < -1$. Hence, the solution to problem (3.33)–(3.36) corresponds to the maximum of $L = f\,(x)$ and the maximum of the objective function (3.33) for an admissible set of solutions. Fig. 3.3*a* illustrates the possibility of a maximiu point to exist for the convex objective function. The objective function $a'b'$ that has the maximum $F_{\max}$ is an intersection of the vertical surface drawn through a nonlinear admissible region of solutions to the problem (the region *ab*), perpendicular to the plane x_1x_2, with the surface of the function $f\,(x)$ above this plane.

An *open active circuit* (with internal sources of effective heads and external sources and sinks) represents a thermodynamic system, whose conditions for interaction with the environment are determined by fixing enthalpy and pressure. In fact, the setting of the vector of nodal flows at fixed circuit resistance uniquely determines pressure (head) differentials between the points of sources and sinks, and between the energy flows as well. For both these and isolated systems, the maximum entropy is achieved at the equilibrium state. In this case the model of flow distribution takes the following form:

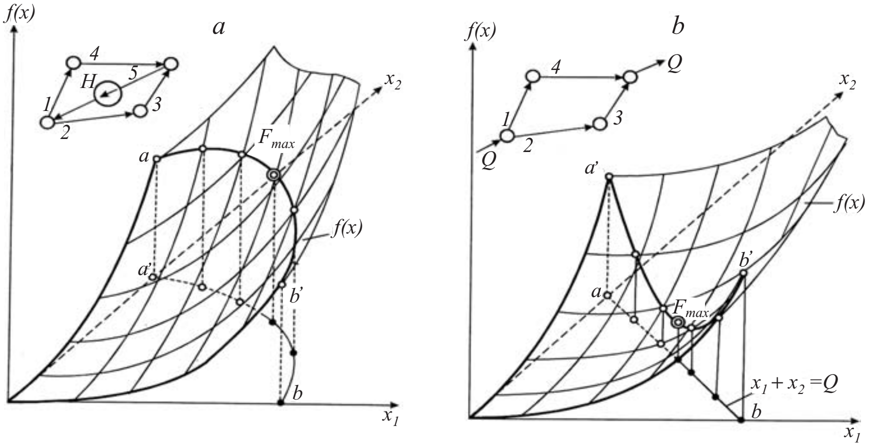


FIGURE 3.3. The objective function and the extremum points on the nonlinear (*a*) and linear (*b*) sets of constraints.

Find

$$\max\left(\sum_{j=1}^{m} P_j Q_j + \sum_{i=1}^{n} H_i x_i = \sum_{i=1}^{n} z_i x_i^{\beta+1}\right) \tag{3.45}$$

subject to

$$Ax = Q, \tag{3.46}$$

$$\sum_{j=1}^{m} P_j Q_j + \sum_{i=1}^{n} H_i x_i - \sum_{i=1}^{n} z_i x_i^{\beta+1} = 0, \tag{3.47}$$

$$P = eP_m - \bar{A}_g^{-1}\left(h_g - H_g\right), \tag{3.48}$$

Where P is a vector of heads at nodes $j = 1, \ldots m-1$; P_m is the fixed head at node $j = m$; h_g and H_g are respective vectors of the head loss and the effective heads in branches of the "circuit tree" comprising the paths from nodes $j = 1, \ldots m-1$ to node m; $\bar{A}_g^{-1}$ is a matrix of "paths" corresponding to this tree that is obtained by inversion of the submatrix of matrix A for branches of this tree; e is a unit vector.

The extreme thermodynamic model of a passive circuit can be obtained as a special case of models (3.33)–(3.36) and (3.45)–(3.48). This can be proved by mentally isolating a passive fragment with n_p branches and m_p nodes from the active circuit. The variables x_i, $i = n_p + 1, \ldots, n$, on branches of the rejected circuit part include flows that determine directions and magnitudes of sources and sinks Q_j, $j = 1, \ldots, m_p$, in the isolated fragment. Then conditions (3.47) and (3.48) are excluded and model (3.45)–(3.48) is replaced by model (3.10), constructed on the basis of the heat theorem. The Lagrange function in this case has the form

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

and its second derivatives are

$$\frac{\partial^2 L}{\partial x_i^2} = \beta (\beta + 1) z_i x_i^{\beta-1} \geq 0. \tag{3.49}$$

Hence, the extremum of $L(x)$ is the point of minimum, and thus the problem of entropy maximization is transformed to the problem of heat minimization, and the Kirchhoff–Maxwell theorem is deduced as a corollary of the second thermodynamics law with its extension to passive circuits. Coincidence of the form of objective functions in the “entropy” models (3.33)–(3.36) and (3.45)–(3.48) with the “energy” model (3.10) is due to the fact that the multiplier $1/T$ is removed from the maximized expression (3.10) on the assumption of constant temperature.

The revealed interrelation of flow distribution problems is a special case of the general thermodynamic law. It states that systems with constant energy tend to maximum entropy, and in systems in which fixation of any parameters results in energy exchange with the environment, the minimum of the corresponding energy kind is achieved. In the considered case of fixed flows of liquid (gas), which the circuit exchanges with its environment, we minimize mechanical energy consumption or, what is the same, quantity of heat liberated in the circuit.

Fig. 3.3*a* and *b* presents a graphical interpretation of the transformation of maximization problem to the minimization problem for the objective function that is convex on the unlimited set of variables.

Here we will not discuss thermodynamic interpretations of the models with regulated and distributed parameters that were considered in [81]. It should only be pointed out that such models can often be reduced to models with lumped parameters, as was explained above.

At the end of our discussion of homogeneous circuits let us show that the extremality criterion (3.11) that was justified above using the principle of virtual works, can be obtained from thermodynamic model (3.33)–(3.36). To do this we perform elementary transformations of the partial Lagrange function:

$$\begin{aligned} L &= \sum_{i=1}^{n} z_i x_i^{\beta+1} + \lambda_m \left(\sum_{i=1}^{n} z_i x_i^{\beta+1} - \sum_{i=1}^{n} H_i x_i \right) \\ &= -\sum_i \frac{\beta+1}{\beta} \left(\frac{z_i x_i^{\beta+1}}{\beta+1} - H_i x_i \right) = \text{const} \sum_i \left(\frac{f_i(x_i)\, x_i}{\beta+1} - H_i x_i \right). \end{aligned}$$

Of course, the constant may be removed from the extremality criterion.

The analysis presented in this section and the previous portion of the book show that extreme models of homogeneous circuits can be constructed on the basis of two competitors: a) the second law of thermodynamics and the principle of virtual works to describe stationary (or nonstationary, if the time variable is excluded from the analysis) flows; and b) the second law and the principle of the least action to describe liquid flow using the time coordinates.

The thermodynamic analysis of closing relations is given in the next section. This section will conclude with several examples of applying thermodynamic models.

Examples of Calculations

Agreement between the solutions of the problem (3.33)–(3.36) and the system of the Kirchhoff equations (3.6)–(3.8) is tested on a number of examples. Table 3.2 presents the calculation results for the circuit presented in Fig. 3.4.

Consideration was given to three variants:

1. the quadratic closing relation $h_i = z_i x_i^2$ for all $i = 1, \ldots, n$;
2. the linear closing relation $h_i = z_i x_i$ for all $i = 1, \ldots, n$;
3. the quadratic closing relation $h_i = z_i x_i^2$ for all $i = 1, \ldots, 15$; $h_{16} = z_{16} x_{16}$.

The effective heads for the three variants are assumed to be equal: $H_5 = 90$; $H_{10} = 60$; $H_{12} = 100$. The resistances z_i of branches coincide for variants 1. and 3. and in variant 2. they are chosen to be 1000 times lower.

For the given circuit the extreme problem solution proved to satisfy the Kirchhoff laws in all the considered variants. It is also valid in case the laminar and turbulent modes of motion are simultaneously present in the circuit (variant 3.).

3.4. Thermodynamic Interpretations of Hydraulic Circuit Theory: Heterogeneous Circuits

Problem Urgency

The theoretical and practical significance of flow distribution calculation in circuits with multiphase chemically reacting flows is conditioned, for example, by the following problems:

- analysis of conditions for self-ignition of combustible components in systems of harmful industrial waste disposal;
- calculation of depositions of heavy hydrocarbons in systems for transporting oil, oil products, and natural gas;
- determination of conditions for condensate formation in long-distance steam pipelines;
- assessment of concentrations of harmful substances in ventilation and air conditioning systems in residential dwellings and in public and industrial places;
- hydraulic calculations of chemical reactors;
- calculation of the schemes of energy carrier travel at energy plants with compound flows (at electrochemical energy converters, integrated gasification combined-cycle power plants, etc.).

Further successful development of the heterogeneous circuit theory will certainly offer many new spheres of its application.

TABLE 3.2. Calculations Results of the Circuit

Branch	z_i	x_i	h_i	$\Delta\lambda_i$	Independent node	λ_j
Variant 1						
1	$0.78\cdot10^{-4}$	799	49.8	—	1	74.7
2	$0.25\cdot10^{-3}$	199	9.9	14.9		
3	$0.64\cdot10^{-4}$	397	10.1	15.1	2	89.6
4	$0.12\cdot10^{-3}$	404	19.6	29.4		
5	$0.64\cdot10^{-4}$	397	10.1	119.8	3	104.7
6	$0.70\cdot10^{-2}$	100	70.0	104.7		
7	$0.24\cdot10^{-3}$	501	60.2	90.5	4	75.3
8	$0.28\cdot10^{-4}$	597	10.0	15.0		
9	$0.64\cdot10^{-4}$	400	10.2	—	5	−44.5
10	$0.64\cdot10^{-4}$	399	10.2	—		
11	$0.18\cdot10^{-2}$	197	69.9	104.9	6	60.2
12	$0.10\cdot10^{-4}$	1001	10.0	135		
13	$0.28\cdot10^{-4}$	601	10.1	15.1	7	−30.3
14	$0.20\cdot10^{-2}$	200	80	119.8		
15	$0.50\cdot10^{-3}$	200	20	30	8	−15.3
16	$0.10\cdot10^{-2}$	97	9.4	14.2	$\lambda_m = -1.5$	
Variant 2						
1	$0.78\cdot10^{-1}$	506	39.5	—	1	79.0
2	0.25	111	27.7	55.3		
3	$0.65\cdot10^{-1}$	155	9.9	19.8	2	134.3
4	0.12	233	27.9	55.8		
5	$0.64\cdot10^{-1}$	72	4.6	170.8	3	154.1
6	$0.70\cdot10$	11	77.0	156.1		
7	0.24	251	60.1	120.2	4	98.3
8	$0.28\cdot10^{-1}$	230	6.4	12.8		
9	$0.64\cdot10^{-1}$	186	11.9	—	5	−72.5
10	$0.64\cdot10^{-1}$	320	20.5	—		
11	$0.18\cdot10$	44	79.2	158.1	6	83.6
12	$0.10\cdot10^{-1}$	462	4.62	190.7		
13	$0.28\cdot10^{-1}$	262	7.3	14.7	7	−36.6
14	$0.20\cdot10$	43	86.0	170.8		
15	0.50	75	37.5	75.1	8	−23.8
16	$0.10\cdot10$	18	18	35.9	$\lambda_m = -2.0$	
Variant 3						
1	$0.78\cdot10^{-4}$	800	49.9	—	1	74.9
2	$0.25\cdot10^{-3}$	202	10.2	15.3		
3	$0.64\cdot10^{-4}$	400	10.2	15.3	2	90.2
4	$0.12\cdot10^{-3}$	351	14.8	22.1		
5	$0.64\cdot10^{-4}$	463	13.7	114.4	3	105.5
6	$0.70\cdot10^{-2}$	97	65.9	98.3		
7	$0.24\cdot10^{-3}$	522	65.4	98.2	4	83.4
8	$0.28\cdot10^{-4}$	602	10.1	15.2		
9	$0.64\cdot10^{-4}$	404	10.4	—	5	−31.0
10	$0.64\cdot10^{-4}$	396	10.0	—	—	—
11	$0.18\cdot10^{-2}$	198	70.6	105.9	6	67.3
12	$0.10\cdot10^{-4}$	953	9.1	136.4		
13	$0.28\cdot10^{-4}$	619	10.7	16.1	7	−30.9
14	$0.20\cdot10^{-2}$	195	76.1	114.4		
15	$0.50\cdot10^{-3}$	202	20.4	30.6	8	−15.7
16	$0.10\cdot10^{-2}$	171	0.17	0.1	$\lambda_m = -1.5$	

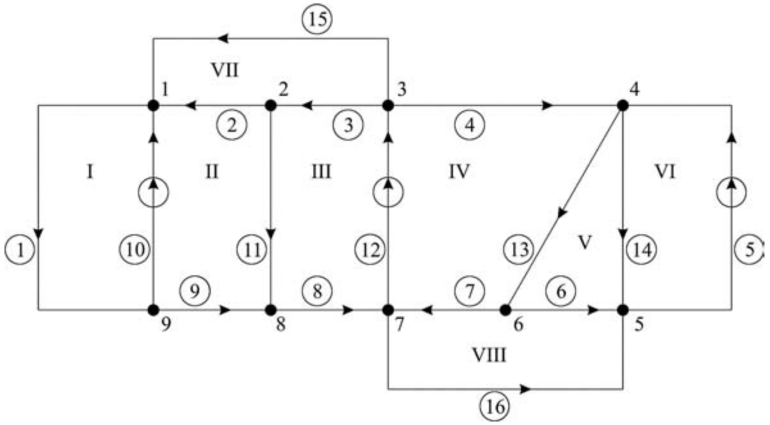


FIGURE 3.4. The calculated circuit scheme. Figures in circles are numbers of branches; 1–9 are numbers of nodes; I–VIII are numbers of loops; arrows in circles are effective heads; arrow show given direction of flow.

In terms of development of extreme thermodynamics models it is precisely the heterogeneous circuits that are the most interesting part of HCT, since presence of chemical reactions makes the problems of searching for the regions of thermodynamic attainability and partial equilibria highly topical[1].

Mathematical Model of a Heterogeneous Network

A model of the closed active heterogeneous network can be represented in a form similar to model (3.33)–(3.36) of the homogeneous system:

Find

$$\max \sum_{i=1}^{n} \frac{z_i x_i^{\beta+1}}{T_i} \tag{3.50}$$

subject to

$$Ax = 0, \tag{3.51}$$

$$\sum_{i=1}^{n} H_i x_i - \sum_{i=1}^{n} h_i x_i = 0, \tag{3.52}$$

$$h_i = z_i x_i^{\beta}, \quad i = 1, \ldots, n, \tag{3.53}$$

$$x_i = (x_{i1}, \ldots, x_{ik})^T, \tag{3.54}$$

$$z_i = f_i\left(\rho_i\left(x_i, T\right)\right), \tag{3.55}$$

$$H_i = \phi_i\left(\rho_i\left(x_i, T\right)\right). \tag{3.56}$$

---

[1] Note: There are many publications on the kind of two-phase flows that do not experience phase transitions and chemical transformations (transport of crushed solid material in water or air, transport of coal in methanol, etc). We do not deal with such flows.

The functional dependences (3.53) and (3.56) indicate that the heterogeneous circuits belong to the models with distributed parameters. In order to reveal properties of system (3.50)–(3.56) and possibilities of its reduction (approximation) to the model with lumped parameters, first, one must study the character of the closing relations (3.53). Such a study is the major subject of this section.

Thermodynamic Analysis of Closing Relations

Availability of physically and mathematically valid closing relations makes it possible to conduct a qualitative physical and mathematical analysis of diverse heterogeneous circuits. For example, these closing relations enable one to determine conditions for occurrence of multiphase flows, possible changes in the type of *piezometric plots* (graphical relationships between head loss and branch length) at chemical transformations and phase transitions, reasons for the many-valued solutions to a flow distribution problem, and so on.

When we derived the closing relations for multicomponent and multiphase flows, we took as the basis premise the equilibrium between different phases, which, in turn, is determined by the equality of chemical and other potentials.

Originally the idea of thermodynamic analysis of relationships between head losses and flow was tested on the example of a homogeneous isothermal flow of incompressible liquid. We considered the phase equilibrium between two conditional flows: a turbulent tube and an annular laminar layer surrounding it: The two move uniformly and in the same direction relative to one another. Thus, the *true* picture of vortex formation and increase in the flow turbulence degree with the growth of flow velocity was substituted by an *imaginary* picture of continuous growth of the turbulent tube diameter d_t from zero to d. The authors borrowed the idea of conditional flows from Landau's theory of quantum liquids [120], in which Landau used the concept of *conditional superfluid* and *normal flow*.

Since the studied flows are homogeneous and isothermal, we naturally reduced the equality of chemical potentials to the equality of hydraulic potentials, namely pressures, and correspondingly, to the equality of pressure losses in the turbulent tube (ΔP_t) and the laminar flow (ΔP_l) between any two tube cross-sections. The value of ΔP_t was calculated by the Darcy–Weisbach formula (1.55) and the Schifrinson formula was applied to determine the friction coefficient

$$\lambda_t = 0.11 \left(k/d_t\right)^{0.25}, \tag{3.57}$$

where k is a roughness coefficient.

When ΔP_l was determined by (1.55), the equivalent diameter d_l of the laminar ring and the coefficient λ_l were calculated from the expressions [3]:

$$d_l = 4\frac{\bar{\omega}}{h} = 4\frac{\pi\left(d^2 - d_t^2\right)}{4\pi\left(d + d_t\right)} = d - d_t, \tag{3.58}$$

$$\lambda_l = \frac{A}{Re} = \frac{96\nu}{w\left(d - d_t\right)}, \tag{3.59}$$

where $\bar{\omega}$ and h are the cross-sectional area of the ring and its perimeter, respectively; A is a form coefficient; Re is a Reynolds number; ν is the kinematic viscosity.

From transforming the equality

$$\Delta P_t = \Delta P_l$$

by means of formulas (1.55) and (3.57)–(3.59), we determined the following relationships:

$$\Delta P = zx^2 = \frac{0.108k^{0.25}l}{f\left(d_t\left(w\right)\right)\rho}x^2, \tag{3.60}$$

$$f\left(d_t\right) = d_t^{1.25}\left(0.6d_t^2 + 0.5d^2\right)^2. \tag{3.61}$$

Comparison of the results calculated by equations (3.60) and (3.61) for pressure losses with water flow in tubes with different diameters to the reference data revealed the close agreement of the two sets of data, which confirmed to some extent the effectiveness of thermodynamic analysis of closing relations.

Multicomponent flows will be addressed now. We start with chemically homogeneous moving media subject to phase transitions. The difference in chemical potential is the driving force for both phase transitions and chemical transformations. Physical and mathematical descriptions of both processes should be similar.

Motion of a condensing ideal gas is the simplest example. As distinct from the analysis of incompressible liquids and homogeneous gases, the assumption of an isothermal flow is inadmissible here. First, if only the gas phase is present in the flow at the initial instant of motion, its conversion to liquid as a result of the isothermal process is impossible (see the isotherm 1–1 in Fig. 3.5). Second, in regions of phase transition, isotherms coincide with isobars, i.e., pressure also remains constant simultaneously with temperature (the isotherm 2–2 in Fig. 3.5), and therefore the process of medium motion becomes impossible.

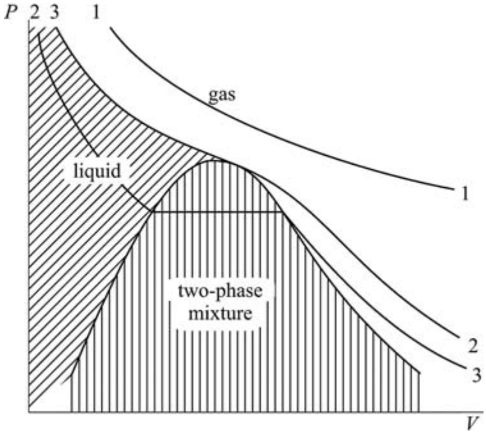


FIGURE 3.5. The diagram of substance state in the coordinates P, V.

Therefore, the flow was assumed to be *polytropic*. For ideal gases the *polytrope equation* has the form

$$PV^{\gamma} \ = \text{const.} \tag{3.62}$$

For the adiabatic process we have

$$\gamma = \frac{c_p}{c_v}, \tag{3.63}$$

where c_p and c_v are the isobaric and isochoric heat capacities, respectively. When γ tends to unity, the process is isothermal at its limit.

The next supposition was that the moving medium represents a spatially homogeneous mixture of gas and suspended fog droplets.

Density of such a medium is determined from the expression

$$\rho = \frac{x}{(x - x_c)\,\rho_g^{-1} + x_c \rho_c^{-1}}, \tag{3.64}$$

where x is the mass flow; and the indices c and g refer to condensed and gas phases, respectivetly.

Since at moderately high flow pressures

$$\rho_g << \rho_c,$$

equation (3.64) can be replaced by the approximate expression

$$\rho = \frac{\rho_g x}{(x - x_c)}. \tag{3.65}$$

The closing relation for the polytropic flow of condensing ideal gas (the flow of the condensed phase at the initial cross-section of tube is equal to zero) can be determined from the Darcy–Weisbach equation written in the differential form

$$-dP = \frac{\lambda \rho w^2}{2d} dl. \tag{3.66}$$

To substitute the variable w by the mass flow x we will express the density ρ at an arbitrary flow cross-section via the density ρ_1 at the initial state.

From the polytrope equation (3.62) follows

$$\rho_g = \rho_{g1} \left(\frac{P}{P_1} \right)^{1/\gamma}, \tag{3.67}$$

since $\rho = 1 \big/ v$.

In terms of (3.65) we have

$$\rho = \rho_1 \left(\frac{P}{P_1} \right)^{1/\gamma} \frac{x}{(x - x_c)}. \tag{3.68}$$

Since

$$x = 0.25 w \rho \pi d^2,$$

then

$$-dP = \frac{8\lambda P_1^{1/\gamma}\ x\,(x - x_c)}{\pi^2 \rho_1 d^5 P^{1/\gamma}} dl. \tag{3.69}$$

Let us introduce the notation

$$\psi = \frac{8\lambda P_1^{1/\gamma}}{\pi^2 d^5 \rho_1}. \tag{3.70}$$

Then

$$\int\limits_{P_2}^{P_1} P^{1/\gamma}\ dP = \int\limits_0^l \psi x\,(x - x_c)\,dl$$

and

$$P_1^{(\gamma+1)/\gamma} - P_2^{(\gamma+1)/\gamma} = \varphi x\,(x - x_c)\,l, \tag{3.71}$$

where

$$\varphi = \psi \frac{(\gamma + 1)}{\gamma}. \tag{3.72}$$

Expression (3.71) is an integral form of the closing relation for the "ideal" two-phase flow from which the final pressure is determined:

$$P_2 = \left(P_1^{(\gamma+1)/\gamma} - \varphi x\,(x - x_c)\,l\right)^{\gamma\ /(\gamma+1)}. \tag{3.73}$$

The closing relation for the single-phase flow ($x_c = 0$) is derived as a particular case of (3.71), namely,

$$P_1^{(\gamma+1)/\gamma} - P_2^{(\gamma+1)/\gamma} = \varphi x^2 l, \tag{3.74}$$

and at $\gamma = 1$ it transfers to the known formula for the isothermal gas flow,

$$P_1^2 - P_2^2 = \varphi x^2 l. \tag{3.75}$$

At the same time equation (3.71) is not symmetric relative to phase transitions: gas → liquid; and liquid → gas. When the gas phase flow rate ($x = x_c$) is equal to zero, the pressure loss in the branch also turns to zero, which is certainly incorrect theoretically. This property of the determined closing relation is quite clear, as it was derived by the ideal gas state equation. But in principle this equation is not adequate for the description of condensed phases. However, when the gas phase disappears in the flow the errors in determination of pressure losses by equation (3.71) are practically negligible. This is due to the fact that the condensate density at a distance from the critical point is much higher than the gas density, and the value of ΔP sharply decreases with condensation. If the tube diameter were chosen with the proviso that a single-phase gas flow passed through it, then, with motion of the same condensate mass in it, ΔP would approach zero.

Let us mention an easily comprehensible fact, namely, that the phase transitions (and the chemical transformations) can lead to both convex (Fig. 3.6, curve 3)

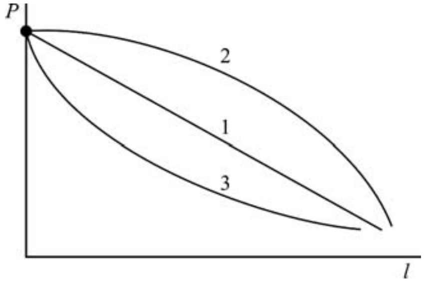


FIGURE 3.6. Possible forms of piezometric plots

and concave (curve 2) forms of the piezometric plots $P = f(l)$. The convex form takes place when the increase of substance density due to condensation exceeds the decrease of ρ as a result of gas expansion.

It is clear that the application of equation (3.71) to practical calculations requires an iterative adjustment of P_2 by determining x_c from the phase equilibrium conditions.

In principle, the closing relation for the polytropic flow of real gas that is obtained by the van der Waals equation (or some other state equation) may be taken with some or another degree of error for calculation of individual components of the vector x_i.

The polytrope equation of the van der Waals gas has the form

$$\left(P + a\rho^2\right)\left(1/\rho - b\right)^{\gamma} = \text{const.} \tag{3.76}$$

Since, analytically, it is difficult to integrate the Darcy–Weisbach formula

$$-dP = \frac{0.811\lambda x^2}{d^5\rho}dl \tag{3.77}$$

($0.811 \approx 8/\pi^2$; see, for example, equation (3.69)) with respect to ρ, let us preliminarily decompose the pressure by powers of density:

$$\begin{aligned} P(\rho) = {} & P(\rho_1) + P'(\rho_1)(\rho - \rho_1) + 0.5P''(\rho_1)(\rho - \rho_1)^2 \\ & + 0.167P'''(\rho_1)(\rho - \rho_1)^3 . \end{aligned} \tag{3.78}$$

Preliminary calculations have shown that the four terms of decomposition (the coefficient of the fourth term is assumed to have a rounded-off value) are sufficient to determine two roots of equation (3.77), obtained as a result of integration to have real values in the region of phase transitions. The determined closing relation has the form

$$a_1\left(\rho_1^4 - \rho_2^4\right) + a_2\left(\rho_1^3 - \rho_2^3\right) + a_3\left(\rho_1^2 - \rho_2^2\right) = \varphi x^2 l, \tag{3.79}$$

where

$$\begin{aligned} a_1 &= 0.125P'''(\rho_1), \\ a_2 &= 0.333\left(P''(\rho_1) - 1.022P'''(\rho_1)\rho_1\right) \end{aligned}$$

and

$$a_3 = 0.5\left(P'(\rho_1) - P''(\rho_1)\rho_1 + 0.501P'''(\rho_1)\rho_1^2\right).$$

It is obvious that for the single-phase flow of ideal gas the second and third derivatives of pressure with respect to density turn out to be zero and equation (3.79) converts to the quadratic relation (3.75).

It is of no doubt that the terms of no lower than the third power should be present in the algebraically expressed closing relations for any flows experiencing phase transitions. Indeed, the region of phase transitions in the state diagrams lies below the critical point, at which the first and second derivatives of pressure with respect to the volume (density) equal zero. This point can be determined only by the equations in which two first derivatives do not vanish identically.

Analytical dependences between pressure loss and flow for chemically reacting flows can be determined only at the limiting idealization of the studied process. To have a clear picture of chemical transformation influence on liquid flow we should also exclude from mathematical description of the problem all factors that are not directly related to transformations of substances (e.g., changes in medium density with variation in temperature and pressure).

Based on the indicated requirements we will consider an isothermal flow of two liquid incompressible isomers 1 and 2 as a model example. In the flow the first component is converted to the second as a result of a *monomolecular reaction of the first order*, i.e., a reaction corresponding to the equation,

$$\frac{dx_1}{d\tau} = -kx_1, \tag{3.80}$$

where x_1 is a mole fraction of component 1, and k is a rate constant of the reaction.

In this case the flow density ρ is determined by the equation

$$\rho = \left(\left(\frac{1}{\rho_2} - \frac{1}{\rho_1}\right)x_2 + \frac{1}{\rho_1}\right)^{-1}, \tag{3.81}$$

x_2 is calculated from the material balance equation

$$x_1 + x_2 = 1, \tag{3.81a}$$

and the solution to equation (3.80) is

$$x_1 = e^{-k\tau}, \tag{3.82}$$

which is true provided that for $\tau = 0$, $x_1 = 1$ and $x_2 = 0$,

$$x_2 = 1 - e^{-k\tau}. \tag{3.83}$$

In terms of (3.83), equation (3.81) can be transformed as

$$\rho = \left(\frac{1}{\rho_2} + \left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)e^{-k\tau}\right)^{-1}. \tag{3.84}$$

If the form of the function $\rho = f(\tau)$ is known, the relationships between ΔP and x can be found from the Darcy–Weisbach equation

$$-dP = \frac{\lambda w^2(\rho)\,\rho(\tau)}{2d} dl(\rho(\tau)) = \frac{8\lambda x^2}{\pi^2 d^5 \rho(\tau)} dl(\rho(\tau)). \tag{3.85}$$

Integration of (3.85) results in

$$\Delta P = \frac{32\lambda x^3}{\pi^3 d^7}\left[\frac{\tau}{\rho_2^2} + \frac{2}{k\rho_2}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)\left(1 - e^{-k\tau}\right) + \frac{1}{2k}\right.$$
$$\left.\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)^2 \left(1 - e^{-2k\tau}\right)\right]. \tag{3.86}$$

Expression (3.86) represents the dependence of pressure loss on the time of liquid motion between the pipeline section that is taken as initial and the current section. However, before passing to the thermodynamic analysis the variable τ should be excluded, i.e., it is necessary to find a relation between ΔP and x at the fixed l that is revealed for the flows with phase transitions. To solve this problem, first the form of the function $l = f(\tau)$ is determined:

$$dl = w(\rho(\tau))\,d\tau,$$
$$l = \frac{4x}{\pi d^2}\left[\frac{\tau}{\rho_2^2} + \frac{1}{k}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)\left(1 - e^{-k\tau}\right)\right]. \tag{3.87}$$

Then a simple transformation of equation (3.86) is performed:

$$\Delta P = \frac{32\lambda x^3}{\pi^3 d^7}\left[\frac{\tau}{\rho_2^2} + \frac{1}{k\rho_2}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)\left(1 - e^{-k\tau}\right)\right]$$
$$+ \frac{32\lambda x^3}{\pi^3 d^7}\left[\frac{1}{k\rho_2}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)\left(1 - e^{-k\tau}\right) + \frac{1}{2k}\right.$$
$$\left.\times\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)^2 \left(1 - e^{-2k\tau}\right)\right]. \tag{3.88}$$

Comparison of (3.87) and (3.88) clearly shows that pressure loss ΔP can be represented as the sum of the term depending on l and the one independent of l:

$$\Delta P = \frac{\varphi x^2 l(\tau)}{\rho_2} + \left[\psi_1\left(1 - e^{-k\tau}\right) + \psi_2\left(1 - e^{-2k\tau}\right)\right]x^3. \tag{3.89}$$

The first term on the right-hand side of (3.89) coincides with classical expressions of closing relations for circuits with lumped parameters, provided the pipe length and the time for the liquid to pass through it are fixed and the liquid density equals the density of the second isomer (the final reaction product). The second term is a correction for the value of ΔP that is determined by the change in density of the moving medium because of the chemical reaction.

Equation (3.89) shows that when τ and l are equal to zero, ΔP also vanishes. At $\tau \to \infty$ the relationship $\Delta P = f(l)$ tends to become linear. This conclusion is clear, since the chemical transformations are completed in an infinitely long time period and the density becomes constant. The sign of "chemical" correction for the variation in ΔP depends on the sign of difference $1/\rho_1 - 1/\rho_2$, i.e., on the density variation during reaction. If the density of the final product ρ_2 exceeds ρ_1, then $\Delta P = f(l)$ on the initial branch section is concave. At $\rho_2 < \rho_1$ the function $\Delta P(l)$ becomes convex. The function $P(l) = P^1 - \Delta P(l)$ is naturally convex when $\rho_2 > \rho_1$ and concave at $\rho_2 < \rho_1$ (see Fig. 3.6).

Note that both the "chemical" and "phase" corrections are cubic (or higher-power) functions of the flow. This fact can be explained physically, since the impact of chemical transformations on hydrodynamics is similar to the impact of phase transitions and is determined solely by the change in the flowing medium density (if the possible variation in viscosity is neglected). Therefore, the mathematical descriptions of the effects of these processes on liquid (gas) flow should also be similar. The impossibility of applying closing relations of a power lower than the third power for flows with a variable phase composition was shown above. The same is naturally true of chemically reacting liquids.

Based on what is said above, let us represent the closing relation (3.89) in a "more thermodynamic" form, excluding from it the time variable that is uniquely related with ρ_1, ρ_2 and l at the fixed x:

$$\Delta P = \varphi_1(\rho_2, l)x^2 + \varphi_2(\rho_1, \rho_2)x^3. \tag{3.90}$$

For the strict derivation of expressions (3.89) and (3.90) we introduced very severe constraints into the initial problem statement. It is clear, however, that the area of qualitative analysis using the obtained equations can be considerably extended in comparison with the area formally corresponding to the accepted mathematical model. Thus, the initial and final compositions of flows can be assumed to be not pure substances, but mixtures and equation (3.81a) in a general form can be supposed to describe a linear material balance. For the flows with $\rho = f(P, T)$ it is natural to assume that the right-hand side of equation (3.90) represents only the two first terms of a more complicated relation that probably includes terms of a powers higher than the third with respect to x.

The obtained closing relations can be applied to show that at least at $k << 1$, the property of "cost function slight slope along the head axes" that was established by V.Ya. Khasilev, does not change essentially at a transition from the flows of incompressible media to the chemically reacting flows (see Section 3.3). Indeed, with the indicated constraint on the reaction rate constant, time τ during which the liquid passes the distance l is expressed approximately by

$$\tau \approx \text{const}\frac{d^2}{x},$$

and the dependence $\Delta P = f(x)$ becomes close to quadratic, which was assumed by V.Ya. Khasilev. It may be supposed that at certain constraints the properties of cost functions of pipeline networks that were determined in [76, 106] hold for the multiphase flows as well.

A fundamental character of closing relations (availability of a "lumped" component of the second power and corrections of higher powers) will apparently not change at a transition from complete to partial equilibria in flows. However, a complex analytical type of these relations indicates that in practical calculations of heterogeneous circuits they should be either determined by the iterative computational procedures or indirectly accounted for at approximation of the models of hydraulic systems on the whole (see below).

In concluding the analysis of closing relations, we will briefly address their derivation for nonsteady flow distribution. The analysis can be based on equation (3.25). The terms of its right-hand side are naturally interpreted as the stationary (the first term) and the nonstationary (the second term) components of head losses.

It is obvious that when we study a steady process, the second term turns out to be equal to zero and equation (3.25) reduces to the traditional form of the closing relation (3.13). Certainly, if the change in the "steady form" for the flows with phase transitions and chemical transformations is taken into account, it seems natural to replace (3.25) by the more general expression

$$h_i(\tau) = f_i(x_i, \tau) + \psi_i \frac{dx_i(\tau)}{d\tau}, \tag{3.91}$$

where the form of terms on the right-hand side is determined by the properties of the moving medium (gas, heterogeneous mixture of gas and condensed particles) and the character of processes running in the flows (phase transitions, chemical reactions, friction, heat exchange, etc.).

The problem of determining the expression for the first term was tackled to a considerable extent above. The problem of searching for the second term form will be not discussed in this book. It should be a subject of independent extensive studies. It should be noted, only, that depending on the disturbance nature the derivative $dx_i(\tau)/d\tau$ in (3.91) may be substituted by the derivative of pressure or temperature, the sum of derivatives of individual components of the vector flow in branch i, and so on.

On the whole the thermodynamic analysis of nonsteady flow distribution proves to be useful, when we are interested in the *results* of transient processes rather than in the *time* of their occurrence, which was considered above. For example, in the analysis of impact of the fast operation of stop valves in a pipeline network, it is important to determine a maximum liquid pressure and to check whether it exceeds an admissible value or not. The question the matter of what fraction of a second or of what seconds such pressure arises—is not so important (if, of course, the choice of the maximum rate of stop valve operation is not dealt with). In the studies of processes of heavy hydrocarbons, precipitation in gas and oil pipelines, or soot in tubes of chemical reactors, thermodynamics helps determine maximum precipitation of harmful substances relative to hourly mass flow of the moving medium and then estimate tentatively the time of tube "overgrowing." At least in a number of cases it is more important to determine the probability that explosive mixtures are formed in communications of energy or other industrial plants than to find the time taken for the corresponding reactions to proceed under favorable conditions.

Examples of Heterogeneous Circuit Application

The methods of constructing thermodynamic models of heterogeneous hydraulic systems to solve applied problems will be illustrated by two examples: 1) *fire spread* in complex air exchange systems; and 2) burning and disposal of harmful pollutants of industrial plants.

Prior to direct modeling of fire spread we will briefly address the topical problem of analysis of normal operation conditions for air exchange systems. This subject was touched upon in [91].

Ventilation and air conditioning systems for residential and industrial premises should provide both the requisite sanitary standards in temperature and moisture and the acceptable chemical composition of air. Whereas until recently the main method of controlling harmful emissions on premises was the intensive dilution of indoor air with outdoor air, now such a purification method may be dangerous. This is because in the "purifying" outdoor air the concentrations of harmful substances may be much higher than the (admissible) standards. Since indoor and outdoor temperature and moisture usually differ considerably, chemical composition of air flows in any building changes significantly. These changes can be calculated by modeling the air exchange systems on the basis of heterogeneous hydraulic circuits.

Modeling of fires in air exchange systems is the most sophisticated and theoretically interesting case when we attempt a "chemical and hydraulic" description of the system. Such systems include ventilation networks of buildings and other structures (such as mines and subways). The appropriate models, if available, will supposedly contribute to working out preventive measures and improving fire control.

The mathematical modeling of fires has been the subject of numerous publications (see, for example, [66]). Originality of the authors' approach consists in the network problem statement and its presentation in terms of HCT and thermodynamics.

Prior to solution of such a complex problem currently we can create just a draft model that should be adjusted successively in the course of further studies.

To make the presentation clear we will first describe fires on the basis of a loop system of hydraulic circuit equations that is similar to system (3.6)–(3.8) and apply it in combination with MEIS; then we will show how to pass from this system to nodal potentials and the extreme model (3.50)–(3.56).

We will not construct equivalent calculated schemes of a real object, and we will suppose that the air exchange scheme (hydraulic circuit) is known. A simplest open double-loop hydraulic circuit is chosen as an example (Fig. 3.7*a*). Assume that the fire occurs on branch 2 and can spread to the rest of the scheme. The difference in densities on individual circuit branches induces gravitational heads denoted by H_{g1} and H_{g2}.

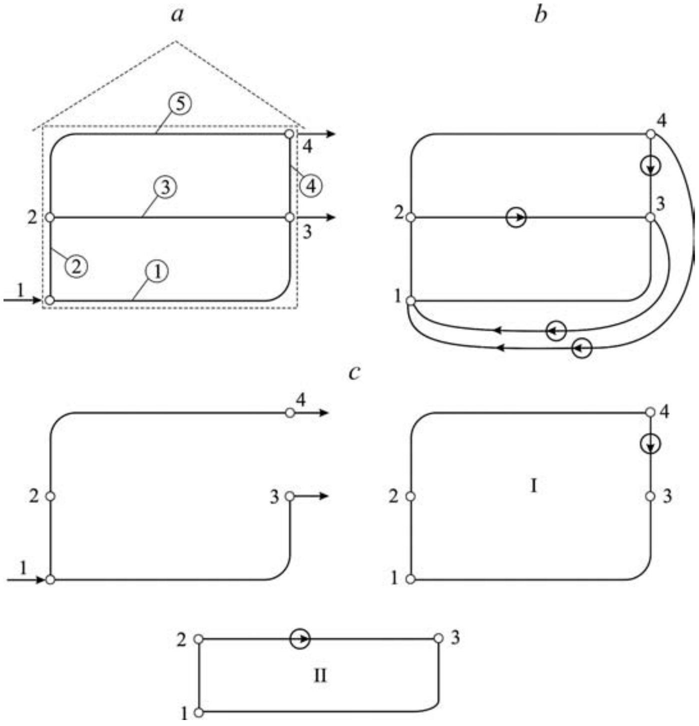


FIGURE 3.7. Hydraulic circuit schemes. *a*) basic calculated scheme, *b*) scheme to study relationships between Q and H_g; *c*) spanning tree and calculated circuit loops. Figures in circles are numbers of branches.

It is clear that if the sources and sinks at nodes of the calculated scheme are not regulated, they are to change with the change in H_g. We can study relationships between the vectors of sources (sinks) Q and the gravitational heads H_g substituting the scheme in Fig. 3.7*a* by the scheme in Fig. 3.7*b*. Here the effective heads of branches 3–1 and 4–1 are taken equal to the pressure difference between the windward and leeward sides of the modeled object. However, the latter scheme will not be used in the theoretical analysis, though in practical calculations similar transformations of schemes may turn out to be necessary. We select loops I and II as independent (Fig. 3.7*c*), which correspond to chords 4 and 3, which were determined as a result of constructing of the spanning tree presented in Fig. 3.7*c*.

The loop system of equations for the considered hydraulic circuit can be represented as:

$$Ax = Q, \tag{3.92}$$

$$Bh = BH_g, \tag{3.93}$$

$$h_i = f_i\left(x_i, \rho_i\left(x_i, T_i\right)\right), i = 1, \ldots, 5, \tag{3.94}$$

$$H_{gk} = f_k\left(z_k, \Delta\rho_k\right), k = 1, 2, \tag{3.95}$$

$$T_i = T_i\left(\Delta T\right), \Delta T_i = T_{bi} - T_{ei} = \varphi_i\left(\alpha_i, F_i, T_{\text{env}}\right), \tag{3.96}$$

$$x_i = \left(x_{i1}, \dots, x_{ie}\right)^T = \psi_i\left(y, T_i, P_i\right), \tag{3.97}$$

where H_g is a vector of the gravitational heads; z_k and $\Delta\rho_k$ are, respectively, the difference of geodetic level marks and the difference of densities of the upward and downward flows in the kth loop; T_{bi} and T_{ei} are temperatures at the inlet and the outlet of the ith branch; T_{env} is an environmental temperature; α_i and F_i are the heat transfer coefficient and the heat exchange surface on the ith branch.

A natural idea of computational algorithms is to construct a circuit model with lumped parameters (3.6)–(3.8) for iterative calculations instead of model (3.92)–(3.97) to adjust the values of components in the vectors x_i and H_g at each iteration.

It seems reasonable to calculate "normal" (before the fire) flow distribution at the first iteration, then to calculate fire on branch 2 and adjust chemical composition, gravitational heads, averaged temperatures, and densities of the moving medium. There are several variants for choosing the model for determination of combustion results, e.g.: 1) stoichiometric description of a small number of basic reactions; 2) determination on MEIS of the final equilibrium point x^{eq} at the given vector y, the given list of the components x and the fixed enthalpy H and pressure P; 3) MEIS application to search for x^{ext} with the same data, as in the second variant, and the setting of the objective function that is the sum of concentrations of the most dangerous substances.

The first stoichiometric variant is the least suitable for assessing fire impact. However, successive sophistication of the considered model and determination of relationships between the mathematical properties and the assumptions made will make it possible to apply the stoichiometric model. Expediency of using the third model (the main block of MEIS – x^{ext}) is due at least to the fact that we are interested in both the fire spread over the circuit branches and the spread of harmful substances beyond its direct zone that can cause poisoning of people at certain concentrations.

Gravitational heads at the first approximation can be determined by the simplest relation

$$H_{gk} = z_k\left(\rho_{ck} - \rho_{hk}\right), \tag{3.98}$$

where ρ_{ck} and ρ_{hk} are the average densities of the upward and downward flows in the kth loop, respectively. They are given by

$$\rho_{ck} = \frac{1}{z_k}\sum_{i\in I_{ck}} \rho_i z_i, \ \rho_{hk} = \frac{1}{z_k}\sum_{i\in I_{hk}} \rho_i z_i, \tag{3.99}$$

where ρ_i and z_i are the average density and the difference of marks along the vertical axis for the ith branch, respectively; I_{ck} and I_{hk} are sets of branches with the downward (*ck*) and upward (*hk*) flows.

Temperatures of the branches and their variations can also be determined the linear approximation from the equations:

$$q_i = \alpha_i F_i \left(T_i - T_{\text{env}}\right) \tau, \ \ T_i = 0.5 \left(T_{bi} + T_{ei}\right), \tag{3.100}$$

$$q_i = c_i x_i \left(T_{bi} - T_{ei}\right) \tau, \tag{3.101}$$

where q_i are heat losses to the environment on the ith branch, and c_i is the specific heat of the multicomponent flow. The estimated time τ corresponding to the supposedly dangerous rate of fire spread should be varied, apparently, to analyze real objects. In terms of the construction principles of thermodynamic models, τ does not belong to the variables sought in the problem.

In addition, the heat balance equations for the circuit as a whole should be satisfied:

$$\bar{A}_b C_b T_b - \bar{A}_e C_e T_e = \bar{A} C T = q, \tag{3.102}$$

where $\bar{A}_b$ and $\bar{A}_e$ are submatrices of the complete $m \times n$ matrix $\bar{A}$ of connections of all circuit nodes and branches that fix separately the initial "b" and the final "e" nodes of the branches; $C_b = [c_{bi}]$ and $C_e = [c_{ei}]$ are diagonal matrices of the heat capacity magnitudes of the medium flowing to the initial node of branch i (c_{bi}) and out of the final node of the same branch (c_{ei}) ; $C = [c]$ is a diagonal matrix of the average heat capacities of flows; T_b, T_e, and T are vectors of the temperatures at the initial and the final nodes and on the circuit branches, respectively; and q is a vector of external heat sources and sinks at the circuit nodes.

When adjusting ρ_i, we determine the density $\rho_{i\theta}$ of every θth component of the ith flow from the thermodynamic equation of state, and calculate the total flow density by the relation

$$\rho_i = \frac{\sum\limits_{\theta} \rho_{\theta i} \ \ x_\theta}{\sum\limits_{\theta} x_\theta}, \tag{3.103}$$

where x_θ is the mole quantity of the θth component.

At the second and following iterations, system (3.6)–(3.8) is calculated with the adjusted values of H_g and ρ. In this case, if for some branch, T_i happens to exceed the ignition temperature T_{fl} of the moving medium, the flame characteristics for it are determined by MEIS (or the stoichiometric model) and then the circuit parameters are adjusted by the algorithm applied at the first iteration. The calculations terminate, if the difference in the values of x_i (or some other variables) at two successive iterations does not exceed a given small value ε.

If the model of fires is constructed on the basis of the method of nodal potentials, equation (3.93) is replaced by the expression

$$h - H_g = \bar{A}^T \bar{P}(x). \tag{3.104}$$

The closing relation for each branch with a nonzero difference of geodetic mark level z_i includes the term

$$H_{gi} = z_i \rho_i. \tag{3.105}$$

It is evident that description of the gravitational heads on the branches by relation (3.105) in the "potential" model is mathematically equivalent to description of the gravitational heads in the loops when the loop system of equations is used.

Of course, relation (3.105) may also be used to describe fires on the basis of the extreme model (3.50)–(3.56), which can obviously be reduced, as well model (3.92)–(3.97), to the model with lumped, iteratively corrected parameters. With system (3.50)–(3.56) the principle of extreme description of hydraulic systems is realized most successively: The MEIS is applied both to the search for the extreme concentration x^{ext} of harmful substances and for the maximum entropy for a closed active circuit.

Note that application of model (3.50)–(3.56) supposes a transformation of the initial calculated scheme of the air exchange system that is similar to the one presented in Fig. 3.7*b*. The variant of "extreme" description of fire is also possible on the basis of the model of an open heterogeneous circuit and choice of the corresponding objective function.

Fig. 3.8 illustrates the modeling of the system of combustion and removal of harmful industrial waste. Here branches 2–5, 3–4, 7–10, and 8–9 model devices in which the combustion process takes place, and branches 1–2, 2–3, 4–5, 5–6, 6–7, 7–8, 9–10, and 1–10 are the incoming and outgoing pipelines. Air is supplied to node 1, products of harmful substance combustion are removed from node 6. Inflows to nodes 2, 3, 9, 10 represent the burnt harmful waste.

The iterative computational process can be represented in a fashion similar to the process considered above, where the model of fires was discussed. At the first iteration the flow distribution is calculated on the assuming that no chemical reactions exist. Closeness of the pressure to atmospheric pressure and its negligible change allow one to take density of the moving medium to be constant and to use

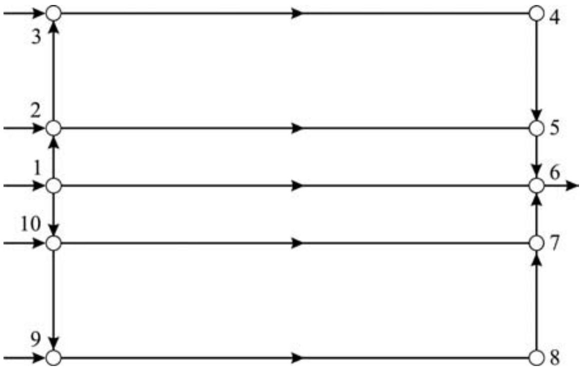


FIGURE 3.8. Hydraulic circuit of the system for removal of harmful industrial waste.

the circuit with lumped parameters. The MEIS-based information on the flow of air and harmful substances through the combustion devices is applied to calculate a combustion process and to adjust density of the moving medium on branches 2–5, 3–4, 7–10, 8–9, 4–5, and 7–8; then, according to the rules of flows mixing, the same is done on branches 5–6 and 6–7. Further, the calculations are repeated iteratively, until the differences in values of the vector x components at a transition from the kth to the $(k + 1)$th iteration become lower than the given small value ε. From the result of the computational process it can be determined, for example, if the products of incomplete combustion are formed at individual combustion devices because of air shortage, and if incomplete combustion leads to appearance of explosive mixtures in the outgoing pipelines.

4

Methods and Algorithms of Searching for Thermodynamic Equilibria

> A small boy asked the mathematician: “How much is twice two?” The mathematician said that he would think and after three days of thinking he shared his joy with the boy: “I have proved that this problem has a solution!”
>
> *A joke*

4.1. E.G. Antsiferov’s General Two-Stage Technique of Searching for Extreme Concentrations

As was noted in Section 2.4, even if we managed to strictly prove reducibility of the problem solved by MEIS to the convex programming (CP) problem, the difficulties caused by the setting of constraints on monotone change of thermodynamic functions presented in implicit form remain. E.G. Antsiferov [4, 7, 8] suggested a two-stage technique of searching for the vector of extreme concentrations x^{ext}. According to his idea, the surface of the thermodynamic function level that contains the point x^{ext} is determined at the first stage, coordinates of this point are sought on this surface at the second stage.

The first stage is based on the analysis of possible locations of the point x^{ext} in the thermodynamic attainability region $D_t(y)$ relative to the points y and x^{eq}. This stage was described in Section 2.4 (see Fig. 2.9).

Different cases are considered in the search for extreme concentration point x^{ext}. The first situation is the case of *monotone decrease of Gibbs energy* (or another characteristic function) on the interval segment $[y, x^{\text{mat}}]$. In this case the second stage is excluded (Fig. 2.9*a*), since the point x^{mat} proves to be a solution to the problem of searching for x^{ext}. The first stage reduces to solution of the canonical linear programming (LP) problem (nonlinear thermodynamic constraints do not influence the location of x^{ext}).

The second situation is the case of *continuous increase of the function* $G(x)$ on the segment y, x^{mat} (Fig. 2.9*b*). In this case the canonical CP problem (2.116) is solved at the second stage.

The third situation is the case of the *minimum point of* $G(x)$ (the thermodynamic “pothole”) on the segment $[y, x^{\text{mat}}]$ (Fig. 2.9*c*). This point is taken as the sought

TABLE 4.1. Calculation results of hexane isomerization ($T = 600$ K, $P = 0.1$ MPa)

		State			
Substance	Gibbs energy kj/mole, kJ/kg	y mole/kg, kg/kg	x^{eq}, mole/kg, kg/kg	x^{mat}, mole/kg, kg/kg	x^{mat}, mole/kg, kg/kg
x_1	−421.034	11.60	3.283	0	1.042
(isomer 1)	−4886	1.00	0.283	0	0.090
x_2	−423.620	0	5.513	11.60	9.670
(isomer 2)	−4916	0	0.475	1.00	0.833
x_3	−420.255	0	2.808	0	0.892
(isomer 3)	−4877	0	0.242	0	0.076
$L = \sum_J c_j x_j$, mole/kg,		0	5.513	11.60	9.670
G, kJ/kg		−4885.7	−4958.8	−4915.7	−4942.8
H, kJ/kg		−1294.0	−1294.0	−1321.0	−1313.0
S, kJ/(kg·k)		6.066	6.006	5.991	5.996
υ,m^3/kg		0.571	0.571	0.571	0.571
ρ,kg/m^3		1.750	1.750	1.750	1.750
x, mole/kg,		11.60	11.60	11.60	11.60

Situation: a thermodynamic "pothole."

level of $G(x^{\mathrm{ext}})$, and the CP problem (2.118) is solved. The function $G(x^{\mathrm{ext}})$ in this situation is determined with some error, as we discussed in Section 3.2 (see Figs. 2.4 and 3.1a).

In order to solve the CP problems at the second stage of searching for x^{ext} Antsiferov developed some algorithms on the basis of methods of the support cone, affine scaling, and generalized linear programming [4, 83]. The further MEIS-based studies of thermodynamic problems were performed using both modified and newly developed algorithms. However, the two-stage scheme of determining x^{ext} by Antsiferov remained invariable [81, 83, 102].

The scheme is highly attractive in terms of the analysis of results of thermodynamic computations as well. It allows their representation in a convenient tabular form, which is illustrated again on the example of hexane isomerization. The data on this process in Table 4.1 describe its thermodynamic features fully enough.

Conditions for attaining the sought extreme concentration ($\max x_2$) are determined from the figures in the columns under "State" and in the footnote "Situation." The case of the thermodynamic "pothole" takes place here. Yield of x_2^{ext} is approximately 80% higher than x_2^{eq} and turns out to be more than 10% lower than x_2^{mat}. The absolute value of difference $|x_2^{\mathrm{mat}} - x_2^{\mathrm{ext}}|$ is the value that cannot be exceeded by the error in calculation of x_2^{ext}, i.e., it is a very rough estimation of solution accuracy. Comparison of the standard values of free enthalpy in the column "Gibbs energy" reveals competitiveness of individual components of the reaction mixture in the contest for a place in the final equilibrium composition. The values of thermodynamic parameters in the lower part of Table 4.1 describe the properties of system states considered in the computation process.

Numerous calculations of most diverse systems (technical and natural) demonstrated high efficiency of the algorithm of stage 1 of Antsiferov's scheme. The results were always logically consistent. In rare cases, when it was possible to *estimate* calculation accuracy more correctly than to find them by comparison between values of x^{ext} and x^{mat}, the estimates were acceptable. This does not mean, however, that in the future one will not run across such situations where the errors in determining $G(x^{\text{ext}})$ will be impermissibly large. Therefore, the problem of devising alternative methods of searching for x^{ext} is topical. Construction of algorithms on the basis of the idea of a thermodynamic tree seems to be a possible alternative to Antsiferov's scheme.

The next Sections of this chapter dwell on algorithms for determination of y^{ext} and x^{ext} (stage 2 of calculations made using Antsiferov's technique) and the alternative algorithm for determination of $G(x^{\text{ext}})$ based on the idea of the thermodynamic tree (stage 1 of calculations made using Antsiferov's technique). The last section, Section 4.5, presents preliminary considerations on the technique for estimating feasibility and stability of the partial equilibria of x^{ext}.

4.2. Optimization of the Initial Composition of Reagents in a Chemical System by the Simplex Embedding Method

It is difficult to apply MEIS (2.43)–(2.50) of systems with a variable initial composition of reagents for choosing an optimal value of y because, in the problem statement, the vectors x and$y$ are analytically independent. Therefore, it is complicated to apply methods requiring that functions and their derivatives—ones that depend simultaneously on the values of these two vectors—be calculated in the iterative process.

To solve a general problem of searching for the point $(x^{\text{ext}}, y^{\text{ext}})$ E.G. Antsiferov applied the *simplex embedding method* to determine y^{ext} [6].

The simplex belonging to the Euclidean space R^n with the vertex at the point x_0 and the edges $x_1 - x_0, \ldots, x_n - x_0$, that form the basis in R^n is a polyhedron, all points of which satisfy the condition

$$x = x_0 + \sum_{i=1}^{n} \alpha_i (x_i - x_0), \ \sum_{i=1}^{n} \alpha_i \leq 1, \ \alpha_i \geq 0. \tag{4.1}$$

Without loss of generality it is assumed that $x_0 = 0$, i.e., x_0 coincides with the coordinate origin. The simplex volume is determined by the formula

$$V = \frac{[\det(x)]}{n}, \tag{4.2}$$

where x is an $n \times n$ matrix whose rows are the transposed vectors of coordinates of the vertices. The simplex center is found from the expression

$$x_c = \frac{(x_0 + \cdots + x_n)}{(n+1)}. \tag{4.3}$$

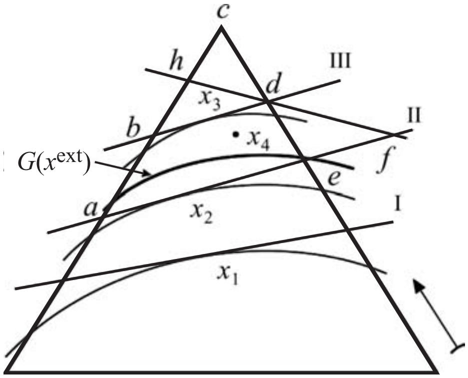


FIGURE 4.1. Geometrical interpretation of the simplex embedding method.

It is convenient to apply the simplex to computational procedures because its topology is so simple compared to other convex polyhedrons. In the simplex, edges connect each vertex every other one, this being another distinctive feature along with (4.1).

At $n = 0, 1, 2, 3$, the simplexes are, respectively, a point, a line segment, a triangle, and a tetrahedron. Note in addition that simplex vertices do not exist in one $(n - 1)$-dimensional plane (where n is simplex dimension). Simplex faces are simplexes of lower dimensionality. A tetrahedron face is a triangle, a simplex of dimension $n = 2$, and so on.

The idea of the simplex embedding method consists in sequential construction of simplexes containing the point $x^{\text{ext}}(y)$. The volume of each subsequent polyhedron turns out to be less than the volume of the preceding one and the solution is progressively localized. The monotone decrease in volumes provides convergence of computations.

The algorithm scheme is explained in Fig. 4.1. It presents the region boundary for admissible solutions of $D_t(y)$ (the bold curve), four simplexes, corresponding to calculation iterations, with simplex centers and the truncating planes used to construct simplexes.

First the simplex with the center x_1 is constructed. Since the objective function $(\sum_j c_j x_j)$ increases toward the admissible region boundary (the direction of increase in Fig. 4.1 is shown by the arrow), it is possible to further localize a solution. To do this, we draw truncating plane I through x_1 or somewhat above it. The plane isolates the simplex with center x_2, in which the objective function value lies higher than in simplex with center x_1. The center of the third simplex x_3 finds itself in the inadmissible region. When we draw the truncating plane III through it, a zone of further search for the solution by the polyhedron *abdea* is limited. For its substitution by the simplex, the segment *bc* is divided in two and a straight line is drawn from the obtained point *h* through the point *d* to the intersection of *f* with the truncating plane II.

The center x_4 of the fourth simplex *ahfa* is now located close to the admissible region boundary and the point with the extreme concentration x^{ext} of desired products of a process that lies on it.

As is seen from equation (4.1), the simplex embedding method requires that the problem constraints be set as non-homogeneous inequalities. Conditions (2.47), which determine admissible relations among the $y$vector components, can apparently be rewritten in the form

$$\sum_{j=1}^{l} \alpha_{kj} y_j \leq 0,\ k \in K. \tag{4.4}$$

To pass from (4.4) to nonhomogeneous inequalities, some variable, the first, for example, will be expressed through the remaining ones based on the normalization condition (2.44):

$$y_1 = 1 - \frac{\sum\limits_{j=2}^{l} M_j y_j}{M_1}. \tag{4.5}$$

Then the initial simplex is determined by the obvious inequality

$$\sum_{j=2}^{l} \frac{M_j}{M_1} y_j \leq 1, \tag{4.6}$$

where all $\frac{M_j}{M_1}$ are strictly greater than zero.

The truncating plane is constructed using the solution $(\bar{x})$ of the following CP problem:

Find

$$\max \sum_{j=1}^{n} c_j x_j \tag{4.7}$$

subject to

$$Ax = b\,(y_c) = \sum_{j=1}^{n} y_j A_j, \tag{4.8}$$

$$G\,(x) = \overline{G}\,(y_c)\,, \tag{4.9}$$

$$x_j > 0, \tag{4.10}$$

where y_c and $\bar{G}(y_c)$ are the simplex center and the associated Gibbs energy level, respectively, and A_j is the jth column of the matrix A. The solution $\bar{x}$ along with (4.8)–(4.10) satisfies the Kuhn–Tucker conditions:

$$c_j = \sum_{i=1}^{m} \lambda_i a_{ij} + \lambda_{m+1} \nabla_j G\,(\bar{x})\,, \tag{4.11}$$

$$\lambda_{m+1} > 0, \tag{4.12}$$

where $\nabla_j G(\bar{x})$ is the jth component of the gradient $G(x)$ at the point $\bar{x}$.

Let us increase the initial component y_c by a small value Δy. This will involve a change in the material balances (4.8), and the relation (4.9):

$$G\,(x) \leq \bar{G}\,(y_c)\,.$$

The optimal solution $\bar{x}$ and the objective function (4.7) will also change. The former will increase by Δx and the latter by $c\Delta x$. If Δy is chosen to be rather small, the set of active constraints and the dual solution to problem (4.7)–(4.10) will remain invariable.

In a linear approximation variation of the solution, Δx will satisfy the conditions:

$$A\Delta x = \sum_{j=1}^{l} \Delta y_j A_j, \tag{4.13}$$

$$\nabla^T G(\bar{x})\,\Delta x = \nabla^T \bar{G}(y_c)\,\Delta y. \tag{4.14}$$

If we multiply equality (4.13) by λ_i, $i = 1, \ldots, m$, equality (4.14) by λ_{m+1}, add the results, and take into consideration (4.11), the objective function (4.7) will be

$$\Delta F = \sum_{j=1}^{l} \left[\sum_{i=1}^{m} \lambda_i a_{ij} + \lambda_{m+1} \nabla \overline{G}(y_c) \right] \Delta y_j. \tag{4.15}$$

Based on (4.11) the formula for the truncating half-space in the y variables can be written:

$$d^T (y - y_c) \geq 0, \tag{4.16}$$

where

$$d_j = \frac{a_j}{\Psi(y_c)} - \frac{\left(c^T \bar{x}\right)}{\Psi(y_c)^2}, \tag{4.17}$$

$$a_j = \sum_{i=1}^{m} \lambda_i a_{ij} + \lambda_{m+1} \nabla \bar{G}(y_c), \tag{4.18}$$

$$\Psi(y_c) = \sum_{j \in J_c} y_j. \tag{4.19}$$

This algorithm can check admissibility of a simplex center at each iteration in terms of yield of substances of interest to the researcher.

4.3. Calculations of Complete and Partial Equilibria by the Affine Scaling Method

The point of the final equilibrium x^{eq} on the material balance polyhedron $D(y)$ is sometimes sought by the Lagrange multipliers method (see, for example, [9]. The system of equations obtained in this case by equating the partial derivatives of L to zero is solved by the Newton method or some other method. Such an approach is suitable when x^{eq} is an interior point of $D(y)$. However, in Chapter 2 it was shown that this condition is not fulfilled when the thermodynamic system contains condensed phases. Besides, the method of multipliers is difficult to apply when inequality constraints are included in the models of final equilibria.

Applicability of the multipliers method to calculate x^{ext} (model (2.38)–(2.42)) becomes even more problematic than searching for x^{eq} because of the necessity to consider a wide diversity of constraints. Therefore, we applied solely the MP methods for searching for x^{eq} and x^{ext}[1]. Here we will dwell on the affine scaling method that has been used most often so far in studies on thermodynamic attainability regions and partial equilibria [34, 35].

The affine scaling method is convenient because it handles only the interior points of $D(y)$, in which an objective function gradient can be calculated and the motion to the extremum point is executed at an acute angle to this gradient taken with the opposite sign. The latter circumstance facilitates convergence of the method at an unfavorable (with the zones of small steepness) surface shape, on which the extremum point is sought. Using the figurative comparison we will explain that when descending the mountain by this method we determine motion direction not by touch, as in the steepest descent method, but by choosing the lowest point in the visible vicinity and adjusting the route after reaching it.

The idea of the above method will be illustrated with the example of searching for the point x^{eq}. An initial point for the computational process is some interior point x^0 of the polyhedron $D(y)$, at which $x_j^0 > 0$ for all $j = 1, \ldots, n$. At each iteration $k = 0, 1, 2, \ldots$, the obvious conditions on conservation of the mole quantities of elements and their positiveness are assumed:

$$\sum_{j=1}^{n} a_{ij}\left(x_j - x_j^k\right) = 0, x_j^k > 0. \tag{4.20}$$

The correction vector $z = (z_1^k, \ldots, z_n^k)^T$ whose components are $(x_j - x_j^k)$ determines direction of the motion at the kth iteration.

The ellipsoid is constructed with center at x^k such that

$$\sum_{j=1}^{n} \frac{z_j^2}{(x_j^k)^2} \le 1, \tag{4.21}$$

which represents a “visible vicinity.” This means the ellipsoid axes are distances from x^k to the positive orthant boundaries that determine a “visibility zone” subject to (4.20).

The point with the minimum Gibbs energy is sought by the linearization technique, i.e., the partial derivatives of the function $G(x)$ are calculated as

$$g_j^k = \frac{\partial G\left(x^k\right)}{\partial x_j}, \tag{4.22}$$

---

[1] Indicating the problems in application of the multipliers method, we mean its application as the basic procedure of computational algorithms. As an auxiliary procedure this method is included in many MP algorithms.

and the minimum value of the linear form is determined to be

$$C = \sum_{j=1}^{n} g_j^k z_j \tag{4.23}$$

subject to

$$\sum_{j=1}^{n} a_{ij} z_j = 0, \tag{4.24}$$

$$\sum_{j=1}^{n} \frac{z_j^2}{\left(x_j^k\right)^2} = 1. \tag{4.25}$$

As compared to (4.21) the strict equality sign is used in (4.25), since the linear function reaches its minimum at the boundary point of the convex set, in this case on the ellipsoid surface or the plane of its intersection with the material balance polyhedron.

The solution z of problem (4.23)–(4.25) is found using the system of equations obtained as a result of equating partial derivatives of the Lagrange functions (4.26) to zero:

$$L(z, \lambda) = \sum_{j=1}^{n} g_j^k z_j - \sum_{i=1}^{m} \lambda_i \sum_{j=1}^{n} a_{ij} z_j + \lambda_{m+1} \left(1 - \sum_{j=1}^{n} \frac{z_j^2}{\left(x_j^k\right)^2} \right). \tag{4.26}$$

The solution thus is represented by the formulas

$$z_j = \left(x_j^k\right)^2 \frac{\sum_{i=1}^{m} \lambda_i a_{ij} - g_j^k}{2\lambda_{m+1}}, \tag{4.27}$$

$$2\lambda_{m+1} = \left(\sum_{j=1}^{n} \left(x_j^k\right)^2 \left(\sum_{i=1}^{m} \lambda_i a_{ij} - g_j^k \right)^2 \right)^{0.5}, \tag{4.28}$$

$$\lambda = gA^{-1}, \tag{4.29}$$

where λ is a vector of the Lagrange multipliers with material balance constraints that include m components of λ_i. The iteration k terminates when the interior point x^{k+1} is determined, at which the minimum of function $G(x)$ is reached on the segment that coincides with its direction and is equal to the absolute value of z.

The process is repeated, until the magnitude

$$F_k = 4\lambda_{m+1}^2 = \sum_{j=1}^{n} \left(x_j^k\right)^2 \left(\sum_{i=1}^{m} \lambda_i a_{ij} - g_j^k \right)^2 \tag{4.30}$$

becomes less than the given small number ε. The sense of a rule that interrupts the process is clear, since the negligibly low value of F_k is associated with the negligibly low value of λ_{m+1} and hence, it is associated with quite an inessential change in the objective function with a change in ellipsoid parameters.

Transformation of system (4.26)–(4.30) results in an alternative statement of the problem on determination of the descent direction on the surface of $G(x)$:

Find

$$\min\left(\sum_{j=1}^{n} g_j^k z_j + 0.5\sum_{j=1}^{n}\frac{z_j^2}{x_j^{k^2}}\right) \tag{4.31}$$

subject to

$$Az = 0. \tag{4.32}$$

To control the method of convergence, the magnitude z can be multiplied by the coefficient α , i.e., from the equation

$$x = x^k + z^k \tag{4.33}$$

it is possible to pass to the equation

$$x = x^k + \alpha^{\,k} z^k \tag{4.34}$$

where step size $\alpha^{\,k} z^k$ is chosen such that $x > 0$. Affine scaling method is illustrated graphically in Fig. 4.2*a* and *b*.

We seek the initial interior point x^0 (the point of introduction in the admissible region) by several specially developed algorithms. Let us consider two of them.

The first (I.I. Dikin's [34, 35]) algorithm applies the idea of the basic affine scaling method and solves the following problem:

Find

$$\min\sum_{j=1}^{n}\frac{z_j^2}{\left(x_j^k\right)^2} \tag{4.35}$$

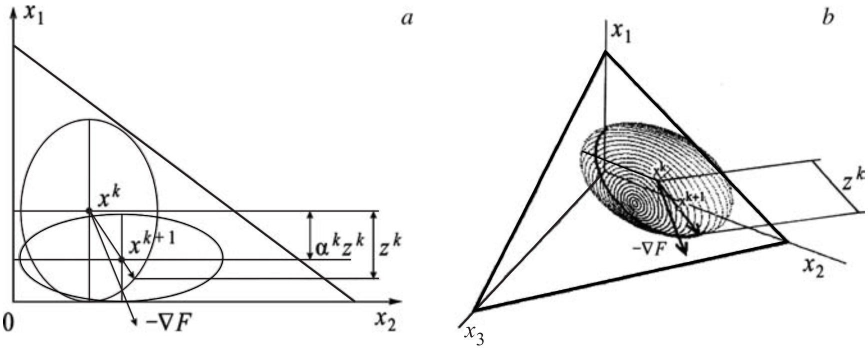


FIGURE 4.2. Graphical interpretation of the affine scaling method in (*a*) two- dimensional and (*b*) three-dimensional spaces.

subject to

$$Az = r^k, \tag{4.36}$$

where

$$r^k = b - Ax^k. \tag{4.37}$$

Transition from x^k to x^{k+1} is performed by equation (4.34), α^k is taken such that x^{k+1} belongs to the interior admissible region. The step size should not exceed unity, in this case. The calculation terminates when the absolute value of the imbalance $|r^k|$ becomes less than the given value ε .

Search for x^0 by the second (E.G. Antsiferov's) algorithm is based on the solution to the following auxiliary LP problem:

$$\left.\begin{array}{l} \text{Find} \\ \qquad \max \Delta \\ \text{subject to} \\ \displaystyle\sum_{j=1}^{n} a_{ij} y_j + \Delta \sum_{j=1}^{n} a_{ij} = b_i \;\; i = 1, \ldots, m, \; y_j \geq 0, \; \Delta \; > 0 \end{array}\right\} \tag{4.38}$$

Components of the vector x^0 are determined by the formula $x_j^0 = y_j + \Delta$. The second algorithm is apparently easier to apply then the first.

The solution of x^0 found by any of the mentioned algorithms can be additionally corrected based on the fact that all the interior points of the segment $[x^0, y]$ are the interior points of $D(y)$. For example, it seems logical to choose a minimum Gibbs energy point on this intercept as an initial approximation in the search for x^{eq}. The choice may contribute to an increase in the convergence rate of computations.

When the affine scaling method is used for searching for the point x^{ext}, the formulas to calculate the coefficients g_j in the objective function (4.23) change, and additional members on the right-hand side of equation (4.26) appear that correspond to constraints on the Gibbs energy values in the models of type (2.116) or (2.118). The general scheme of algorithm application, however, remains invariable.

Despite the fact that the affine scaling method proved to be highly efficient for solving a large number of applied thermodynamic problems, there are cases of extremely slow convergence such as in the solution of environmental problems, where the spread in values of the sought variables reaches 10–12 orders of magnitude and higher.

This problem was solved by I.A. Shirkalin [156]. He revealed a sharp deceleration of convergence of the discussed method near the point x^{eq} when concentrations of part of the reaction mixture components approach zero. In the search for a direction of optimal descent (z) he formulated the simplest two-dimensional problem, introducing three assumptions: 1) the initial point x^0 is close to the solution; 2) the objective function is strictly convex and twice continuously differentiable; 3) the value of the second coordinate (r) is much lower than that of the first (R).

Shirkalin determined the coordinates z by expansion of the objective function into the Taylor power series, $z = x - x^0$, and employed just the first three members of the series, i.e.

$$F(x) = F\left(x^0\right) - (\nabla, z) + 0.5\left(\nabla^2 z, z\right), \tag{4.39}$$

where ∇ is an antigradient and

$$\nabla^2 = \left[\frac{\partial^2 F(x)}{\partial x_1, \partial x_2}\right]$$

is a Hessian matrix at the point x^0.

Based on the minimization of $F(x)$ Shirkalin determined that

$$z_1 \approx \nabla_1 \quad \text{and} \quad z_2 \approx -r. \tag{4.40}$$

Transition to formulas (4.40) in the affine scaling method was performed using the auxiliary model he constructed:

Find

$$\max\left(\nabla_1 z_1 + \nabla_2 z_2\right) \tag{4.41}$$

subject to

$$\frac{z_1^2}{R^{2\beta}} + \frac{z_2^2}{r^{2\beta}} = 1, \tag{4.42}$$

where β is a sought parameter of the method.

Solution to problem (4.41), (4.42) reduces to (4.40) at $\beta = 0.5$. This value of β was applied to accelerate convergence of the computational process, i.e., when approaching the point x^{eq} expression (4.25) was replaced in the procedure of transition from the kth to the (k+1)th iteration by the expression

$$\sum_{j=1}^{n} \frac{z_j^2}{x_j^k} = 1, \tag{4.43}$$

which may be interpreted as an ellipsoid equation with axes $x_j^{0.5}$.

Since β was determined on the basis of the expansion in (4.39), the algorithm applied by Shirkalin can be treated as a realization of the general Newton method for minimization problems:

$$x^{k+1} = x^k - \left[\nabla^2 f\left(x^k\right)\right]^{-1} \nabla f\left(x^k\right). \tag{4.44}$$

Under Shirkalin's assumptions fit to a physical nature of the problems discussed in the book, the Newton method shows fast convergence [94, 142]. This explains the efficiency of substituting the parameter $\beta = 0.5$ into the ellipsoid equation applied in the affine scaling method. The calculating advantages of Shirkalin's algorithm were confirmed by its application to the thermodynamic analysis of anthropogenic air pollution (see Chapter 5) and the solution of some other problems.

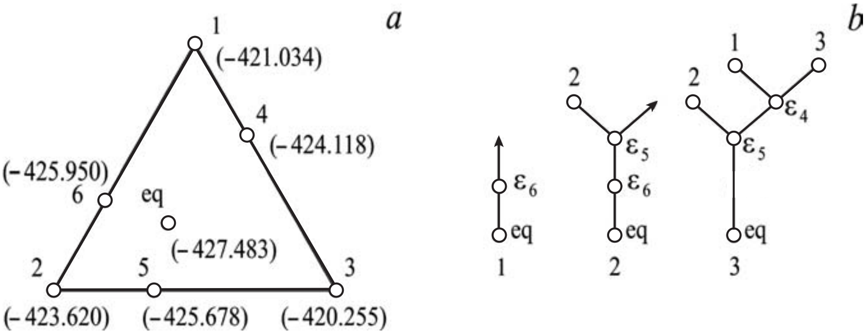


FIGURE 4.3. Construction of the thermodynamic tree of hexane isomerization reaction.

4.4. Construction of Algorithms Using the Thermodynamic Tree Idea

In this Section we present potential schemes of the algorithms for constructing a thermodynamic tree, whose efficiency was discussed briefly in Chapter 3. At first, consideration will be given to the exact algorithm described in *Equilibrium Encircling* [58] and then the algorithm will be explained on the examples of hexane isomerization and hydrogen combustion in oxygen of Section 3.2.

The tree construction for converting the isomers C_6H_{14} is illustrated in Fig. 4.3*a* and *b*. According to [58] we introduce the notation:

$D_0 = \{\upsilon_1, \ldots, \upsilon_l\}$is a set of the vertices of $D(y)$;
$D_1 = \{d_1, \ldots, d_k\}$is a set of the edges of $D(y)$;
ε_d is the minimum Gibbs energy value at the edge d.

First of all calculations, are made of the Gibbs energy values for all vertices υ and the minimum values of G (in kJ) at all edges ε_d. These values are presented in Fig. 4.3*a* (see, also, Fig. 3.1). The values ε_d are arranged in increasing order (ε_d may coincide with the Gibbs energy value at one of the vertices adjacent to the edge d).

The tree construction ("growth") starts with its root, i.e., the equilibrium point x^{eq}. Relative to x^{eq} the whole triangle 123 is the single component of arcwise connectedness, since there is a thermodynamically admissible path to x^{eq} from any of its points. We connect the point x^{eq} by the segment (the tree branch) with the point ε_6 that corresponds to the minimum Gibbs energy level from the calculated point ε_d (that maps the line $G(x) = \varepsilon_6$ within the appropriate component of arcwise connectedness). Relative to the point ε_6 the triangle part, for which $G(x) \geq \varepsilon_6$, is also the single component of arcwise connectedness. It results from the fact that all the triangle vertices are connected by edges (or a chain of edges), at which $\varepsilon_d > \varepsilon_6$, and hence, any point of the triangle with $G(x) \leq \varepsilon_6$ can be reached from any vertex by the thermodynamically admissible path. Thus, the point ε_6 is not a ramification point and the line $x^{\mathrm{eq}} - \varepsilon_6$ is extended to the next point ε_5 in increasing order of $G(x)$.

Relative to the level ε_5 there is vertex 2, which cannot be connected with other vertices by the edges with $\varepsilon_d > \varepsilon_5$. Therefore, part of the triangle between the line $G(x) = \varepsilon_5$ and vertex 2 is an arcwise connectedness component with respect to ε_5. The rest of the polyhedron $D(y)$ is another component. Hence, the point ε_5 is a branch point. One branch of the tree connects it with the end vertex 2 and another leads to the next in increasing order of $G(x)$ at the point ε_4.

Relative to the level ε_4 none of the triangle vertices is connected to other edges with $\varepsilon_d > \varepsilon_4$. This level of $G(x)$ separates in $G(y)$ two additional components of arcwise connectedness adjacent, respectively, to vertices 1 and 3. After connecting the point ε_4 to the end vertices 1 and 3, construction of the thermodynamic tree is completed.

Stages of the "growth" of such a tree for hydrogen combustion are shown in Fig. 4.4. The numbers ε_d of the edges of $D(y)$ are arranged as follows:

$$\varepsilon_3 < \varepsilon_1 < \varepsilon_6 < \varepsilon_2 < \varepsilon_4 < \varepsilon_5 < \varepsilon_8 < \varepsilon_7 < \varepsilon_{14} < \varepsilon_{13} < \varepsilon_9 < \varepsilon_{10} < \varepsilon_{12} < \varepsilon_{11} < \varepsilon_{15}$$

(the numbers of edges are presented in Fig. 4.4).

Because of the multidimensionality of the space ($n = 6$) in this case, as distinct from the description of the tree of hexane isomerization, we will sequentially represent graphically the removed edges of the graph $D(y)$ rather than the components corresponding to new branches of arcwise connectedness. Such graphical interpretation of tree growth is clear, since connection of each new branch to the tree means simultaneous substitution of some multidimensional region $D(y)$ by the one-dimensional segment. Disappearance of multidimensional regions leads to disappearance of the corresponding edges.

As in the previous case, construction will start with the root x^{eq}. We connect it with the least one among $\varepsilon_d - \varepsilon_3$. After removal of edge 3 the graph of the balance polyhedron remains connected. Hence, any two vertices of $D(y)$ can be connected with each other by an edge, a chain, or chains with max min ε_d on the parallel chains, max min $\varepsilon_d > \varepsilon_3$. The point ε_3 in this case is not a branch point. A similar situation is observed after removal of edges 1, 6, 2, and 4.

Only after rejection of edge 5 is the graph $D(y)$ broken into two components: the vertex H_2O and "the remainder." Then it becomes possible to draw two twigs of the tree: $x^{\mathrm{eq}} - \varepsilon_5$ and $\varepsilon_5 -$ H_2O. The next tree growth (the branches $\varepsilon_5 - \varepsilon_{14}$ and $\varepsilon_{14} -$ H_2, O_2) is executed after removal of edge 14. After sequential removal of edges 13 and 9 the vertex H_2, OH is separated from the graph, and becomes a new endpoint of the tree. Then the new vertices appear, respectively, after removal of edges 12 (H, OH) and 11 (H_2, O). The tree construction is completed after removal of edge 15, leading to formation of two last components of arcwise connectedness that border on the vertices (H, O) and (H, O_2).

The first example of converting the balance polyhedron to a tree (for the isomerization reaction) can evidently be explained as a process of sequential removal of edges from the graph $D(y)$.

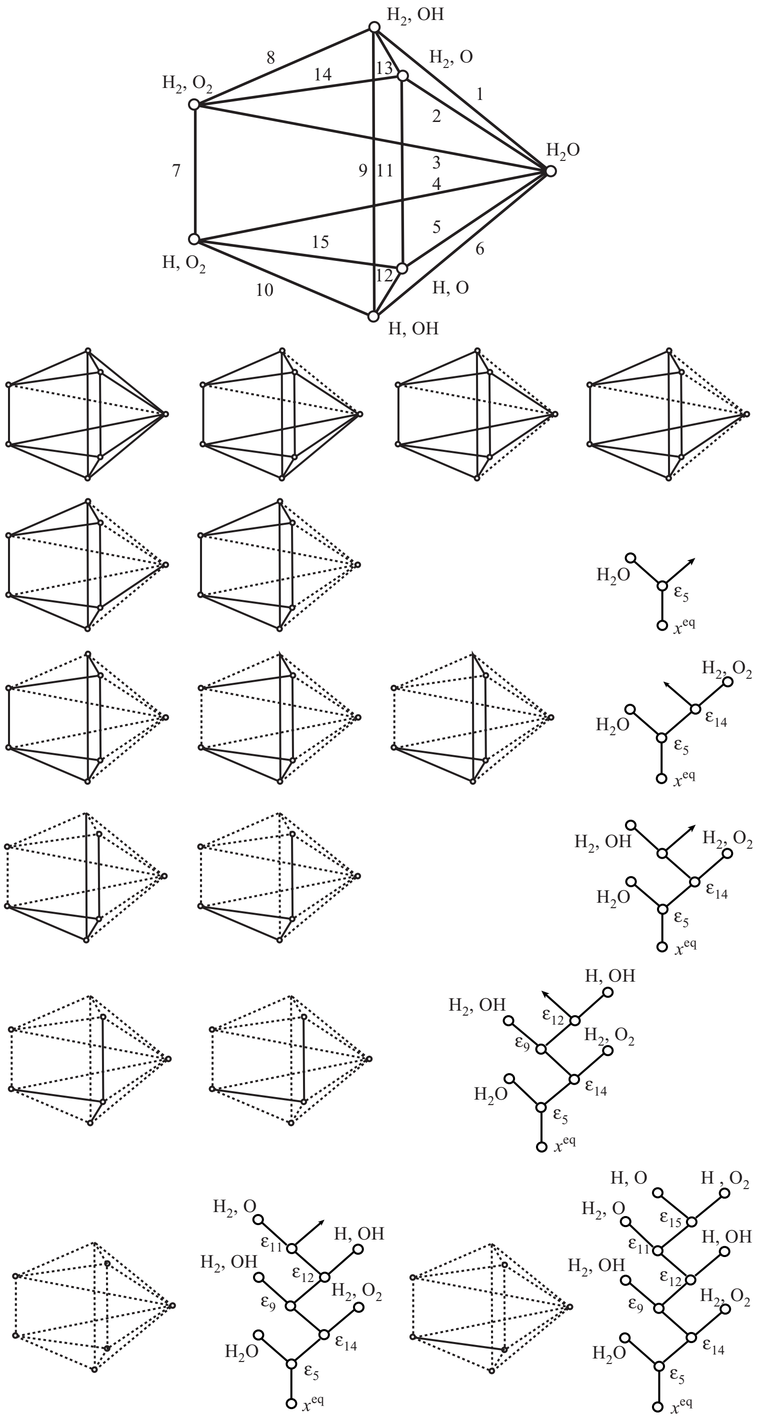


FIGURE 4.4. Construction of the thermodynamic tree for hydrogen combustion in oxygen.

After we have given graphical illustrations of the algorithm of tree construction, it is relevant to note that the equilibrium point x^{eq} can be a ramification point only at the one-dimensional $D(y)$, i.e., at $n - m = 1$. It is obvious that from the part of such a polyhedron to the left of x^{eq} we cannot reach the part to the right and vice versa. Therefore, both parts turn out to be different components of arcwise connectedness with respect to the equilibrium point.

Now we present a brief formal description of the exact algorithm of constructing a thermodynamic tree:

1. Construction of the graph of balance polyhedron $D(y)$.
2. Formation of the list of vertices of $D_0 = \{\upsilon_1, \dots, \upsilon_l\}$.
3. Formation of the list of edges of $D_1 = \{d_1, \dots, d_k\}$.
4. Calculation of the minimum values of $G(x)$ at the edges ε_d.
5. Arrangement of the values of ε_d in increasing order.
6. Calculation of the value of x^{eq} (by the affine scaling method, for example).
7. Connection of the point x^{eq} with the least ε_d.
8. Check of whether removal of the edge d results in separation of some vertex (vertices) υ from the polyhedron, i.e., whether ε_d is a ramification point.
9. If yes, connection of the ramification point ε_d to the vertex (vertices) υ and determination of the next tree branch (branches).
10. Check of whether ε_d is the highest level of ε . If yes, termination of the algorithm work.
11. Connection of the point ε_d to the next point ε (in order of increasing value) and transition to item 8.

The simplest examples presented in addition to the analysis in Section 3.2 illustrate an extreme complexity of the algorithm described. Apart from knowing the graph (remember that it can have an astronomic number of vertices), we need information about the Gibbs energy values at all the vertices and about the minimum values of $G(x)$ at all the edges prior to construction of the tree.

Possibilities for development of simplified numerical algorithms for constructing the tree that result in approximate solutions will be illustrated again with the example of isomerization (though, in this case, in a space of five variables). It is convenient to apply this example to a small-dimensional problem, because $D(y)$ as described by the single equation of the material balance is always a simplex and its graph is easily constructed by connecting each vertex with all the remainders.

A simplex of the process comprising mutual transformations of five isomers to each other is presented in Fig. 4.5*a*. It has 5 vertices (C_1^5) and 10 edges (C_2^5). If the minimum values of $G(x)$ at the edges are ordered as

$$\varepsilon_1 < \varepsilon_2 < \varepsilon_3, \dots, < \varepsilon_9 < \varepsilon_{10}.$$

then the tree of this simplex takes the form presented in Fig. 4.5*b*. It is clear that the point ε_7 is the first (lower) ramification point, since the simplex with 5 vertices turns into a tree in which the number of edges is equal to 4.

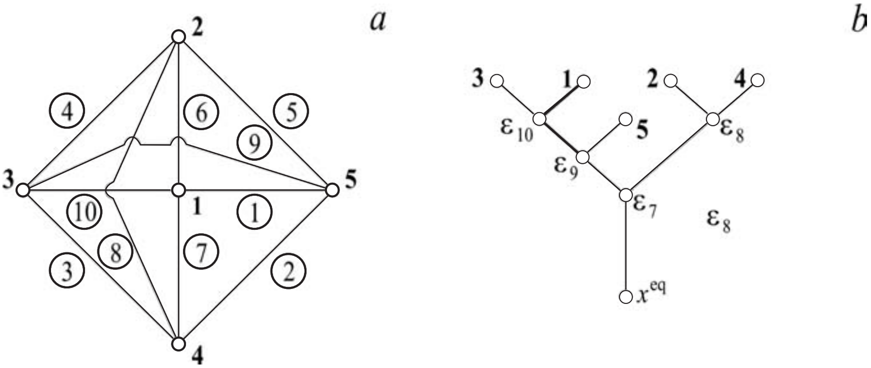


FIGURE 4.5. Simplex (*a*) and thermodynamic tree (*b*) of mutual transformations of five isomers.

If we assume that $y = (1, 0, 0, 0, 0)^T$, i.e., the initial state is represented by point 1 and the process goal is to obtain the maximum quantity of the fifth component, then the level ε_9 will be the surface level of $G = G(\max x_5)$.

Now we will try to find this level in accordance with the idea formulated in Section 3.2, constructing trees not for the whole polyhedron $D(y)$, but for its separate faces. Fig. 4.6 presents trees constructed for the three-dimensional faces, whose set D_0 contains vertices 1 (y) and 5 (x^{mat}). Using two trees from the obtained ones, we determine the same optimal level $G(x) = \varepsilon_9$ as we found in the tree of the whole simplex (Fig. 4.5). The trajectories of motion from y to $\max x_5$ along the tree branches are shown in Fig. 4.5–4.7 by bold lines.

If the trees are constructed at the two-dimensional faces with vertices 1 and 5, the optimal problem solution is also found in one of the three possible cases (Fig. 4.7).

Thus, these examples demonstrate the possibility for decreasing dimensionality of the problem of thermodynamic tree construction: substitution of the problem by one of determining projections of this tree on individual faces of the balance polyhedron. Even for complex real systems such substitution essentially decreases dimensionality of the problem of searching for the optimal level of $G(x)$ (or some other thermodynamic function). So, for the studied system with $n = 200$ and $m = 20$, the number of two-dimensional faces with two equal fixed vertices (y and x^{mat}) at the same edge makes up 179 (from $C_B^A = C_{178}^{179} = 179$, where A is the power of intersection of the sets of zero components at y and x^{mat} and B is the dimensionality of the set of zero components for the two-dimensional faces). Construction of about 200 trees for comparatively simple polyhedrons seems now to be a realizable problem.

Certainly it may happen that to determine $G(x^{\text{ext}})$, trees should be constructed at faces with dimensionality higher than 2.

To further analyze the idea on algorithm simplification two additional examples were considered: 1) combustion of pure carbon and 2) coal combustion in the air. To analyze both examples one and the same sequence of procedures was applied:

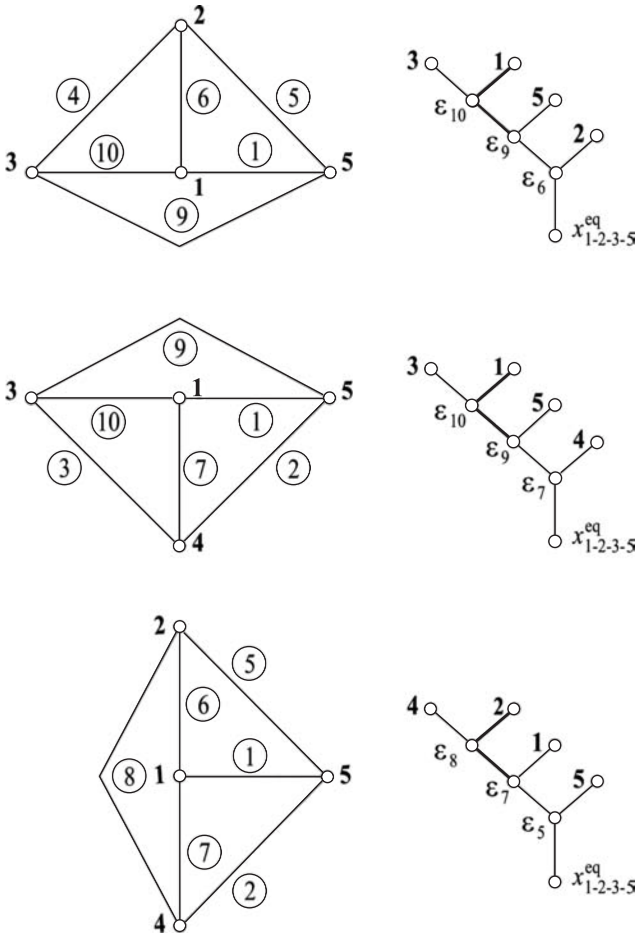


FIGURE 4.6. Three-dimensional faces of the simplex and the associated thermodynamic trees.

- The (intuitive) choice of a subset of solutions to the system of material balance equations, i.e., determination of part of the vertices of $D(y)$ (a subset of the set $D_0(y)$; in this case the choice of sample space necessarily included the vertices y (or the nearest one to y, if the initial system state does not coincide with one of the vertices of $D(y)$ and x^{mat} (the point of the maximum concentration of a given set of substances on $D(y)$).
- Application of the criterion

$$I_j \cap I_i = n - m - 1 \tag{4.45}$$

to check which segment connecting the determined vertices are the edges of $D(y)$ (here I_j and I_i are sets of indices of the zero components of x at the

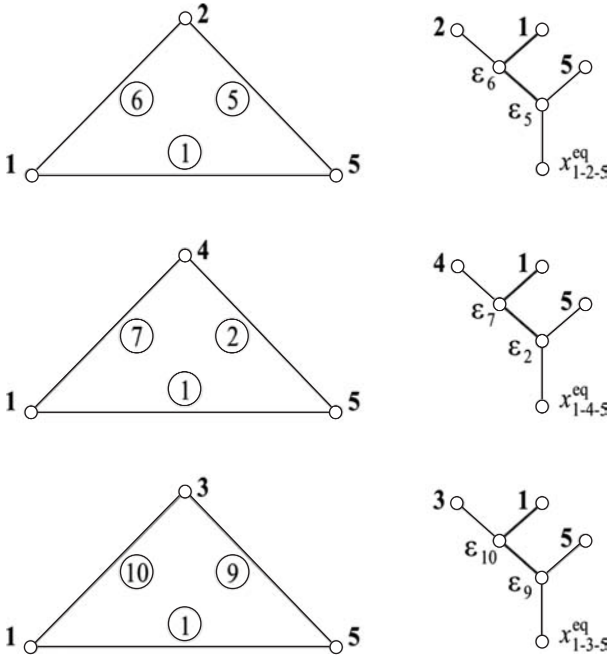


FIGURE 4.7. Two-dimensional faces of the simplex and the associated thermodynamic trees.

vertices j and i, respectively); then construction of a partial graph of the balance polyhedron (criterion (4.45) can be replaced by the criterion $I_j \cup I_i = m + 1$, where I_j and I_i are already sets of the nonzero components).

- Selection of connected parts of lower dimensionality (if possible) from the determined partial graph (preferably in the form of triangles) that contain the points y and x^{mat}.
- Construction of trees for the obtained parts and determination at them of the maximum ε_d on the thermodynamically admissible paths from y towards x^{mat}.

The solutions to the problem (searching for max ε_d for the considered examples) are interpreted by the plots in Figs. 4.8 and 4.9.

The graph with 7 vertices in Fig. 4.8*a* is part of the complete graph $D(y)$ of a system with 8 variables (x_{CO}, x_{CO_2}, x_{N_2}, x_{NO}, x_{NO_2}, x_{O}, x_{O_2}, x_{C}) and 3 material balances (for carbon, oxygen, and nitrogen) having 12 vertices. The vertices of the drawn graph correspond to maximum concentrations of substances forming a system.

Two triangular faces (Fig. 4.8*b* and *c*) and one quadrangular face (Fig. 4.8*d*) including the vertices y (7) and $x^{\text{mat}}_{\text{NO}}$ (4) were separated from the graph in Fig. 4.8*a* to construct trees. In this case, in accordance with the problem conditions, $y = (y_{\text{N}_2} = 25.5; y_{\text{O}_2} = 6.8; y_{\text{C}} = 5.7)^T$ and $x^{\text{mat}}_{\text{NO}} = (x_{\text{N}_2} = 18.7;$

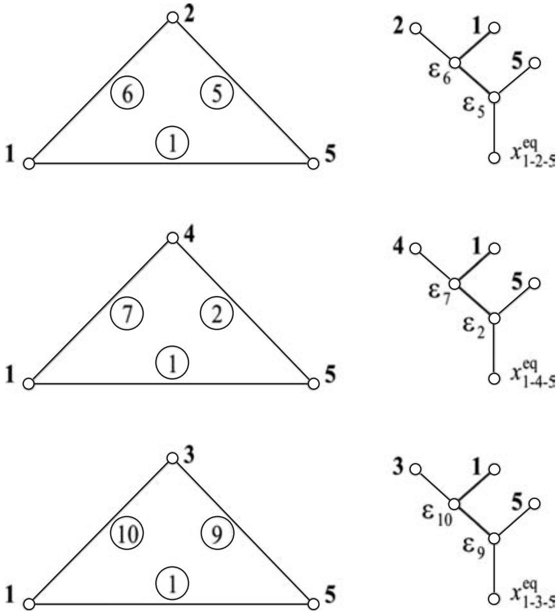


FIGURE 4.8. Construction of thermo-dynamic trees for carbon combustion reaction.

$x_{\mathrm{NO}} = 13.6; x_{\mathrm{C}} = 5.7)^T$. The same maximum value of $\varepsilon_d = -15.207$kJ was determined with the help of each the constructed tree (in Fig. 4.8 and 4.9 the values of $G(x)$ are given on the edges of polyhedrons and at the points of tree branching). This value turned to be somewhat higher than that determined by E.G. Antsiferov's [4, 7, 8] approximate algorithm (-15.211).

Though the graph in Fig. 4.9*a* is not more complex in structure than the graph in Fig. 4.8*a*, it belongs to a much more complex system. Coal combustion was modeled by the system comprising 23 components (CH_4, CN, CN_2, CO, CO_2, H, H_2O, H_2O_2, HO_2, N, N_2, N_2O, NH, NH_3, NO, NO_2, O, O_2, O_3, OH, SO_2, C, coal) and satisfying 5 material balances (for carbon, oxygen, nitrogen, hydrogen, and sulfur). Coal was represented by the conditional molecular formula: $CH_{0.833}O_{0.233}N_{0.012}S_{0.002}$.

The graph (Fig. 4.9*a*) was obtained from another partial graph containing 23 vertices by elimination from the latter those edges that did not belong to the triangular faces including the vertices y (23) and $x^{\mathrm{mat}}_{\mathrm{NO}}$ (15). The tree of the triangular face 12–15–23 determined the level of $G(x)$ that corresponded to the maximum concentration of NO (-15.571 kJ) and coincided with that obtained by Antsiferov's algorithm.

Thus, two last examples also confirmed the efficiency of simplified algorithms for constructing a thermodynamic tree. More accurate values of $G(x^{\mathrm{ext}})$ obtained in some examples than what was obtained by Antsiferov's algorithm raise hopes for the effective application of such algorithms.

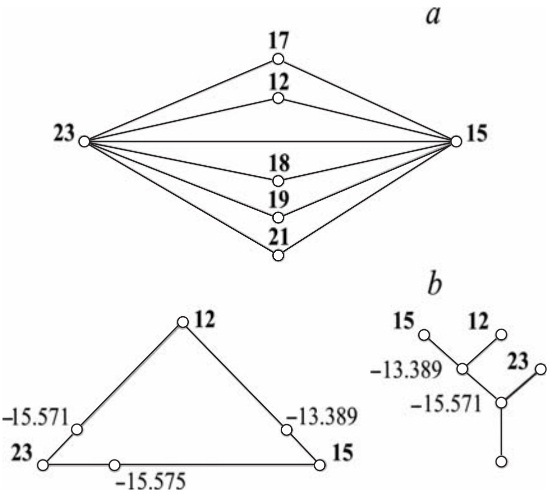


FIGURE 4.9. Construction of thermodynamic trees for coal combustion reaction.

The computational procedures describing two last examples may surely be considered only as drafts of these algorithms.

Their creation calls for further theoretical comprehension of the problem and practical tests of the outlined computational approach. Formalization of the problem of searching for the partial graphs for which thermodynamic trees are constructed will apparently be central in development of the approach.

4.5. Analysis of Feasibility and Stability of Partial Equilibria

The most difficult and frequent questions among those arising in MEIS application are the following: “How complicated is it, and is it possible in general to implement the determined extreme state?” and “Is this state maintained long enough to extract or register the target products?” In many cases the positive answer is suggested by the available experience of studying processes similar to the considered one. Possibilities for production of hydrocarbons, these being intermediate products of fuel processing discussed in the final chapter (Chapter 5) of the book, are confirmed, for example, by operating data of numerous technological installations. Experiments also reveal the presence of harmful substances in the atmosphere, whose calculated extreme concentrations are presented in Section 5.1.

However, in the analysis of new technologies that were not tested experimentally and in the calculations of poorly studied processes of environmental pollution, the response to the question on feasibility of extreme partial equilibria is not known in advance. Along with the question on duration and retainability[2] of the sought states the question often arises of their stability in the face of different disturbances, such as changes in initial composition, pressure, temperature, and so on.

This section presents preliminary considerations on possible algorithms of analysis performed after calculations on MEIS; our aim is to estimate the achievability (realizability) of determined intermediate extreme states. We suppose that the described sketch of the technique variant for such an analysis will find application to further studies on stability and retainability of partial equilibria.

The key premise consistent with the preliminary nature of subsequent reasoning is that the considered thermodynamic system is closed and, hence, does not comprise processes of matter and energy transit throughout the system. Such processes were discussed in Chapter 6 of *Equilibrium Encircling* (see Section 1.5).

The first stage of the analysis on achievability of the state x^{ext} should certainly entail checking its stability. To do this, first of all it is necessary for us to choose "suspicious" chemical reactions, ones whose rates may turn out to be high enough for the system to move in a short period of time by a considerable distance from the partial equilibrium determined by MEIS. Here one should take into account possible formation of active particles in the process of reaching x^{ext}, which can stimulate further conversions of substances. A list of "suspicious" reactions can be used sometimes for an aggregate description of the entire studied process from initial state y to reactions proceeding after the sought extreme point is passed.

Reactions can be written in the conventional kinetic form, i.e., with the help of derivatives of concentration with respect to time, or in thermodynamic form (1.88), (1.101), as when rates are represented as functions of thermodynamic potentials. In the latter case the check of conditions for coordination (1.93) and balancing (1.94), which can also be described by inequality (1.95), appears useful in the retainability analysis of the state x^{ext}.

If the rate of chosen reactions proves to be high enough, it can be concluded that the determined x^{ext} is not achievable or that it should be provided by some artificial means (the sharp decrease of process temperature at the required instant, selection of catalysts, etc.).

The kinetic analysis of the retainability of x^{ext} will be illustrated on two examples. Hexane isomerization, which was handled many times above in all its aspects, will be the first example. Let us turn again to Fig. 3.1. Suppose that only monomolecular reactions are possible at the point $x_2^{\text{ext}} = (0.075, 0.860, 0.065)$:

1) $x_1 \to x_3$,
2) $x_2 \to x_3$,
3) $x_2 \to x_1$.

---

[2] Here we use the word "retainability" to express the ability of extreme states to preserve over time—distinct from their ability to be reached at a variation of some conditions, i.e., stability.

TABLE 4.2. Methane pyrolysis at one volume percent of air at $T = 1273$ K and $P = 0.1$ MPa. Substance concentrations, mole/kg

				$x^{\text{ext}}_{C_2H_2}$	
Substance	Initial composition	Composition in 2 hours	Equilibrium composition	kinetic	thermodynamic
C_2H_2		**$3.637 \cdot 10^{-3}$**	**$4.898 \cdot 10^{-5}$**	**8.471**	**21.76**
C_2H_3		$1.353 \cdot 10^{-9}$	$1.248 \cdot 10^{-8}$	$9.901 \cdot 10^{-7}$	$9.332 \cdot 10^{-9}$
C_2H_4		$7.021 \cdot 10^{-6}$	$1.892 \cdot 10^{-4}$	$1.514 \cdot 10^{-2}$	$1.283 \cdot 10^{-4}$
C_2H_5		$1.535 \cdot 10^{-10}$	$1.013 \cdot 10^{-8}$	$1.052 \cdot 10^{-7}$	$6.225 \cdot 10^{-9}$
C_2H_6		$3.650 \cdot 10^{-6}$	$1.273 \cdot 10^{-5}$	$6.668 \cdot 10^{-3}$	$7.094 \cdot 10^{-6}$
CH_2		$6.749 \cdot 10^{-15}$	$7.322 \cdot 10^{-12}$	$3.934 \cdot 10^{-14}$	$6.038 \cdot 10^{-12}$
CH_3		$1.062 \cdot 10^{-5}$	$1.673 \cdot 10^{-5}$	$3.514 \cdot 10^{-4}$	$1.251 \cdot 10^{-5}$
CH_4	**61.07**	**0.9185**	**1.139**	**36.12**	**0.7719**
CO		$2.372 \cdot 10^{-2}$	0.2313	$3.092 \cdot 10^{-2}$	0.2318
CO_2	1.753E-4	$2.830 \cdot 10^{-5}$	$3.176 \cdot 10^{-6}$	$7.321 \cdot 10^{-3}$	$3.180 \cdot 10^{-6}$
H		$5.419 \cdot 10^{-5}$	$8.593 \cdot 10^{-5}$	$1.702 \cdot 10^{-5}$	$7.815 \cdot 10^{-5}$
H_2		**118.24**	**119.9**	**44.10**	**98.83**
H_2O		0.2104	$2.750 \cdot 10^{-3}$	0.1886	$2.265 \cdot 10^{-3}$
H_2O_2		$8.103 \cdot 10^{-19}$	0	$2.580 \cdot 10^{-16}$	0
HCO		$5.847 \cdot 10^{-7}$	$7.813 \cdot 10^{-10}$	$2.144 \cdot 10^{-7}$	$7.099 \cdot 10^{-10}$
O_2	0.1169	$1.481 \cdot 10^{-20}$	0	$1.417 \cdot 10^{-13}$	0
OH		$1.184 \cdot 10^{-9}$	$2.257 \cdot 10^{-11}$	$5.068 \cdot 10^{-10}$	$2.051 \cdot 10^{-11}$
C (cond.)		**60.12**	**59.70**	**7.924**	**16.55**

Note: The inert components x_{Ar} and x_{N_2} are not shown.

It is clear that the processes leading to an increase in concentration of the component x_2 cannot start from the point x_2^{ext}, since the Gibbs free energy increases in this case.

After obvious transformations of equation (1.101) the rate of the above stages (e.g., the third) will have the form

$$w_s = k\left(e^{-\frac{\mu_2^0}{RT}} e^{m_2} - e^{-\frac{\mu_1^0}{RT}} e^{m_1}\right).$$

Since the rate constants k of monomolecular reactions have an order of 10^{13}–10^{14} s^{-1} [135], it is easily seen that the numerical value of w_s is extraordinary high and hence, the state x_2^{ext} will be unstable (inretainable).

The methane pyrolysis process aimed at acetylene production, which was studied in [99], was taken as the second example. The calculation results of this process are presented in Table 4.2 and Fig. 4.10. The most important components are presented in the table in bold typeface.

The computational experiment was based on the formal kinetic description of 95 reactions with participation of 25 substances. The calculated partial equilibrium (the column "$x^{\text{ext}}_{C_2H_2}$ kinetic" in Table 4.2) can be interpreted to correspond to the extreme concentration of C_2H_2 at the existing kinetic constraints. The acetylene concentration in it turned out to be approximately 2.5 times lower than at the thermodynamically attainable state, where there are no kinetic constraints (the column "$x^{\text{ext}}_{C_2H_2}$ thermodynamic").

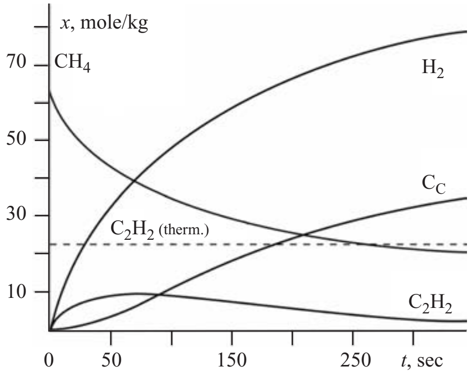


FIGURE 4.10. Calculation of methane pyrolysis.

Table 4.2 and Fig. 4.10 show that in this case, the extreme state displays retainability probably sufficient for extraction of the desired process product from the reactor. Approximately for a minute after the extremum point is reached, concentration of C_2H_2 does not vary essentially.

If an extreme state obtains for a noticeable amount of time, then it is necessary to evaluate its stability, to check the feasibility of a sharp decrease in retainability as a result of possible disturbances of the process or change of the extreme point position with the corresponding change in concentrations.

Strict physical and mathematical formulations of the problems to be solved are also complicated at the present time. Thus, the feasibility and expediency of describing these problems in terms of stability theory are far from obvious. Indeed, in traditional formulations of the problem where we are searching for global thermodynamic equilibrium in closed systems with equilibrium environment, we deal with Lyapunov functions tending to the stationary point (the point of system's stable equilibrium). All possible trajectories in the thermodynamic attainability region $D_t(y)$ are usually stable. It becomes senseless to apply criteria and methods to check this fact.

It may be apparently reasonable to employ a technique of the stability theory, but only when some nonthermodynamic factors that distinguish particular admissible directions of motion in $D_t(y)$ are taken into account. Such factors may include retardation of all possible physicochemical processes after the point x^{ext} is reached; or limitation of the reaction mechanism by several basic stages, as we presented in the above example of isomerization.

When we analyze the impact of disturbances on solutions obtained by MEIS, it seems most simple and logical to initially estimate sensitivity of these solutions. This may be the second step of the algorithm for determination of properties of the found extreme intermediate state.

At the first stage of this step, in turn, the presumably most dangerous disturbances for this specific case should be chosen (changes in the initial data of MEIS). Disturbances may occur due to deviations from the accepted initial values of the vector y, the environmental temperature and pressure, and other factors. Variations in the raw material quality (e.g., the composition of fuel burnt in boiler furnaces) is a typical reason for change in technological systems. In natural objects such changes can be caused by nonstationary meteorological conditions or unstable anthropogenic loads.

The sensitivity analysis for the selected disturbances can be most easily performed by variant calculations on MEIS, determining, for example, the functions $\Delta\, x^{\text{ext}} = f(\Delta y)$, where $\Delta\, x^{\text{ext}}$ and Δy denote changes in the values of the vectors x^{ext} and y with respect to the basic calculated variant.

In the sensitivity analysis the use of the thermodynamic tree may prove to be highly useful. Let us turn again to Fig. 3.1. It is easily seen how the optimal level of the Gibbs energy $G = G(x^{\text{ext}})$ changes as a function of $y$when searching for the maximum concentration of the third component (x_3^{ext}) of the reaction mixture. At $y = (1, 0, 0)^T$ (vertex 1) this level is equal to -424.118 kJ, and at $y = (0, 1, 0)^T$ (vertex 2) it is -425.678 kJ (Fig. 3.1*b*). The values of x_3^{ext} change correspondingly (Fig. 3.1*a*).

The last (third) step of the mentioned technique consists apparently in the stability analysis itself. Some preliminary considerations can also be applied to this analysis. For example, it is preferable to use the first (direct) Lyapunov method, since the type and properties of the studied functions are known to a considerable extent beforehand. However, more detailed representation of suppositions on the contents of the third step is premature yet. In order to exactly formulate the problem solved at this stage we need a sufficient experience in the study on properties of extreme partial equilibria.

In conclusion we note that, after the problem of estimating the properties of extreme states in closed systems is solved successfully (we look to the success), it is necessary to analyze specific features of MEIS-based solutions for open systems. These are, first of all, cases in which transit flows of energy make up an essential portion of the converted energy in the system, and where modeling of real open systems by closed ones can lead to significant errors. Here it is convenient to take advantage of the approach developed in Chapter 6 of *Equilibrium Encircling* [58] (see Section 1.5).

5
Application of Extreme Models

> Physicists always have a habit of taking the simplest example of any phenomenon and calling it "physics", leaving the more complicated examples to become the concern of other fields—say, of applied mathematics, electrical engineering, chemistry, or crystallography.
>
> *"The Feynman lectures on physics"*

5.1. Thermodynamics of Atmosphere

Objectives of Study

This section and, indeed, whole chapter are offered to illustrate the use of *extreme thermodynamic models* in applied problems, on the one hand, and to reveal the difficulties arising from such mpdel's application. We also consider methods eliminating these difficulties.

Capabilities of thermodynamic modeling can be shown by the detailed description of the inferences of modeling, explanation of their originality, formulation complexity without using thermodynamics principles, usefulness for understanding the studied process nature, and elaboration of measures for its improvement.

Presentation of the problems of applying these models implies disclosure of secrets of their construction regarding specific features of the object under study; description of computational experiments on their basis and application of other models in these experiments and information collected from different sources.

Why is it interesting to analyze air pollution processes to exemplify and illustrate the capabilities of extreme thermodynamic modeling? There are several reasons.

First of all, *chemical processes in the atmosphere proceed at low temperatures* in comparison with the majority of technological and many other natural processes. Except for photochemical transformations, they are also characterized by extremely low rates and do not reach a final equilibrium point (see Section 1.4). Live nature and harmful anthropogenic substances in the atmosphere are in partial equilibrium states. This helps explain the skepticism of many specialists concerning possible application of thermodynamics to atmospheric chemistry. In terms of development of applied thermodynamics and choice of models to study pollution of the atmosphere and the environment as a whole, it is highly important that we explain invalidity of such skepticism, doing so by using examples of problems that were earlier considered beyond the sphere of thermodynamic analysis.

The next reason to study the air pollution with the help of MEIS is associated with the *complexity of the atmosphere as a thermodynamic system*. "Complexity" in this case means both a great number of variables influence the values of thermodynamic functions, and the corresponding mathematical model is complex with respect to its construction, our analysis of its specific features, and the execution of numerical experiments on its basis.

The atmosphere is an open heterogeneous system that interacts with the nonequilibrium environment. It comprises a gas phase, as well as water droplets and aerosols (solid and liquid, anthropogenic and natural) [36, 166]. The latter can be pure condensed substances, but more often they have a heterogeneous spatially non-uniform structure, in particular, they are solutions on the surface of solid particles. Both gaseous and condensed matter of the atmosphere is distributed unevenly with respect to height (mainly due to decrease of air density with height) and on the horizontal plane (because of air flow).

The nonequilibrium nature of the environment is conditioned by the difference of temperatures between the aquatic and terrestrial surfaces and radiation (solar and reflected), and also by pressure variation in horizontal direction under the influence of heat and mass transfer.

The composition and spatial distribution of substances change in response to highly diverse physical forces, including chemical affinity, gravity, wind pressure, surface tension, electrical interactions, and others. The transfer processes of energy, substance, and charge that are caused by these forces are often characterized by pronounced irreversibility and have in some cases a clearly defined nonstationary character.

Successful qualitative and quantitative analysis of such a complex system as the atmosphere using rather simple models is surely the best demonstration of the competence and efficiency of thermodynamic idealization of a problem.

Unfortunately, this interest has also been generated by great *practical* significance of the problem. Air pollution is known to be a major part of the bigger problem of maintaining life on Earth.

Finally, this example is interesting because the anthropogenic impact on the atmosphere is the subject of very extensive studies on theoretical models and full-scale experiments. And though the results of these studies do not allow a unique assessment of the consequences of our current influence on nature, they provide rich material for the analysis of thermodynamic modeling results. The information obtained by nonthermodynamic models and measurements of real atmospheric states can be used to check correctness of thermodynamic methods for solving similar problems, and to set up schemes for their joint application with kinetic and hydrodynamic models in computational experiments.

We will address three particular problems within the general problem of atmosphere thermodynamics: 1) assessment of the limiting concentrations of water vapor; 2) determination of relationships between concentrations of primary and secondary pollutants; 3) determination of distribution of harmful substances in a vertical air column.

Assessment of Limiting Concentrations of Water Vapor

As distinct from the two following problems and most of the problems on atmospheric chemistry, this one is traditionally described in terms of thermodynamics. The section entitled "Humid Air" is commonly included in manuals on technical thermodynamics and heat engineering (see, for example, [114]). However, the air humidity dependence on temperature and enthalpy is analyzed in them on the basis of the simplest relations assuming that pressure is constant and there is no impact of microcomponents contained in the atmosphere on concentration and phase state of water.

MEIS-based studies for different combinations of T and P have shown first of all the correctness of the applied mathematical descriptions. Discrepancy between the results by the known L.K. Ramzin's Id-diagram (enthalpy vs. moisture content) and the data of full-scale measurements in [25] was no more than 0.5%. A variant of calculations is given in Table 5.1.

Note that the calculations were performed on the model of the ideal gas phase. In this case the parameters of the modeled system at the points located on the curve of phase transitions (gas-to-liquid) were determined with high accuracy. Though such an excellent result of calculations is easily explained by the very low partial pressure of saturated water vapor, the considered fact expands our understanding of the capabilities of ideal models (with a logarithmic nature of change in the values of thermodynamic functions at deviation of parameters from the standard values). For comparison the last column of the table contains the results of similar calculations regarding the real sizes of water droplets, i.e., regarding the surface tension for the condensed phase. The value of $x^{\text{eq}}_{\text{H}_2\text{O(c)}}$ in the example is seen to change considerably (by 4.6%), and this should be borne in mind in the analysis of atmospheric processes.

TABLE 5.1. Calculation of the limiting concentration of water vapor in the atmosphere ($T = 293.15$ K, $P = 98.0$ kPa)

	State, mole		
Substance	y	$x^{\text{eq}}(r_{\text{H}_2\text{O}} \to \infty)$	$x^{\text{eq}}(r_{\text{H}_2\text{O}} = 0.1\ \mu\text{m})$
Ar	0.93	0.93	0.93
N_2	78.08	78.08	78.08
O_2	20.95	20.95	20.95
CO_2	0.03	0.03	0.03
NO	0.00	$1.0 \cdot 10^{-14}$	$1.0{\cdot}10^{-14}$
NO_2	0.00	$1.0{\cdot}10^{-8}$	$1.0{\cdot}10^{-8}$
$H_2O_{(g)}$	0.00	2.35	2.38
$H_2O_{(c)}$	3.00	0.65	0.62

Practical significance of the problem of searching for $x^{\text{eq}}_{\text{H}_2\text{O(g)}}$ is dictated by the fact that only its solution will make it possible to determine conditions for forming fogs, smog, and acid rain [133]. A lot of harmful substances are formed in water solutions, namely on the surface of aerosols, rain droplets, haze and fog [36, 159]. Thermodynamic modeling allows estimation of the impact of anthropogenic change in chemical composition of the atmosphere in industrial centers on water film formation around aerosols, mist formation, composition of rudimentary germ drops, content of secondary pollutants in them, and, finally, air quality and climate of a city. It should be stressed that drops of fog and clouds appearing at humidity close to 100% are usually very diluted solutions and the effect of solution composition and drop radius on the maximum content of water vapor above them is on the whole negligible [15, 36]. The flooding of aerosols is known to start at relative humidity (f) equal to around 30% and to lead to variation in the optical characteristics of the atmosphere. On the average haze appears at a relative humidity of about 80% [179]. Haze drops are just a diluted solution of electrolytes, however, the solution composition still influences essentially a condensation process. Therefore, the calculated composition of a haze droplet is given as an example. Table 5.2 gives an indication of the possible "harmfulness" of solution. Its data were obtained on the basis of high idealization of real phenomena. The sorption processes, for example, were not dealt with at all. The action of surface tension forces was taken into consideration approximately, i.e., by making adjustments calculated for the fixed radii of particles. The calculation results are given for both the condensed phase evenly distributed in some volume of the atmosphere ($r \to \infty$) and drops with the radius $r = 0.1\,\mu\text{m}$ (10^{-7} m). Since the available model describes in principle only diluted solutions, changes in the surface tension are considered solely for water.

However, despite some simplifications the model of liquid phase aerosol qualitatively correctly simulates the processes of equilibrium heterogeneous condensation in the real atmosphere [119].

In particular, change in the concentration of electrolyte solution with decrease in the relative humidity of air is determined within a sufficient range of accuracy (Fig. 5.1). The results for different initial compositions (0.5 of AQS[1] NO_2 and 5

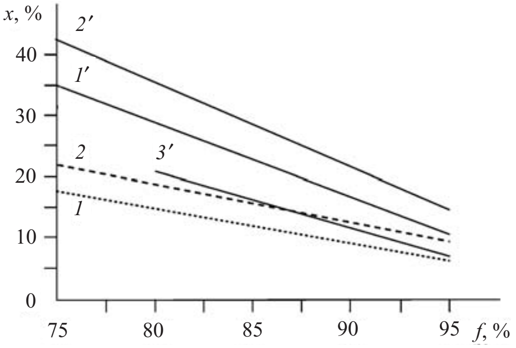


FIGURE 5.1. Change in the total concentration of ions in a drop with an increase of relative humidity ($T = 298$ K). 1, 2 – calculation results, 1′, 2′, and 3′ – published data.

TABLE 5.2. Modeling results of the liquid phase aerosol in the atmosphere ($T = 298$K, $f = 99\%$, $P = 1$ atm)

Substance	$G_0(r \to \infty)$, J/mole,	y, mole/kg	$x^{eq}(r_{H_2O} \to \infty)$, mole/kg	$x^{eq}(r_{H_2O} = 0.1\mu m)$, mole/kg
		Gas phase		
HNO_3	−213410	$5.11{\cdot}10^{-8}$	$7.22{\cdot}10^{-12}$	$5.83{\cdot}10^{-12}$
H_2O_2	−205732	$6.55{\cdot}10^{-9}$	$4.35{\cdot}10^{-16}$	$1.16{\cdot}10^{-16}$
O_3	70613.5	$1.42{\cdot}10^{-6}$	0.0	0.0
O_2	−61110	7.18	7.16	7.16
NO_2	−37345.4	$4.58{\cdot}10^{-7}$	$1.44{\cdot}10^{-11}$	$3.89{\cdot}10^{-12}$
NO	28486.8	$6.06{\cdot}10^{-12}$	$4.62{\cdot}10^{-10}$	$1.24{\cdot}10^{-12}$
N_2O_5	−92682	$2.91{\cdot}10^{-10}$	0.0	0.0
HNO_2	−154133	$7.88{\cdot}10^{-13}$	$1.16{\cdot}10^{-10}$	$3.11{\cdot}10^{-11}$
CO	−169407	$7.11{\cdot}10^{-6}$	0.0	0.0
H_2	−38904.9	$1.96{\cdot}10^{-5}$	0.0	0.0
N_2	−57071.6	26.7	26.7	26.7
H_2O	−298051	1.03	1.04	1.04
CH_4	−130107	$6.13{\cdot}10^{-3}$	$1.28{\cdot}10^{-17}$	$3.44{\cdot}10^{-18}$
CO_2	−457182	$1.19{\cdot}10^{-2}$	$1.80{\cdot}10^{-2}$	$1.80{\cdot}10^{-2}$
C_2H_4	−12921.6	$1.74{\cdot}10^{-9}$	0.0	0.0
C_3H_6	−59130.2	$1.87{\cdot}10^{-9}$	0.0	0.0
SO_2	−370743	$6.55{\cdot}10^{-7}$	$4.64{\cdot}10^{-12}$	$1.25{\cdot}10^{-9}$
CH_3Cl	−151824	$3.50{\cdot}10^{-7}$	0.0	0.0
HCl	−147978	0.0	$2.05{\cdot}10^{-8}$	$1.41{\cdot}10^{-9}$
		Solution		
$H_2\,O_{(c)}$	−306714	$3.50{\cdot}10^{-5}$	$5.16{\cdot}10^{-4}$	$1.45{\cdot}10^{-4}$
$H^+NO_3^-$	−243873	$3.50{\cdot}10^{-14}$	$1.25{\cdot}10^{-7}$	$1.36{\cdot}10^{-7}$
$H^+HCO_3^-$	−713359	$3.50{\cdot}10^{-14}$	$1.28{\cdot}10^{-7}$	$3.44{\cdot}10^{-8}$
$H_2^+SO_4^-$	−1800384	$3.50{\cdot}10^{-14}$	$6.55{\cdot}10^{-7}$	$6.55{\cdot}10^{-7}$
$H^+\,Cl^-$	−177537	$3.50{\cdot}10^{-14}$	$3.30{\cdot}10^{-7}$	$3.49{\cdot}10^{-7}$
M, kg	—	0.0286	0.0286	0.0286
G, J	—	−66641.1	−66782.3	−66782.3
Ionic strength	—	—	$2.74{\cdot}10^{-1}$	$9.48{\cdot}10^{-1}$

of AQS of NO_2 at a gas phase) that were obtained by the authors on the model of solutions are under 1 and 2; the curves 1′, 2′, 3′ [119] are the published data for different compositions of components of the liquid-phase aerosol, respectively for the background conditions, polluted atmosphere and laboratory model representing a mixture of dry air and NaCl solution.

As distinct from other models, thermodynamic modeling makes it possible to vary a composition of gaseous pollutants and components of the electrolyte solution over a wide range. As a result the relationship between concentrations of different solution components, the limiting content of water vapor directly in the drop vicinity, and correspondingly the drop sizes can be determined. Besides, it becomes

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[1] Here the value of the Russian national air quality standard (AQS) is used as a unit of concentration

feasible to study the effect of the initial concentration of gaseous pollutants on solution composition as well as absorptive capacities of drops with different radii.

The thermodynamic models of change in air humidity are to be applied to the study of atmospheric pollution processes and to calculate air conditioning systems and different-purpose drying installations. In this case, unlike the use of diagrams, we can vary parameters of air composition or drying agent (the latter may contain products of fuel combustion). The topicality of thermodynamic modeling of air exchange in buildings was shown in Section 3.4.

Analysis of Secondary Atmospheric Pollution

This problem refers to the "illicit" sphere of thermodynamics application, since in the final equilibrium state the concentrations of the majority of known pollutants turn out to be some orders of magnitude lower than the admissible ones and are practically equal to zero, which does not correspond to reality.

Solving the problem requires that we overcome certain numerical difficulties. One of them, i.e., a wide scatter in the values of sought parameters, was discussed in Section 4.3. Another one consists in a great number of primary and secondary pollutants and dependence of their conversion reactions in the atmosphere on several factors (temperature, air pressure and humidity, solar radiation, etc.). Determination of dependences in formation of many pollutants on different parameters naturally gives rise to the problem of reducing the number of calculation variants, i.e., the problem of conducting computational experiments. Therefore, the secondary pollution problem should be discussed starting with the technique of studies to be performed.

Its basic point is certainly the choice of an initial thermodynamic model. In this case a closed spatially uniform heterogeneous system with a fixed initial composition of reagents that interacts with the environment at the constant T and P was considered. The premise on the system closedness is equivalent to the assumption that all processes manage to reach the states of partial or complete equilibria. The spatial uniformity means that surface tension forces at phase transitions are neglected. Assumption of constant temperature and pressure limits the analysis to a ground layer of the atmosphere, whose pollution is the most dangerous for nature and humans. With these assumptions made the mathematical formulation of the problem is apparently reduced to the simplest MEIS modification, i.e., (2.38)–(2.42).

A natural way to decrease the volume of computational experiments is to make a small number of calculations of some typical states and to extend their results to other possible states based on the simplest analytical dependences. Such dependences can be determined from the fact that since the atmosphere is an oxidizing medium, the danger of primary emissions in terms of secondary pollution of the atmosphere is caused to a considerable extent by their reactivity in oxidization processes. Indeed, the energy necessary to drive the reaction of secondary pollutant formation may come only from the reactions of primary pollutant oxidation. As far as we consider the system with the constant T and P, the concentration of the jth secondary pollutant changes directly as a function of change in *Gibbs energy surface shape of the system* (ΔG) due to increase (decrease) in concentration of the pth primary pollutant.

It can be admitted that

$$\Delta G = \Delta G_p^{\mathrm{ox}}, \tag{5.1}$$

where ΔG_p^{ox} is the Gibbs energy change in the oxidization reaction of the pth component; then

$$\Delta G_p^{\mathrm{ox}} = \alpha G_{pO} - \beta G_p - \gamma G_O, \tag{5.2}$$

where α, β and γ are stoichiometric coefficients; the indices pO, p, and O at the values of G refer to the oxidization product, pollutant, and oxygen, respectively.

Since the absolute values and the increases in pollutant concentrations are very small quantities, the following expression seems admissible:

$$x_j^{\mathrm{ext}} - x_j^b = \frac{\Delta G_p^{\mathrm{ox}}}{\left(\partial G_p^{\mathrm{ox}} / \partial x_j^b\right)}, \tag{5.3}$$

where x_j^b is the extreme concentration of the jth secondary pollutant in the background (conventionally clean) atmosphere.

Assuming that the reacting gases are ideal, we have

$$\frac{\partial G_p^{\mathrm{ox}}}{\partial x_j^b} = G_j^0 + RT \ln x_j^b - RT \ln \sigma \approx a' + RT \ln x_j^b, \tag{5.4}$$

since the total quantity of moles σ in the atmosphere is virtually constant.

As the value of x_j^b is given, then

$$x_j^{\mathrm{ext}} - x_j^b = a \Delta G_p^{\mathrm{ox}}. \tag{5.5}$$

The letter a in (5.4), (5.5) and elsewhere in this section denotes constant coefficients.

To interpret relation (5.5) graphically let us consider an idealized system in which the initial reagents are monatomic gases and the reactions result in formation of the monoxide of primary pollutant and the monoxide representing a secondary pollutant. For this system $x = (x_{\mathrm{O}}, x_p, x_j, x_{p\mathrm{O}}, x_{pj})^T$ and $y = (y_{\mathrm{O}}, y_p, y_j)^T$. It is easy to apply, because it does not depend on the choice of primary pollutant (p), oxidized component (j) and secondary pollutant (*pj*), and therefore the material balance polyhedron $D(y)$ does not change and the concentration $x_{pj} = x_{j\mathrm{O}}$ is determined only by the thermodynamic properties of the components.

Figure 5.2 represents a two-dimensional face of $D\,(y)$ whose vertices correspond to the initial mixture composition and the maximum concentrations of oxides of the primary ($x_{p\mathrm{O}}^{\mathrm{mat}}$) and the secondary ($x_{j\mathrm{O}}^{\mathrm{mat}}$) pollutants. Two surfaces of the Gibbs energy are put over the plane $y - x_{p\mathrm{O}} - x_{j\mathrm{O}}$. The upper surface (the index s) refers to the system with a low oxidizing capacity of the primary pollutant and the lower surface (the index l)—refers to the system with a large value of ΔG_p^{ox}.

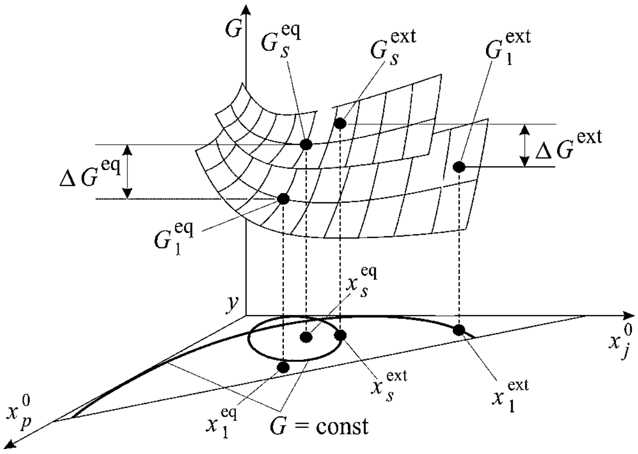

FIGURE 5.2. Graphical interpretation of atmosphere's sensitivity versus oxidizing capacity of the primary pollutant.

Fig. 5.2 shows that moving along the trajectory $y - x_{jOl}^{\mathrm{ext}}$ we approach closer the vertex x_{jo} and hence, achieve a much higher concentration of the secondary pollutant than when moving along the trajectory $y - x_{jOs}^{\mathrm{ext}}$.

However, relation (5.5) is difficult enough to apply to computational experiments despite its simplicity, since

$$\Delta G_p^{\mathrm{ox}} = f\left(A_p^{\mathrm{ox}}, \ln x_1, \ldots, \ln x_n\right),$$

where A_p^{ox} is the standard chemical affinity of the oxidation reaction for the pth pollutant. Hence, it is desirable to pass from ΔG_p^{ox} to another function that does not depend on the partial pressures of the reaction mixture components. *Enthalpy* is such a function for ideal gases. Its application in this case proves to be convenient, because at temperatures of Earth's atmosphere, $H_j \gg \mathrm{TS}_j$, and it can be admitted that

$$\Delta G_p^{\mathrm{ox}} = \Delta H_p^{\mathrm{ox}} - \Delta\,(TS)_p^{\mathrm{ox}} \approx \Delta H_p^{\mathrm{ox}}. \tag{5.6}$$

Therefore, we can pass from (5.5) to the expression

$$x_j^{\mathrm{ext}} - x_j^b = \alpha \Delta H_p^{\mathrm{ox}}. \tag{5.7}$$

Application of equation (5.7) sharply decreases the volumes of thermodynamic calculations. In essence it is necessary to calculate the values of extreme concentrations of secondary pollutants in the background atmosphere (x_j^b) by MEIS and to determine the coefficients α based on several calculations.

Some results of computational experiments that are obtained using the linear dependence (5.7) are presented in Figs. 5.3 and 5.4. The values

$$r_{pj} = \frac{x_{pj}^{\mathrm{ext}} - x_j^b}{x_j^b} = \frac{\Delta x_{pj}}{x_j^b}, \tag{5.8}$$

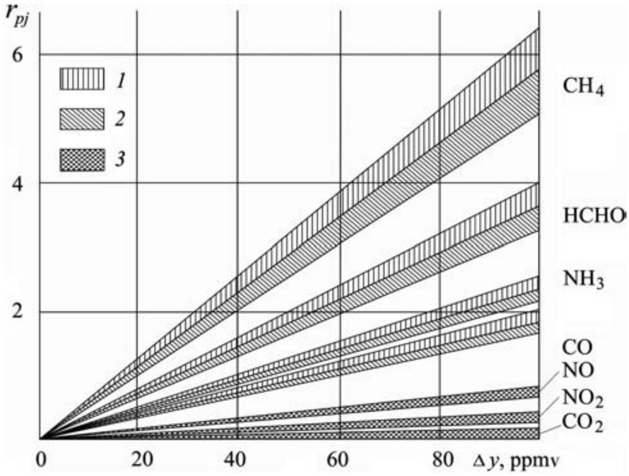

FIGURE 5.3. Relative responses of the atmosphere to emission of particular pollutants (the pollutants are denoted on the right). Secondary pollutants:
1—organic, 2—inorganic, 3—organic and inorganic.

are plotted along the vertical axis in dimensionless units in Fig. 5.3 and can be interpreted as the environmental responses to emissions of the pth pollutant. Figure 5.4 presents the dependence on ΔH_p^{ox} of the value

$$K_{pj} = \frac{\Delta x_{pj}}{y_p} = \frac{r_{pj} x_j^b}{y_p} \tag{5.9}$$

which characterizes the atmosphere's sensitivity to the pth pollutant.

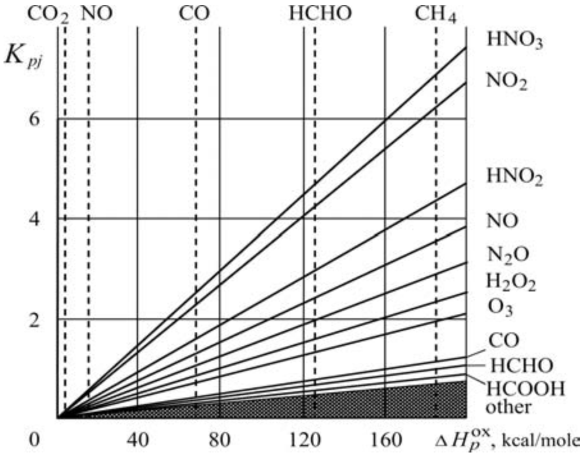

FIGURE 5.4. Coefficients of chemical sensitivity of the atmosphere versus the oxidation heat of primary pollutant.

Figures 5.3 and 5.4 show the effect of oxidation heat of primary pollutants on the secondary pollution of the atmosphere. The highest values of the coefficients K are typical of methane. The conclusions drawn from the thermodynamic analysis on the higher sensitivity of the atmosphere to hydrocarbon emission are in good agreement with the results of kinetic and experimental studies [12, 163, 164, 169].

The danger of secondary environmental pollution is determined both by the relations $\Delta x_{pj}/y_p$ and the relationships between the toxicity of the jth and pth substances. Hence, it does make sense to characterize every primary pollutant by the individual (D_{pj}) and integral (D_p) coefficients of environmental danger:

$$D_{pj} = \frac{\Delta x_{pj}/\mathrm{AQS}_j}{y_p/\mathrm{AQS}_p}, \tag{5.10}$$

$$D_p = \frac{\sum\limits_{j=1}^{n} \left(\Delta x_{pj}/\mathrm{AQS}_j\right)}{n\left(y_p/\mathrm{AQS}_p\right)}, \tag{5.11}$$

where AQS_j and AQS_p are the limiting guideline concentrations of the jth and pth substances; and n is the number of considered secondary pollutants.

The coefficients D_{pj} and D_p show how much the formation of the jth secondary pollutant (or the sum of pollutant in the case of D_p) in the atmosphere is more dangerous than that of the initial pth substance. At $D_{pj} > 1$ and $D_p > 1$ the products of transformation processes in the atmosphere are more dangerous than the initial reagents. It is obvious that for the case of emission of several primary pollutants the denominators of formulas (5.10) and (5.11) should contain the sums of their concentrations. Thus, the indices D_{pj} and D_p can characterize in full measure a risk of the secondary pollution of the atmosphere with anthropogenic emissions.

Table 5.3 presents the results of calculating D_{pj} for the most typical components in the energy-related emissions: methane (CH_4), carbon monoxide (CO), formaldehyde (HCOH), nitrogen monoxide (NO) and ammonia (NH_3). The table shows that in many cases the products formed can be more hazardous than the initial substances ($D_{pj} \gg 1$). This pertains first of all to methane emissions. Special attention should be paid to the risk of secondary atmospheric pollution by benzpyrene, ozone, and prussic acid. Even with an error in determination of D_{pj} one or two orders of magnitude, the conclusions drawn are invariable.

Among other things, the results of the presented thermodynamic analysis can be used to specify the directions that the experimental and numerical kinetic studies may take. Kinetics and experiments in turn can help in the formulation of constraints for the further thermodynamic modeling of harmful emission behavior in the atmosphere.

Distribution of Harmful Substances in a Vertical Air Column

Solution to this problem has already been dealt with in Section 2.3 as an illustration of one possible application of MEIS for spatially nonuniform structures. Therefore, here we will limit ourselves to several remarks only.

Table 5.3. Average values of the coefficient of additional environmental hazard due to energy-related emissions (D_{pj})

Secondary pollutant		Primary emissions				
		CH_4	CO	HCHO	NO	NH_3
Ozone	O_3	13000	280	13	300	180
Carbon monoxide	CO	34	0.8	0.5	0	0.5
Hydrogen peroxide	H_2O_2	1200	20	1.3	33	13
Nitrogen oxide	NO	100	2.2	0.1	1.2	1.5
Nitrogen dioxide	NO_2	2500	36	2.3	47	13
Dinitrogen oxide	N_2O	450	8.6	0.4	7.0	7.5
Ammonia	NH_3	30	0.5	0	0.5	0.6
Nitric acid	HNO_3	1100	37	1.1	22	9.4
Prussic acid	HCN	1100	28	1.3	37	14
Hydrazine	N_2H_4	4300	46	5.1	63	47
Formaldehyde	HCOH	810	18	0.9	17	8.3
Formic acid	HCOOH	630	19	0.6	17	8.9
Acetaldehyde	CH_3COH	40	0.8	10	1.0	0.5
Acetic acid	CH_3COOH	56	1.3	0.1	1.0	0.7
Ethylene	C_2H_4	1.7	0	0	0.1	0
Butadiene-1,3	C_4H_6	1.0	0	0	0	0
Acetone	CH_3COCH_3	0.7	0	0	0	0
Methanol	CH_3OH	63	0.5	0.1	1.2	1.0
Benzene	C_6H_6	4.7	0.1	0	0.1	0
Toluene	$CH_3C_6H_5$	1.4	0	0	0	0
Phenol	C_6H_5OH	240	3.6	0.3	5.2	1.2
Ethyl benzene	$C_6H_5C_2H_5$	1.1	0	0	0	0
Pyridine	C_5H_5N	18	0.3	0	0.4	0.1
Ethylamine	C_2H_5N	8	0.1	0.1	0.1	0.1
Naphthalene	$C_{10}H_8$	0	0	0	0.1	0
Phenanthrene	$C_{14}H_{10}$	0.5	1.2	0.1	0.8	0.3
Benzpyrene	$C_{20}H_{12}$	150000	3600	210	3200	1900

The first of them elucidates the given problem in the literature. The data that are theoretically justified by the Boltzmann distribution and confirmed experimentally concern only basic macrocomponents of the atmosphere (N_2, O_2, Ar, CO_2). The theoretical analysis was limited to consideration of the only force—gravity. Distribution of microcomponents was studied solely for individual substances, for example ozone, whose concentrations in the upper and lower atmospheric layers have different effects on the environmental state.

The general model for distribution of gaseous microcomponents and aerosols in the vertical air column with an account for their chemical transformations and phase transitions and the effects of different forces is certainly interesting from both the theoretical and applied standpoints. Of special concern is a nonisothermal model of the atmosphere that would help us study formation of cloudy and aerosol layers in the stratosphere, where processes are relatively stable in comparison to the lower layers. The concentration of pollutants in lower layers is determined primarily by the intensity of turbulent motion of a different scale. In the last decade the problems of possible human-induced impact on the global climate has become extremely topical. An important aspect of the problem is to assess a role of the troposphere and stratospheric aerosol in the processes of scatter and reflection of short- and long-wave radiation and also condensation, i.e., formation of the cloud cover [1]. The most difficult problem here is determining the contribution of anthropogenic particles or the indirect human-induced effect on aerosol formation and transfer and on atmospheric chemistry in general [11]. The thermodynamic model of the vertical air column would possibly assist in revealing some laws concerning specific features in formation of the aerosol layers regarding their dispersion and chemical composition.

Depending on the objectives of the study, the thermodynamic modeling can examine different column heights at different steps in the vertical plane. Variation of the sizes and structure of cells in the modeled system provides an idea of both distribution of harmful substances in the ground layer of the atmosphere (under certain conditions) and processes extending over the whole column of the troposphere and even in the middle atmosphere.

It was shown in [92] that MEIS for spatially inhomogeneous structures could be applied to the analysis of substance distribution over the horizontal plane as well. In this case, terrain relief and other factors can be taken into consideration.

Application of spatial thermodynamic models in combination with models of chemical kinetics and *transfer* (motion induced by pressure drop, molecular and turbulent diffusion, heat exchange) proves to be the most effective. Increase in the number of quite different models to describe one and the same system we may suppose will give a deeper insight into the processes occurring in that system and lead to accurate forecasting of processes' results.

5.2. Thermodynamics of Combustion

Introductory Notes

Unlike atmospheric chemistry, the chemistry of combustion was not a forbidden area for thermodynamic analysis. As was mentioned in the Introduction (Section I.23), the main features of hydrogen combustion thermodynamics were discovered by D. Gibbs. Now the thermodynamic interpretations of oxidation of the main combustible components in fossil fuel are clear. However, currently, environmental characteristics of furnaces and combustion chambers are studied almost solely by kinetic models and full-scale experiments. And the necessity for thermodynamic methods to penetrate into this sphere of studies has yet to be demonstrated. In this section of the book the authors make one more attempt (the previous ones are presented, e.g., in [50, 80, 81]) to explain a certain technique of using thermodynamic models and reveal the model's effectiveness for the analysis of harmful substances formed at fuel burning.

In terms of revealing the capabilities of thermodynamics, the processes of both combustion and atmospheric pollution are highly interesting because of their complexity and great practical significance. Besides, the available abundant data on release of pollutants during fuel burning allows the estimation of thermodynamic modeling accuracy and facilitates elaboration of algorithms of joint application of the kinetic and thermodynamic models and full-scale experiments to study physicochemical processes. We now describe the factors determining the scientific significance of combustion thermodynamics in greater detail.

Fuel is burnt in open systems with a nonequilibrium environment. Mass is exchanged with the latter by flows of fuel, air (oxidant), recirculating and flue gases, slag, and ash of different temperature. As a rule these systems are heterogeneous. Heterogeneity proves to be highest at solid fuel combustion, first among these being coals that consist of both organic and diverse mineral matter. Reactions with participation of the mineral part of fuel can result in formation of gaseous and condensed compounds. The number of reaction mixture components may reach many hundreds. Design of a combustion appliance and the arrangement of fuel burning in it stipulate both chemical and other interactions: mechanical, thermal, gravitational, electrical and electromagnetic, and radiative.

Periodic processes of fuel combustion at small boiler plants and furnaces are not steady. However, insteadiness is most typical of operation of transport engines. A revelation of the specific features of such complex real objects by comparatively simple models of equilibria seems highly instructive to the task of mastering the art of thermodynamic modeling.

The practical importance of environmental analysis of fuel combustion processes, it being a key source of pollution in nature, requires no comment. Thermodynamics, however, allows both estimation of the potential negative impact of production installations on the environment and determination of the factors influencing the reliability and security of equipment operation. Thermodynamic studies on slag formation at water pipes of furnaces, as well as sulfuric acid corrosion of the rear heating surfaces of boiler units, are examples of problems related to the reliability problem. We may recall the practical significance of such traditional thermodynamic analysis applied in the energy sector for determining specific fuel consumption for production processes.

Combustion is a better illustration than atmospheric pollution, when we tend to compare thermodynamic models to kitetic models and full-scale experiments. In human-organized processes as compared to natural ones, it is much easier to determine initial system state, conditions of interaction with the environment, and possible ranges of initial data variation. When we study atmospheric pollution it turns out to be rather difficult to estimate composition prior to anthropogenic impacts and the extent of these impacts (emissions of harmful substances). It is extremely difficult to take into account the effect of infinitely diverse natural factors (solar radiation, air flows, mass exchange with water and ground surfaces, etc.) on all the microcomponents present in the atmosphere.

A wide experience has been gained by now on MEIS application to the analysis of combustion processes for different types of coals, heavy oil, gas, production waste, designs of boiler furnaces and stoves, and furnace regimes. Environmental characteristics of energy and public utility installations for fuel combustion have been studied to the greatest extent [50, 81, 138]. Nonequilibrium plasma ignition and lightening of pulverized-coal torches have been also analyzed.

Here we will dwell on only two problems: 1) analysis of nitrogen oxide formation at coal combustion; and 2) study of the environmental characteristics of periodic processes of solid fuel combustion at small boiler plants and stoves.

Theoretically interesting issues of MEIS application to the study of nonequilibrium plasma processes are considered briefly in the next section.

Thermodynamic Modeling of Nitrogen Oxides Formation in Coal Furnaces

The processes of NO_x formation at fuel combustion have long been the subject of systematic studies for many specialists in different countries [48, 147, 165, 169, 176]. Such studies resulted in accumulation of a wide range of experimental data. There are theoretical achievements and practical recommendations, and many of them have already been implemented. However, many problems call for further investigation in this sphere. They are, for example, raising the efficiency of technologies for NO_x emission reduction, evaluation of the potential for improving these technologies, prevention from formation of other harmful substances due to NO_x suppression, and so on.

MEIS was used for the thermodynamic analysis of forming thermal, fuel, and prompt nitrogen oxides [2] at coal combustion [50, 81]. The analysis was made on the Kansk–Achinsk coal of the Irsha–Borodinsk deposit. The conventional chemical formula for the organic mass of this coal has the form: $CH_{0.833}O_{0.233}N_{0.012}S_{0.002}$. The greatest efforts were made to study dependences of the NO_x concentration on a) thermodynamic parameters, b) the composition of the reaction mixture, c) the process mechanism, and d) conditions of energy and mass exchange.

In the analysis the general MEIS was the basis for constructing models representing a real combustion process in sufficient detail and those employing utmost idealization of the mechanism of chemical reactions. The most detailed model comprised 200 components formed by 12 chemical elements. Coal's organic and mineral parts were presented. The vector x included 50 gaseous and condensed nitrogen compounds along with sulfur compounds, hydrocarbons, heavy metals, and other substances. Studies on reaction mixtures with such a wide composition of substances by kinetic modeling gives rise to many difficulties.

The results of calculation of equilibrium concentrations of nitrogen compounds (at the point x^{eq}) with the *air excess* coefficient[3] $\alpha_{air} = 1.2$ obtained by the detailed model are presented in Fig. 5.5. Nitrogen monoxide (NO) prevails among these compounds, which agrees with experimental data. Figure 5.6 illustrates

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[2] Thermal oxides are formed at fuel burning from atmospheric nitrogen and oxygen. Fuel oxides are the result of oxidation of nitrogen-containing compounds of coal. Prompt oxides are formed from atmospheric nitrogen as a result of its interaction with active species emerging at thermal destruction of the organic part of fuel.

[3] The ratio between the available air and the stoichiometrically needed amount of it.

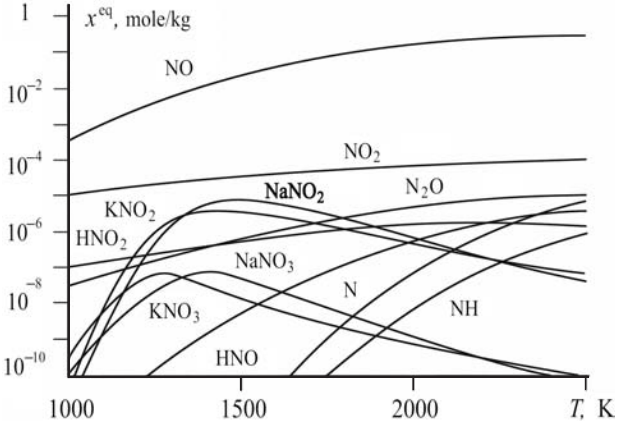


FIGURE 5.5. Equilibrium concentrations of nitrogen compounds in the products of the Kansk–Achinsk coal combustion ($\alpha_{air} = 1.2$).

dependences $x_{NO} = f(T)$ and $x_{NO} = \varphi(\alpha_{air})$. The figure shows a strong effect of temperature on the NO concentration and a sharp change of NO amount at the instant when the value of α_{air} exceeds unity (i.e., at a transition from the reductive to the oxidative medium). Figure 5.7 illustrates the interrelation between concentrations of NO and another dangerous pollutant—carbon monoxide (CO). The detailed model allowed the increasing yield of other incomplete combustion products to be determined at NO suppression; many of these are environmentally more hazardous than NO.

Now we will successively discuss the technique and the results of modeling the formation of thermal, fuel, and prompt NO_x.

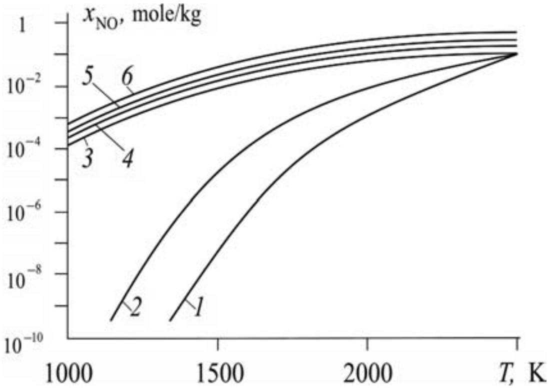


FIGURE 5.6. The equilibrium yield of NO versus combustion temperature and air excess α_{air} : 1, 0.95; 2, 1.00; 3, 1.05; 4, 1.10; 5, 1.20; 6, 1.40.

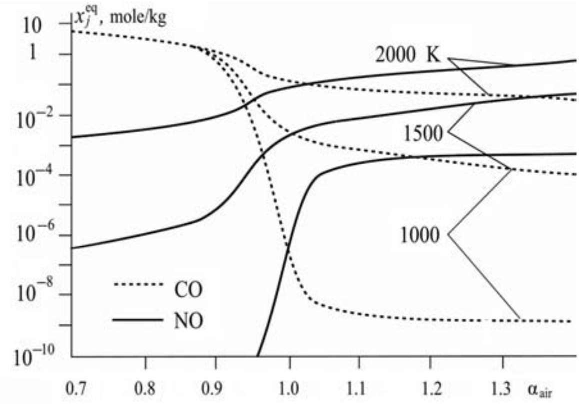


FIGURE 5.7. Equilibrium concentrations of NO and CO versus the air excess α_{air} at different combustion temperatures.

The fundamental laws in formation of thermal oxides were revealed with idealized models corresponding to the simplest systems of reagents:

$$[O_2, N_2] \rightarrow [O_2, N_2, O, N, NO], \tag{5.12}$$

$$[C_c, O_2, N_2] \rightarrow [C_c, O_2, N_2, CO_2, O, N, NO, CO], \tag{5.13}$$

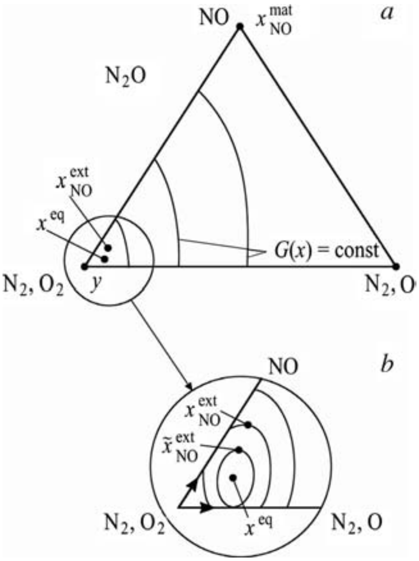
$$[CO_2, O_2, N_2] \rightarrow [C_c, O_2, N_2, CO_2, O, N, NO, CO], \tag{5.14}$$

where the initial reagents (vector y) are given in the left-hand side brackets and the total compositions of the reaction mixture (vector x) are in the right-hand side brackets.

The simplest system (5.12) allows one to abstract from the reactions of fuel burning and study a pure process of molecular nitrogen oxidation at T and P typical of these reactions. System (5.13) reflects the key specific features of N_2 oxidation in the real coal-burning process. System (5.14) corresponds to Ya.B. Zeldovich's theory [173, 175] on the thermal nature of NO formation reactions at burning and explosion. According to this theory the difference in reaction rates causes formation of thermal oxides after the organic coal mass oxidation is completed. This system offers a better explanation of the available experimental data on the thermal NO_x formation than the two preceding ones.

The results of analysis for system (5.12) are illustrated in Fig. 5.8*a* and *b*. It presents the face $N_2, O_2(y) - NO - N_2, O$ of the material balance polyhedron $D(y)$ (Fig. 5.8a) and its small part adjacent to vertex y (Fig. 5.8*b*). The vertex NO corresponds to the state x_{NO}^{mat}. From Fig. 5.8*b* it is seen that thermodynamics assumes a concentration of x_{NO}^{ext} that is somewhat higher than the equilibrium x_{NO}^{eq}. The extent of the excess depends on equilibrium location. The highest value of x_{NO} is reached when moving along $y - NO$ to the point with a minimum value of $G(x)$ at this edge (the thermodynamic "pothole") and then along the curve $G(x) = \text{const}$. The calculations have shown that superequilibrium concentrations of NO can take

FIGURE 5.8. To the thermodynamic analysis of NO formation in the system [O_2, N_2, O, NO] $T = 2000$ K, $P = 0.1$ MPa.



place only starting with $T = 1600$ K and the difference ($x^{ext}_{NO} - x^{eq}_{NO}$) increases with the temperature rise. However, even at $T = 2000$ K this concentration still remains rather low (about 28%, Table 5.4). The thermodynamic attainability region $D_t\,(y)$ for system (5.12) is extremely small. The system enthalpies at the states x^{eq} and x^{ext} are approximately the same. But the inequalities $H\left(x^{ext}\right) > H\,(x^{eq}) > H\,(y)$ are observed, i.e., for the process to be realized a small energy inflow is required from the outside.

Specific features of systems (5.13) and (5.14) are explained from Fig. 5.9*a* and *b*. In (5.13) in comparison with (5.12) the thermodynamic attainability region (the nonhatched part of the triangle $y - x^{mat}_{NO} - CO_2, N_2$ in Fig. 5.9*a*) sharply increases, resulting in a considerable rise of the value of x^{ext}_{NO} (Table 5.4). At $T = 1000$ K the point x^{ext}_{NO} lies on the intersection of the curve $G = G\,(y)$ with the edge $x^{mat}_{NO} - CO_2, N_2$. At $T > 1000$ K the thermodynamic "pothole" occurs. The point x^{ext}_{NO} has a very high enthalpy level $H(x^{ext}) \gg H\,(y)$. Hence, this point can be reached by the additional supply of a large amount of energy (520–970 kJ/kg at $T = 1000 - 3000$ K) to the reaction mixture. In boiler furnaces such conditions are possible only in local zones, e.g., in the torch core.

In system (5.14) the point $y \approx \tilde{x}^{eq}$ is the initial point (Fig. 5.9*b*). It corresponds to equilibrium state (5.13), provided NO starts to form only after completion of carbon burning. The segment $[y, \tilde{x}^{eq}]$ in this case represents oxidation of C_c. The point x^{eq} corresponds to the final equilibrium of system (5.13), where there are no constraints on the process mechanism. When we pass to system (5.14), the thermodynamically attainable region (where a superequilibrium concentration of NO is possible) decreases considerably. In Fig. 5.9*b* the region is limited by the curve $G = G\,(\tilde{x}^{eq})$ and the straight line *AB*. The maximum NO concentration

TABLE 5.4. Formation of thermal nitrogen monoxide (NO) ($T = 0.1$ MPa)

	x, mole/kg			$H(x) - H(y)$,kJ/kg			$G(x) - G(y)$,kJ/kg			$S(x) - S(y)$,kJ/(kg·K)		
T, K	eq	ext	mat	eq	ext	mat	eq	ext	mat	eq	ext	mat
						System (5.12)						
1000	0.0011	0.0011	14.56	0.1	0.1	1331	0	0	1099	0.0001	0.0001	0.2328
1250	0.0098	0.0098	14.56	1.0	1.0	1332	–0.10	–0.10	1040	0.0009	0.0009	0.2334
1500	0.0424	0.0427	14.56	4.0	4.0	1332	–0.50	–0.50	982	0.0030	0.0030	0.2333
1750	0.1206	0.1377	14.56	11	13	1332	–1.80	–1.80	924	0.0073	0.0085	0.2333
2000	0.2629	0.3399	14.56	27	34	1331	–4.60	–4.40	866	0.0158	0.0192	0.2327
2250	0.4787	0.7278	14.56	59	81	1330	–10.10	–9.00	807	0.0307	0.0400	0.2323
2500	0.7652	1.4020	14.56	127	184	1329	–20.90	–16.30	750	0.0592	0.0801	0.2318
2750	1.1030	2.4680	14.56	270	385	1326	–41.70	–26.50	692	0.1133	0.1496	0.2307
3000	1.4530	3.9750	14.56	544	729	1323	–81.00	–3980	634	0.2083	0.2563	0.2296
						System (5.13)						
1000	0.0004	10.18	13.6	–2236	520	1243	–2268.6	0	1027	0.0329	0.5203	0.2168
1250	0.0037	10.61	13.6	–2238	631	1244	–2276.5	–0.1	927	0.0308	0.5049	0.2175
1500	0.0161	10.99	13.6	–2240	704	1244	–2283.9	–0.5	918	0.0294	0.4697	0.2175
1750	0.0457	11.31	13.6	–2239	765	1244	–2291.2	–1.7	863	0.0297	0.4381	0.2175
2000	0.0998	11.58	13.6	–2227	819	1243	–2299.2	–4.1	809	0.0362	0.4116	0.2170
2250	0.1875	11.83	13.6	–2163	865	1242	–2311.2	–8.5	755	0.0661	0.3882	0.2165
2500	0.3307	12.03	13.6	–1964	906	1241	–2336.7	–15.2	701	0.1491	0.3685	0.2161
2750	0.5492	12.21	13.6	–1583	939	1239	–2391.0	–24.7	647	0.2938	0.3504	0.2153
3000	0.8138	12.37	13.6	–1062	967	1236	–2486.8	–37.3	593	0.4749	0.3348	0.2143
						System (5.14)						
1000	0.0004	0.0011	13.6	0.0	0.0	3479	0	0	3295	0.0000	0.0000	0.1839
1250	0.0037	0.0101	13.6	0.0	0.0	3482	–0.10	0	3249	0.0001	0.0000	0.1868
1500	0.0161	0.0440	13.6	1.5	4.1	3485	–0.20	0	3202	0.0011	0.0027	0.1892
1750	0.0457	0.1277	13.6	5.3	13	3489	–0.80	0	3154	0.0035	0.0073	0.1914
2000	0.0998	0.3080	13.6	21	41	3491	–2.40	0	3106	0.0119	0.0204	0.1927
2250	0.1875	0.7106	13.6	89	145	3494	–8.50	0	3058	0.0434	0.0642	0.1939
2500	0.3307	1.5830	13.6	292	454	3497	–28.6	0	3009	0.1282	0.1816	0.1952
2750	0.5492	3.1410	13.6	679	1042	3501	–77.9	0	2960	0.2752	0.3788	0.1967
3000	0.8138	5.2340	13.6	1207	1743	3505	–169.3	–0.1	2911	0.4588	0.5810	0.1982

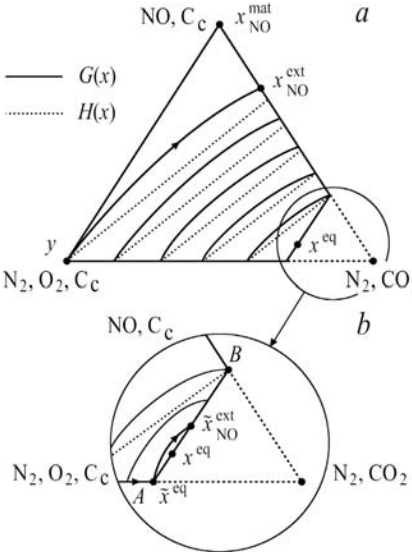


FIGURE 5.9. To the thermodynamic analysis of NO formation in the system [C_c, O_2,N_2, NO, CO_2]. $T = 1500$ K, $P = 0.1$ MPa.

(the point $\tilde{x}^{ext}_{NO}$) also decreases in a pronounced fashion. This outcome is typical primarily of low temperature burning ($T < 1500$ K).

The negative thermal effect of NO formation in system (5.14) increases sharply with rising temperature (Table 5.4). Constraints on energy and mass exchange are the main reason for discrepancy in the theoretical and experimental data on the NO yields at $T > 1500$ K.

Comparison of systems (5.13) and (5.14) results in the key conclusion that a new mechanism of NO formation (*Fenimore's mechanism*) originates at injection of condensed carbon into the reaction volume [48]. Nitrogen oxides formed by this mechanism are called "prompt." Thus, in system (5.13) the value ofx^{ext}_{NO} is the sum of thermal and prompt nitrogen oxides. In the whole region $D_t(y)$, except for its negligible part, limited by the curve $G = G(\tilde{x}^{eq})$ and the segment AB, the nitrogen monoxide is formed by the "prompt" mechanism.

Fig. 5.9*b* illustrates the second important conclusion of the analysis. In the case of kinetic slowdown of formation reactions, emissions of thermal NO lower than the equilibrium emissions are possible if the fuel is burnt completely. The corresponding states lie in the region limited by the lines AB and $G = G(\tilde{x}^{eq})$ below the point x^{eq}. At the point A the NO concentration is close to zero. With increasing combustion temperature, the point x^{eq} is displaced along AB toward B, i.e., toward the region of higher concentrations (Fig. 5.9*b*). The same regularity is observed with respect to the extreme states x^{ext}_{NO} and $\tilde{x}^{eq}$.

With the expansion of system (5.13) (increase of the vector x dimension to $n = 200$, which is quite enough to describe the oxidation of organic part of coal) the equilibrium and extreme concentrations of NO at $T < 2000$ K change negligibly.

Divergence does not exceed 4% for $x_{\mathrm{NO}}^{\mathrm{eq}}$ and 15% for $\tilde{x}_{\mathrm{NO}}^{\mathrm{ext}}$ (in a real system the NO yields are lower). At $T > 2000$ K divergence increases, making at $T = 3000$ K 10% for $x_{\mathrm{NO}}^{\mathrm{eq}}$ and 60% for $\tilde{x}_{\mathrm{NO}}^{\mathrm{ext}}$. As to differences in $x_{\mathrm{NO}}^{\mathrm{ext}}$, they do not exceed 10–20% over the whole studied range of temperatures. The experimental data on $x_{\mathrm{NO}}^{\mathrm{ext}}$ are somewhat higher.

The thermodynamic analysis performed contributes to substantiation of ways to lower the formation of thermal oxides ($\mathrm{NO_x}$) during fuel combustion, namely: 1) decrease of combustion temperature ($T < 1500$ K); 2) decrease of the time for the flue gases to stay in the high temperature zone of the furnace; 3) decrease of α_{air} in the furnace (however, α_{air} should be higher than unity at its outlet); 4) limitation of energy liberation in the high-temperature zone (by more intensive heat removal from it); 5) elimination of carbon injection into the high-temperature zone of the furnace.

According to the up-to-date concept [147, 165], fuel nitrogen oxides are obtained from nitrous substances of coal in the starting section of torch, when temperatures reaches 900–1000 K. During thermal destruction of nitrous substances of fuel the intermediate gaseous substances $\mathrm{R_N}$—the molecules of HCN, $\mathrm{NH_3}$, and the radicals CN, NH, and $\mathrm{NH_2}$—are formed first. Then these products react with the atmospheric oxygen and the flame components O and OH with partial oxidation to NO. In general, the fuel NO formation can be represented in the form:

$$\text{Organics} + Q \rightarrow \mathrm{R_N} : [\mathrm{HCN}, \mathrm{CN}, \mathrm{NH_3}, \mathrm{NH_2}, \ldots], \tag{5.15}$$

$$\mathrm{R_N} + [\mathrm{O_2}, \mathrm{O}, \mathrm{OH}] \rightarrow [\mathrm{CO_2}, \mathrm{N_2}, \mathrm{NO}, \mathrm{H_2O}], \tag{5.16}$$

where Q is thermal energy.

The calculations show that, in terms of thermodynamics, between the temperatures 600–1000 K, the fuel nitrogen may virtually completely turn into the gaseous nitrogen species HCN, CN, $\mathrm{NH_3}$, etc.; i.e., process (5.15) has no thermodynamic constraints. Hence, the condition $x_j^{\mathrm{ext}} = x_j^{\mathrm{mat}}$ is met for all $\mathrm{R_N}$. In Fig. 5.10 this conclusion is illustrated on the example of $\mathrm{NH_3}$.

The maximum (thermodynamically permitted) total concentration of the nitrogen compounds in products of thermal destruction of coal is about 0.24 mole N/kg.

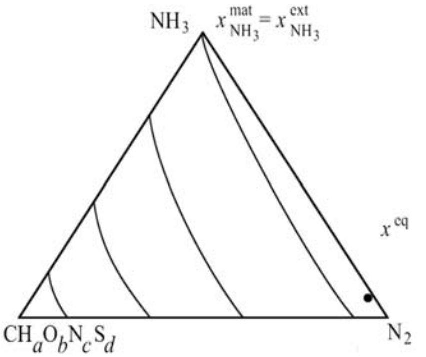
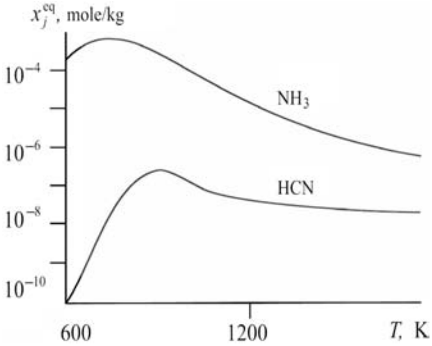


FIGURE 5.10. To the thermodynamic analysis of thermal destruction of nitrogen species of coal ($\alpha_{\mathrm{air}} = 0.8$; $P = 0.1$MPa, $T = 1000$ K).

FIGURE 5.11. The equilibrium concentrations of gaseous nitrogen substances in the products of thermal coal destruction ($\alpha_{\text{air}} = 0.8$; $P = 0.1$ MPa).



The concentration does not depend on T and α_{air}: it is determined entirely by the content of the bound nitrogen in fuel. It should be noted here that the point x^{eq} is closely "held" against the edge $NH_3 - N_2$ inside $D(y)$.

After the complete equilibrium is reached, the concentrations of R_N sharply fall (by 3–5 orders of magnitude and more) and do not exceed $5 \cdot 10^{-4}$ mole/kg at $\alpha_{\text{air}} = 0.8$. Among the considered substances in the equilibrium mixture, NH_3 and HCN are present in the greatest amounts. Their equilibrium concentrations depend on T and particularly on α_{air}. At $T < 1000$ K the concentrations of HCN fall rapidly, while those of NH_3 on the contrary remain constant and are the highest (Fig. 5.11). The influence of air excess is more unambiguous. The increase in α_{air} leads to a decrease in the yields of NH_3 and HCN, and at $\alpha_{\text{air}} > 1$ the concentrations of these substances are virtually equal to zero (Fig. 5.12).

The thermodynamic analysis of R_N oxidation into NO (5.16) reveals that thermodynamic constraints are also inessential for this process. Hence $x_{\text{NO}}^{\text{ext}} = x_{\text{NO}}^{\text{mat}}$ (Fig. 5.13). The material balance constraints on oxygen are more significant (the segment AB in Fig. 5.13). When the oxygen content in the system decreases, the line AB shifts downward, and, correspondingly, the values of $x_{\text{NO}}^{\text{ext}}$ decrease. Note that in this case the solution is degenerate. At any point of the segment AB, $x = x_{\text{NO}}^{\text{ext}}$. The extreme NO yield does not depend on temperature in the range from 600 to 2400 K.

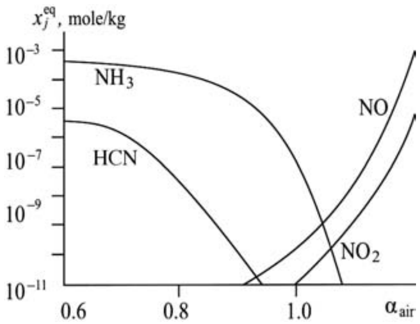


FIGURE 5.12. Dependence of equilibrium concentrations of nitrogen species R_N in the products of thermal coal destruction on α_{air} ($T = 1000$ K; $P = 0.1$ MPa).

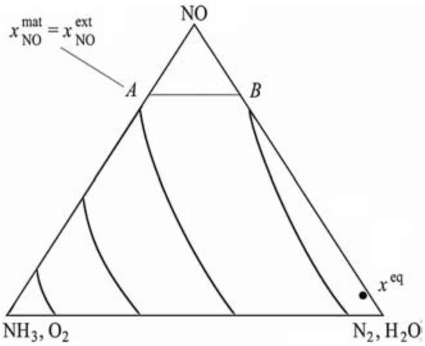


FIGURE 5.13. To the thermal analysis of fuel NO formation.

At the state x^{eq} of the process (5.16) the NO concentration is by several orders of magnitude lower than it is in x_{NO}^{ext}. Here, the equilibrium concentrations of NO depend strongly enough on T, especially in the region $T < 1000$ K. They show weaker dependence on α_{air} (at $\alpha_{air} > 1$), increasing with its rise. This dependence is inverse to that in the process (5.15), where the R_N yield decreases with the rising α_{air} (Fig. 5.12).

Results of the thermodynamic analysis of the processes (5.15) and (5.16) allow the conclusion that the yield of fuel NO_x depends rather weakly on T and very strongly on oxygen content in the combustion zone. This is in a good agreement with experimental data [165].

From the aforesaid follow some recommendations on reduction of fuel NO_x formation: 1) change in the composition of primary products of thermal decomposition of nitrogen species to enhance the extent of fuel nitrogen transition to molecular nitrogen (in particular, by more intensive elimination of volatiles, their thorough premixing with air, and creation of an oxidizing medium in the heating zone of coal particles); 2) more extended period for thermal destruction products to stay in the torch volume to achieve more complete reactions of R_N transition to N_2 and NO reduction (to the point of complete equilibrium state); 3) decrease of the oxidizer content in the combustion zone until the reducing atmosphere is created in it; 4) use of fuel without bound nitrogen.

According to C.P. Fenimore [48], prompt nitrogen oxides are formed at the flame front from atmospheric nitrogen by the following mechanism: As a result of the thermal destruction of organic coal matter, the carbon sustances R_C (CH, CH_2, C) are formed first. They are bound with molecular nitrogen, forming substances such as R_N (HCN, CN, NH, N, etc.). The latter react with the active species of flame O, H, and OH, resulting in formation of the prompt oxides. The overall process can be represented in the form

$$\text{Organics} + Q \rightarrow R_C : [CH, CH_2, C], \tag{5.17}$$

$$R_C + N_2 \rightarrow R_N : [HCN, CN, NH_3, NH_2, NH], \tag{5.18}$$

$$R_N + [O_2, O, OH] \rightarrow [CO_2, N_2, NO, H_2O, \ldots]. \tag{5.19}$$

The MEIS-based studies revealed the possibility for forming O, H, and OH in the flame at coal burning in amounts that exceed their equilibrium concentrations by several orders of magnitude. This is, however, a very energy-capacious process. Without constraints on energy supply to the reacting system the limiting (thermodynamically allowed) concentrations of O, H, and OH in the products of coal combustion in the temperature range 600–1200 K vary as follows (at $\alpha_{\text{air}} = 1.2$): The volumetric fractions of O and H increase linearly from 5.8 and 10.2% to 10.8 and 16.1%, respectively, and the OH fraction decreases linearly from 10.8 to 5.2%. Energy consumption for formation of such quantities of O, H, and OH and the corresponding changes in the composition of the whole reacting system within the same temperature range (600–1200 K) linearly increase from 660 to 1650 kJ/kg. It is usually impossible to supply such quantities of energy in real furnaces. The yield of active species sharply falls with decrease of heat supplied. For the equilibrium state at low T it is close to zero. In a boiler, sources of additional energy may comprise: a) radiation from the high-temperature flame zone, b) hot recirculating gases, and c) exothermal chemical reactions running directly in this zone.

Thermodynamic constraints on the formation of extreme concentrations of O, H, and OH are significant. The points x^{ext} lie on the curve $G = G(y)$. The temperature rise causes extention of the thermodynamic attainability region $D_t(y)$. The equilibrium concentrations of O, H, and OH are in strong dependence on T and α_{air} (Fig. 5.14). All of them intensively increase at the increase of T. Increase of α_{air} leads to yield increases of O and OH and yield decrease of H.

We carried out a study on thermodynamic regularities in the formation of R_C radicals at the thermal destruction of organic coal mass by scheme (5.17). The point x^{ext} is located on the initial surface of the Gibbs energy $G(y)$ (Fig. 5.15). It can be reached by the considerable quantity of energy supplied from the outside. The value of $x^{\text{ext}}_{\text{CH}}$ smoothly increases with rise in temperature.

At $\alpha_{\text{air}} > 1$ the equilibrium concentrations of R_C are negligible within the considered temperature range 750–2000 K. The point x^{eq} in this case lies near the vertex CO_2 of the polyhedron $D(y)$.

The thermodynamic analysis of process (5.18) lets us conclude the following: There are no thermodynamic constraints for this process, therefore, the states

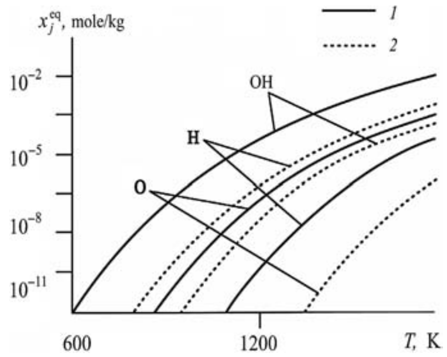


FIGURE 5.14. Equilibrium concentrations of O, H, OH in the flame at coal burning α_{air} : 1, 1.2; 2, 0.8.

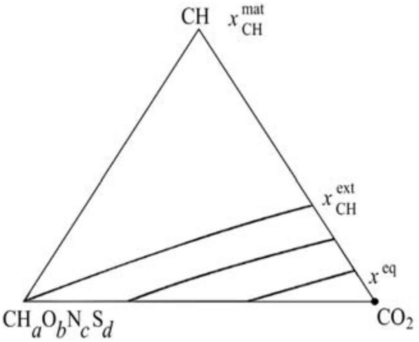


FIGURE 5.15. Thermodynamics of CH radical formation at thermal destruction of coal: $T = 1000$ K; $P = 0.1$ MPa; $\alpha_{air} = 1.2$; y, mole: $y_{OCM} = 1$, $y_{O_2} = 1.312$; x, mole/kg: $x_{CH}^{eq} = 0$, $x_{CH}^{ext} = 9.02$, $x_{CH}^{mat} = 14.18$; $G(x)$, kJ/kg: $G(y) = -4695$, $G(x^{eq}) = -13160$, $G\left(x_{CH}^{ext}\right) = -4695$, $G\left(x_{CH}^{mat}\right) = 1125$.

$x_j^{ext} = x_j^{mat}$ are attainable for all compounds of the R_N type. The extreme concentrations of R_N depend neither on α_{air} nor T and are wholly determined by the concentrations of R_C radicals in the system. The equilibrium concentrations of R_N are by several orders of magnitude lower than the extreme ones. Comparatively speaking, they relatively weakly depend on temperature and strongly on α_{air} in the range $0.8 < \alpha_{air} < 1.2$. At $\alpha_{air} < 0.8$ the equilibrium concentrations of R_N stabilize and make up approximately 10 mole/kg; there is a prevalence of NH_3 in these amounts. The concentrations of R_N rapidly decrease with increasing α and with $\alpha > 1$ do not exceed 10^{-9} mole/kg.

The regularities in formation of prompt nitrogen oxides by scheme (5.19) are similar to those in the oxidation of the products of thermal coal destruction into fuel nitrogen oxides represented in process (5.16).

Small changes in the yield of carbon radicals CH and the total concentration of active species O, H, and OH at the flame front within the wide temperature range explain the weak dependence of the yield of prompt NO on temperature, a conclusion that agrees with experimental data [157].

The analysis of specific features in the formation of prompt NO_x determines potential measures for eliminating this situation: 1) operation of the process of thermal coal destruction at the low temperature and $\alpha_{air} > 1$ (to decrease the yield of carbon radicals); 2) implementation of "cold" flame regime in the reductive medium (which will contribute to decrease in concentrations of O, H, and OH); 3) limited supply of high-temperature energy to the zone of thermal destruction of coal organics and to the flame front from the outside (to reduce the yield of CH, O, H, and OH); 4) prevention of the reactions of atmospheric nitrogen-binding by the carbon radicals (by creating an oxidative medium in the corresponding furnace zone); 5) change in the mechanism of fuel burning to decrease concentrations of O, OH, H, R_C, and R_N in the reacting volume (e.g., implementation of low-temperature catalytic oxidation); 6) application of pure oxygen rather than air as an oxidizer; 7) changeover to carbon-free fuel combustion (e.g., hydrogen produced from coal).

The thermodynamic analysis of mechanisms for forming individual types of nitrogen oxides reveals the following general approaches to reduction of the

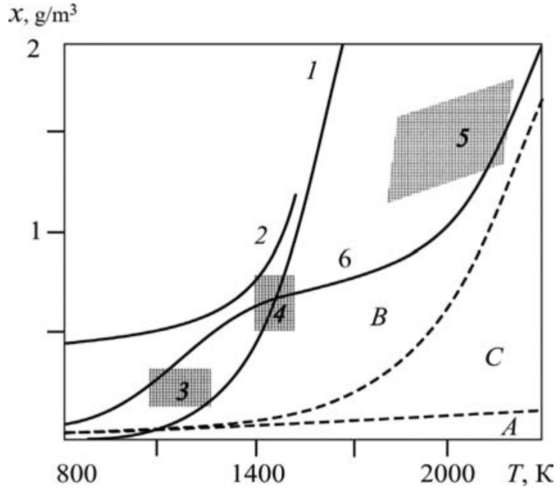


FIGURE 5.16. Comparison of the theoretical and experimental yields of NO at coal combustion: equilibrium (1), extreme (maximum) (2); actual data (3–6): fluidized-bed combustion (3); low-temperature burning of brown coals (4); high-temperature burning of hard coals (5); average NO emissions by pulverized coal-fired boilers (6); A: "prompt" NO_x; B: "fuel" NO_x, C: "thermal" NO_x.

thermodynamic feasibility region of NO_x formation reactions:

1. Limitation of energy supply to the zones of intensive formation of NO and R_C.
2. Limitation of oxygen consumption by the reaction mixture at the initial combustion stage.
3. Increase in duration of combustion products presence in the reduction zone.
4. Decrease in the temperature level at the initial combustion stage (to minimize active flame components O, H, and OH).
5. Decrease in the temperature and the air excess coefficient in the torch center.

MEIS-based theoretical concentrations of NO (equilibrium, maximum, and minimum) were compared with generalized experimental data taken from [14, 68, 157] (Fig. 5.16). Joint analysis of sufficiently well-corresponding calculated and experimental data explains basic regulations of formation of nitrogen oxides and allows the conclusions on the possibility of applying thermodynamics to, potentially, improve fuel combustion technologies aimed at reduction of NO_x yield.

In the region of low combustion temperatures ($T < 1500$ K) total NO_x emissions consist basically of fuel and prompt NO. Thermal NO yields prevail at $T > 2000$ K. In the temperature range 1500–2000 K (the region of torch-furnace boiler operation) the greatest contribution is made by fuel and thermal NO.

At $T < 1500$ K the actual NO emissions by pulverized coal-fired boilers can considerably exceed equilibrium values. The reason is the superequilibrium formation of fuel and prompt NO in the boilers. At high-temperature fuel combustion the NO yield does not reach, as a rule, an equilibrium value because of insufficient duration of reaction mixture presence in the region of maximum temperatures.

However, not all theoretical methods mentioned to reduce NO_x yields are of practical importance (for example, by reason of increasing concentrations of other harmful substances) and some of them contradict one another. Choice of tradeoff decisions for specific type of furnaces and kind of fuel involved is an engineering problem whose successful solution may demand additional experimental and kinetic studies. The aim of these studies is to search for and realize on the thermodynamically attainable set D_t (y) a process trajectory leading to the desirable result. The theoretical results discussed above may form a basis for this search.

After describing the considered example's significance in the direct solution of the problem of NO_x suppression in fuel combustion processes, we will take advantage of a visualization of the example to demonstrate the "art of the possible" in the thermodynamic analysis of technical systems.

In the given case such an analysis was made based on solely the fragmentary kinetic information on the studied process mechanism: an aggregated description of forming three types of nitrogen oxides. In real systems these processes are interrelated and in addition to this, their implementation depends on the whole set of reactions running in the system.

The fragmentary character of information was taken into account by applying the following scheme of thermodynamic modeling: Idealized models of the least dimension were used to study independently every parallel branch of the total mechanism of NO_x formation. The study of an individual branch, in turn, was reduced to the thermodynamic analysis of components of its aggregate stages. The influence of nonideality was evaluated by detailed models including nitrogen oxides and many other harmful compounds.

It is precisely such a stage-by-stage joint application of thermodynamics and kinetics, ideal and detailed "real" models, that allowed the fundamental regularities of running the considered processes to be revealed and the potential changes in the actual characteristics to be evaluated. The most important applied result of the analysis performed was the substantiation of measures on control of separate stages.

In our opinion the conclusions drawn proved to be more informative than those reached by the use of only kinetic models and full-scale experiments with a comparable scope of studies. The original results of the analysis carried out that were obtained by its "thermodynamic decomposition" are: 1) explanation of the reasons for changing sizes of the thermodynamic attainability region D_t (y) with indication of possible quantitative relationships between x_{NO}^{mat}, x_{NO}^{ext}, x_{NO}^{eq}; 2) determination of the effect of nonthermodynamic factors (energy and mass exchange, air surplus) on NO_x concentrations; 3) appraisal of the possibility to decrease NO_x yield below the equilibrium values in the case of complete combustion of fuel carbon; 4) thermodynamic derivation of a weak temperature dependence of ptompt NO_x formation.

Analysis of Environmental Characteristics of Periodic Fuel Combustion in Small Furnaces

Coal- or wood-fired utility boiler plants and home heating stoves with manual fuel loading are chosen as the object of study. In many cities these small heat sources make the greatest contribution to air pollution by carbon monoxide, nitrogen and sulfur oxides, particulates (ash) and other harmful emissions.

The theoretical, in particular thermodynamic, analysis of combustion processes in these heat sources is apparently even more sophisticated than the study of pulverized fuel combustion in large furnaces. The first difficulty is caused by the unsteady and periodic behavior of the combustion process, characterized by small (between fuel loadings) and long (between cleanings of the fire grate) cycles. Periodic poking of the fuel as it burns in the bed is an additional source of the unsteadiness.

Periodicity makes an essential contribution to increase in a reacting system's nonequilibrium, and to temperature difference that arises between newly loaded and burning fuel, between solid and gas phases in the bed, and between the bed and furnace space over it.

Unfortunately, the problems in modeling are aggravated by the low technological level of equipment at small heat sources, the poor quality of fuel used, and in many cases by the low level of their operation. Because of highly nonuniform coal particle size distribution and low-quality poking, the layer of burning fuel becomes spatially nonuniform, conditions of mass exchange between phases and, hence, conditions of fuel ignition and burning, sharply deteriorate. Correspondingly, difficulties arise when we try to represent such "abnormal" conditions in theoretical models.

In comparison to the analysis of processes in large boilers another problem in studying the periodic combustion in small fixed-bed furnaces arises from the obvious insufficiency of theoretical and experimental data on the kinetics of the formation of harmful substances during such burning.

The mentioned specific features of the given example lead to distinctions in its thermodynamic analysis as compared to the previous example. Whereas, in the considered case of stationary burning, thermodynamics was used jointly with kinetics, the study presented below incorporates three interrelated elements: thermodynamics, kinetics and full-scale experiments. Surely, the experimental data are applied in virtually in all cases of thermodynamic modeling of complex real systems. However, here a full-scale experiment is directly included in the scheme of analysis.

MEIS application to periodic nonequilibrium combustion processes studies was based on an assumption about low variation of the macroscopic parameters in every local furnace (bed) volume—sufficiently low that it was possible to consider the processes running in the furnace as passing through the continuous sequence of equilibrium states.

The process mechanism was broken down into three aggregate stages [138]. Two of them ("come-out" and combustion of volatiles, and combustion of residual coke) refer to the bed; the third represents chemical transformations in the furnace space.

The first two stages were analyzed on the basis of a joint application of thermodynamics and full-scale experiments. Kinetic modeling was unnecessary because of the rather fast processes of coal thermal destruction. Such modeling would also be rather difficult because of the highly sophisticated kinetic description of a heterogeneous coal burning. Experiments resulted in determination of: 1) temperature variations in the bed as a function of time and average temperature for individual stages of the total process; 2) time dependences of α_{air} and variations of this magnitude on the bed surface; and 3) concentrations of individual substances (O_2, CO, CO_2, etc.) at the bed boundary. The experimental data helped prepare correctly a list of the vector x components and specify the temperature of the reaction mixture by the MEIS-based variant calculations.

We carried out analysis of the third stage (the processes in the furnace space above the bed) by using all three mentioned elements of the applied technique: thermodynamic, kinetic, and full-scale experimentation. Kinetic calculations were applied to determine concentrations of substances (e.g., NO_x), whose formation time can presumably exceed the time during which the gas flow passes through the furnace space. Since there are no reliable data on the mechanism and constants of chemical reaction rates with participation of aromatic hydrocarbons, in particular polycyclic aromatics (PAH), their formation was determined by MEIS. As in the analysis of the first two stages, the experimental data on the time-dependence of T, α_{air}, and concentrations of particular substances (e.g., CO) at the furnace outlet were also applied to the MEIS-based variant calculations.

Some results of the analysis on the estimation of concentrations of harmful substances formed at combustion are presented in Figs. 5.17, 5.18, 5.19, and 5.20.

Formation of nitrous substances (Fig. 5.17) was studied in accordance with the real course of reactions in time. As a result of the fixed-bed combustion almost all fuel nitrogen passes to molecular N_2, which is favored by reductive conditions in the bed. Thermal NO_x yields make up only a small fraction of the total yield of NO_x. In the thermodynamic calculations the volatile nitrous substances were modeled by ammonia (NH_3) and prussic acid (HCN). The region of intensive formation of NH_3 and HCN (sources of fuel NO) corresponds to low temperatures and small α_{air} (Fig. 5.17*a* and *b*). The intermediate compounds are converted to fuel NO owing to high temperatures and higher air excess (Fig. 5.17*c*). Such conditions are observed in the bed during come-out and burning of volatile substances. The highest NO concentrations in the flue gases are noted precisely during burning of volatiles, which was confirmed by the authors' experiments.

Analysis of the composition of sulfur-containing compounds revealed that hydrogen sulfide (H_2S) and carbonyl sulfide (COS) can be formed along with SO_2 at fixed-bed combustion (Fig. 5.18). With the lack of oxidizer they can be formed in a rather wide temperature range, which causes a danger from high-temperature corrosion of the radiation heating surfaces.

The analysis also allowed us to determine conditions for formation of carbon monoxide CO, a most dangerous product of fuel combustion in the fixed bed at the stage of residual coke combustion (Fig. 5.19).

The results of analysis of changes in the PAH concentrations during combustion proved to be interesting. The experiments carried out by the authors jointly with A.G. Gorshkov and L.I. Belykh revealed that the PAH concentrations, which are products of incomplete combustion, depend to a greater extent not on the properties of fuel burnt, but on process conditions (Fig. 5.20). According to experimental

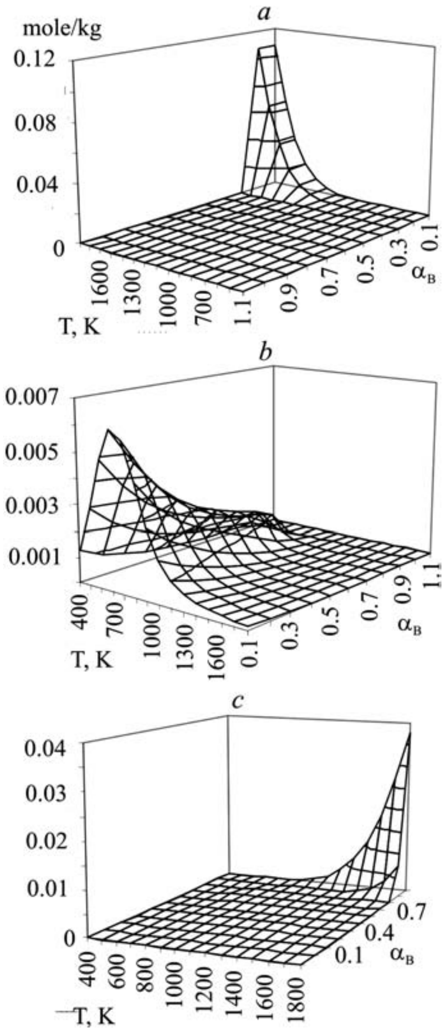


FIGURE 5.17. Equilibrium concentrations of nitrous products versus temperature and oxidizer excess. *a*) HCN, *b*) NH_3, *c*) NO.

data, during the combustion cycle the PAH amount changes in a way similar to the way that concentration of particulates is effected. Therefore, it can be supposed that aromatic polycyclic hydrocarbons precipitate on solid particles. This relation is particularly clear at the initial stage of the combustion cycle, where, by the data of element analysis, soot constitutes 65–70% of the mass of solid particles. Thermodynamic calculations confirmed the supposition that PAH presence in coal combustion products was more likely the result of PAH synthesis at the gas phase oxidation of volatiles than the consequence of incomplete destruction of the carbon matrix of fuel.

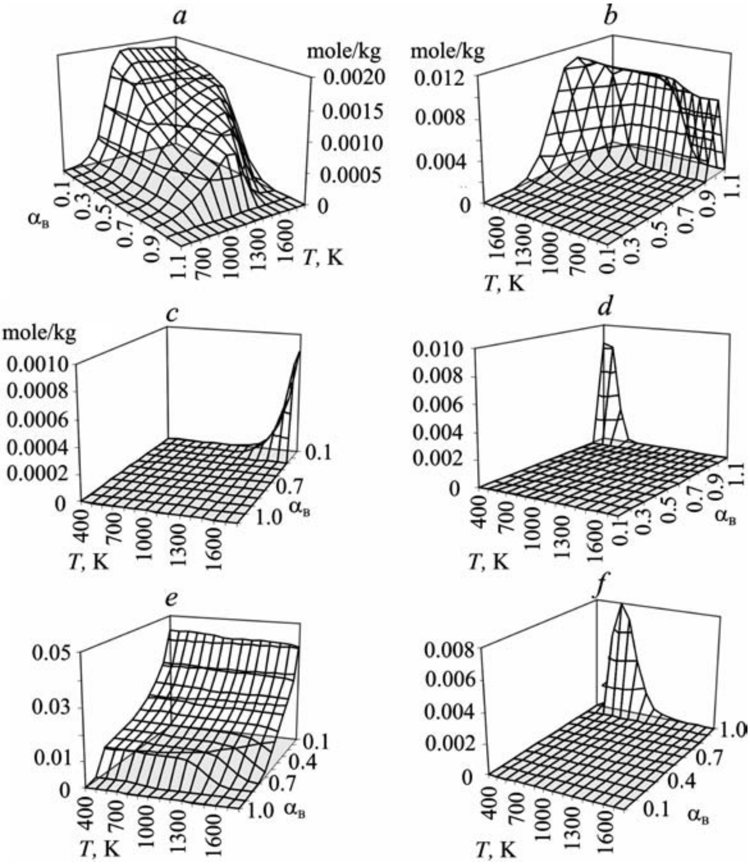


FIGURE 5.18. Equilibrium concentrations of sulfur-containing products versus temperature and oxidizer excess. *a*) – COS, *b*) SO_2, *c*) CS_2, *d*) $H_2\ SO_4$, *e*) $H_2\ S$, *f*) SO_3.

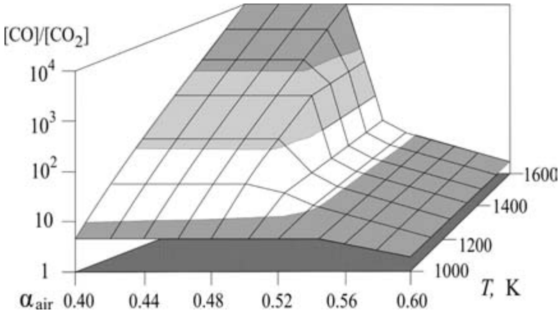


FIGURE 5.19. Dependence of the ratio $[CO]/[CO_2]$ on the air excess and temperature (thermodynamic equilibrium).

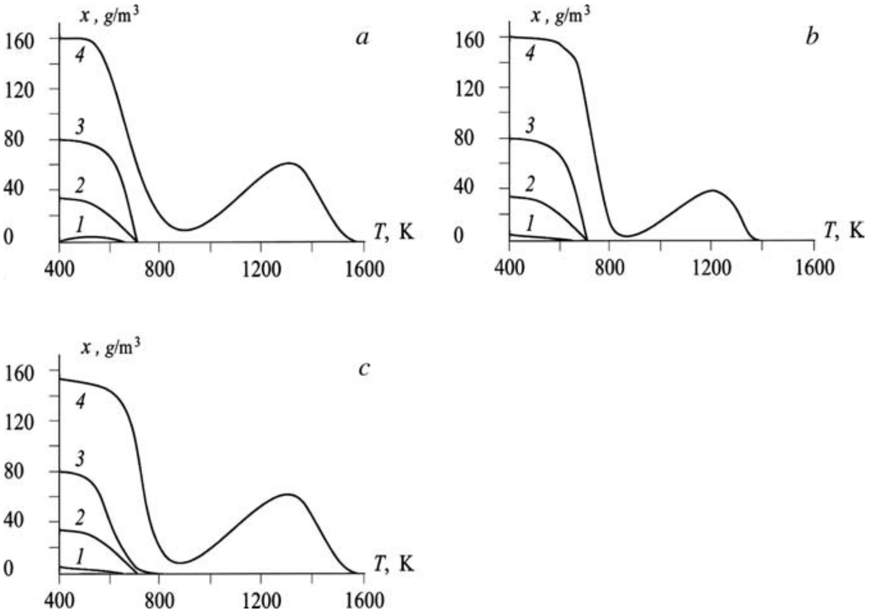


FIGURE 5.20. Equilibrium PAH concentrations versus combustion temperature at different air excesses. *a*) $\mathbf{C}_{14}\mathrm{H}_{10}$, anthracene gas; *b*) $\mathbf{C}_{14}\mathrm{H}_{10}$:c, condensed anthracene; *c*) $\mathbf{C}_{14}\mathrm{H}_{10}$, phenanthrene gas. α_{air}**:** 1, 0.4; 2, 0.3; 3, 0.2; 4 , 0.1.

In modeling coal pyrolysis none of PAH is found in the state x^{eq}, when we include the condensed carbon $\mathrm{C_c}$ into vector x. In modeling transformations of volatiles, when we exclude C_c from the vector x, a number of PAH are found in the reaction mixture both in gaseous and in condensed phases at low α_{air}. The nature of change in calculated PAH concentrations versus temperature proved to be close to experimental data. The revealed relationships confirmed that the greatest amount of PAH is formed at the initial stage of combustion at lower temperatures and air excesses.

On the whole, the analysis of periodic fuel burning in fixed-bed furnaces enabled us to obtain sufficiently full information on the conditions for formation of harmful substances at different process stages and to determine environmentally optimal conditions of its implementation.

It was established that the real temperatures and air-excess coefficient in the bed at the initial combustion stage correspond to conditions of the low-temperature oxidation pyrolysis of solid fuel that leads to formation of products of incomplete combustion: carbon monoxide, soot, PAH, etc. Despite the high values of α_{air} in the furnace volume, the products of incomplete combustion formed due to low temperature and their short residence in the boiler do not have reasonable time for further oxidation; they are emitted to the atmosphere with flue gases. The quantity of these products can be reduced by feeding fuel in small portions and maintaining the temperature at a level sufficient for its fast ignition in the combustion zone.

Increase in average (for the cycle) furnace temperature causes some increase in thermal NO_x emissions. However, the thermodynamic calculations showed that this increase is negligible, since even at the maximum temperatures (1500–1600 K) in the fixed-bed furnaces the yield of thermal oxides is only a small portion of the total NO_x. High-temperature fuel pyrolysis at the initial stage of the combustion cycle fosters a decrease in concentrations of fuel nitrogen oxides owing to reduction of nitrogen substances to molecular nitrogen. The level of reduction is determined by the time, as nitrogen substances are found in the high-temperature zone.

Change in fuel combustion conditions virtually has no influence on SO_2 emission mass, since the atmosphere in the furnace space is oxidative. Increase in combustion temperature, however, makes it possible to prevent high-temperature corrosion of the furnace heating surfaces by sulfur oxides. A sufficiently high temperature maintained in the bed and the furnace space of boilers and stoves during the whole combustion period leads to a decrease in emissions of harmful substances (except for nitrogen and sulfur oxides) at all process stages.

Thermodynamic analysis of periodic fuel combustion processes in fixed-bed furnaces is undoubtedly useful to the task of recommending (in general) choice of heat supply schemes for residential districts, types of heat sources, kinds of fuel consumed, and so on.

5.3. Fuel Processing

We present some more examples on MEIS application to fossil fuel processing in order to form something close to a comprehensive notion of the capabilities of thermodynamic equilibria models.

The authors have already used MEIS extensively for the analysis of basic technologies of deep coal conversion: hydrogenation and hydrogasification, pyrolysis, successive gasification and synthesis of liquid and gaseous hydrocarbons and methanol from the mixture of CO and H_2, and hydrogen production to determine the limits of their perfection [81]. As in the study of combustion processes, Kansk–Achinsk coal was taken as the main object of study.

Here we present a brief thermodynamic analysis of two processes of methane production from coal: one by hydrogasification and steam conversion and the other by plasma gasification.

Hydrogasification of Coal

The first example, and the examples that follow, were analyzed on the simplest of models, ones in which coal was represented by condensed carbon, and the vector x included only key macrocomponents of the reaction mixture.

In a generalized form the hydrogasification process can be presented as follows:

$$C + H_2 + O_2 \rightarrow CH_4 + H_2O + CO + CO_2. \tag{5.20}$$

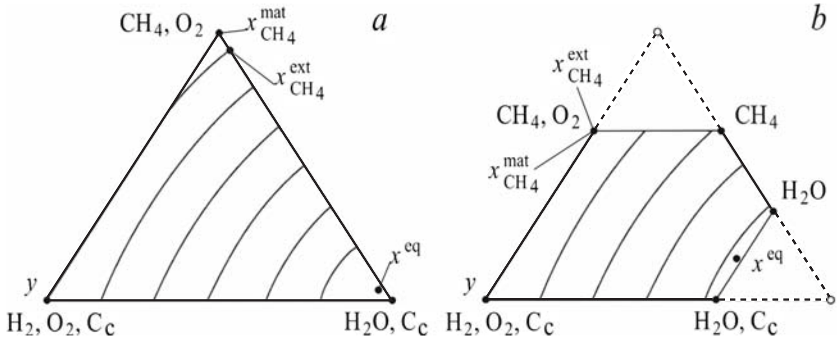


FIGURE 5.21. Geometrical interpretation of coal hydrogasification process. $P = 10$ MPa, $T = 800$ K; initial composition, mole: a) y: 1 C_c, 2 H_2, 1 O_2; b) y: 1 C_c, 3 H_2, 1 O_2.

Fig. 5.21 represents graphically this process for the case when only CH_4 and H_2O are the reaction products.

When oxygen is consumed in large amounts, the final equilibrium point x^{eq} lies immediately adjacent to the vertex H_2O. The equilibrium yield of CH_4 is close to zero. When the system passes from vertex C_c, H_2, O_2 (y) to vertex CH_4, O_2 (corresponding to the maximum concentration of methane on $D(y) - x^{\text{mat}}_{\text{CH}_4}$, a thermodynamic "pothole" occurs. Therefore, the condition

$$x^{\text{ext}}_{\text{CH}_4} < x^{\text{mat}}_{\text{CH}_4}$$

is met (Fig. 5.21*a*).

At certain ratios of H:C, H:O and C:O there appear material balance constraints on carbon (the segment [CH_4, O_2 – CH_4] in Fig. 5.21*b*) and oxygen (the segment [H_2O, C – H_2O]). Conditions when these constraints appear can be determined based on the technological ratios for the reaction synthesis of substances from the initial elements:

- at H:C > 4 we have a carbon constraint;
- at H:O > 2 we have an oxygen constraint (assuming that O_2 completely converts to H_2O);
- at C:O > 0.5 we also have an oxygen constraint (on the assumption that O_2 completely converts to CO_2). The latter constraint takes place when CO_2 is included in the list of reaction products instead of H_2O.

With the carbon constraint, the solution $x^{\text{ext}}_{\text{CH}_4}$ proves to be degenerate and can be situated at any point of the segment [CH_4, O_2 – CH_4] beloning to the thermodynamic attainability region $D_t\ (y)$ (Fig. 5.21*b*). This means an increasing degree of freedom in the choice of chemical process trajectories in the space of compositions that provide the same maximum yield of methane.

With the more strict constraint on oxygen, the segment [H_2O, C – H_2O] moves toward the edge [y – CH_4, O_2] (Fig. 5.21*b*). The region accessible for the hydrogasification process decreases. The final equilibrium point x^{eq} shifts, approaching the vertex CH_4, C_2 and the edge $[y - CH_4, O_2]$. In the limit, when O_2 is not consumed, the point x^{eq} lies at this edge and the equilibrium detour becomes impossible.

If the oxygen is excluded from the vector y in system (5.20), at $T < 900$ K and $P > 1$ MPa, the point x^{eq} closely approaches the vertex CH_4. In this case, if we assume a small error, we can consider that

$$x^{eq}_{CH_4} = x^{ext}_{CH_4} = x^{mat}_{CH_4}.$$

At $T > 900$ K and $P > 1$ MPa the equilibrium yield of CH_4 begins to decrease and the point x^{eq} shifts to the vertex y.

With the growing dimensionality of the vector x (in particular, with inclusion of CO_2 in it), the thermodynamic constraints are removed and, in the studied temperature range 400–1200 K, the extreme yields of CH_4 depend only on the material balance constraints, i.e.,

$$x^{ext}_{CH_4} = x^{mat}_{CH_4}.$$

However, the equilibrium concentrations of CH_4 herewith decrease with the growing amount of oxygen in the system. This conclusion also holds for the case of coal hydrogasification by pure hydrogen, when coal is the oxygen source.

The presented analysis can obviously be useful when choosing conditions for the processes in real gasifiers.

Steam Coal Conversion

The generalized equation of this process is

$$C + H_2O + O_2 \rightarrow CH_4 + H_2 + CO + CO_2. \tag{5.21}$$

Fig. 5.22 graphically presents steam conversion for the simplest case: The initial substances include C and H_2O. The reaction products are presented by CH_4, H_2, and CO.

The process proved to be very sensitive to temperature variation with simultaneous change of the Gibbs energy surface shape, the thermodynamic attainability region, the position of the final equilibrium point and the extreme point, and the character of thermodynamic situation on the segment [1–2], i.e., at the transition

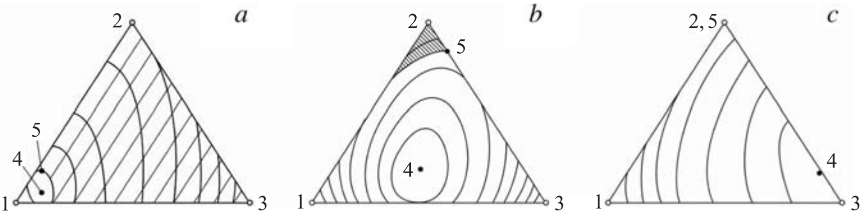


FIGURE 5.22. Steam conversion of carbon. Vertices: 1 – y : C_c, H_2O; 2 – CH_4 ; 3 – CO, H_2 . Thermodynamic states: 4 – x^{eq} , 5 – $x^{ext}_{CH_4}$. Thermodynamic parameters: $P = 5$ MPa; T, K: *a)* 700, *b)* 800, *c)* 900. The region of thermodynamic inaccessibility is hatched.

from the initial point (vertex 1) to the vertex with the maximum possible yield of CH_4 (vertex 2).

At a low temperature (<700 K) the thermodynamic attainability region is negligible (Fig. 5.22*a*). The points x^{eq} and $x_{CH_4}^{ext}$ lie near the vertex y. There is a thermodynamic pothole on the segment [1–2]. When the temperature rises to 800 K, $D_t\,(y)$ sharply increases. The point $x_{CH_4}^{ext}$ shifts to vertex *2* ($x_{CH_4}^{mat}$). The thermodynamic constraints become increasingly less strict. At $T > 900$ K they disappear. The extreme point reaches the vertex 2, i.e., the following equality is met:

$$x_{CH_4}^{ext} = x_{CH_4}^{mat}.$$

The final equilibrium point shifts to the vertex *3* that corresponds to the process products H_2 and CO.

For the total system (5.21) the thermodynamic constraints are significant. The solution $x_{CH_4}^{ext}$ lies on the curve $G = G\,(y)$ and in the whole studied range of external parameters (change of T from 400 to 1200 K and the mole ratio O_2:C from 0 to 0.5) the condition

$$x_{CH_4}^{ext} < x_{CH_4}^{mat}.$$

is satisfied. Here the extreme yield is no more than 52% of the maximum possible yield subject to the material balance. This quantity determines the extent of initial carbon transition to methane (Table 5.5).

Fig. 5.23 illustrates the effect of process temperature on methane yield (at the states x^{eq} and $x_{CH_4}^{ext}$). It shows that a temperature of about 800 K is optimal for the process from the thermodynamic viewpoint. The methane yield in this case reaches 90% of the extreme yield.

Plasma Gasification

This example is interesting first of all because it deals with *high-energy chemistry* [26], which is characterized by the most crucial case of nonequilibrium—a sharp deviation in distribution of some microscopic quantity from equilibrium distribution. It is clear that the successful application of the models of equilibrium

TABLE 5.5. The extent of initial carbon conversion to methane ($P = 5$ MPa, $T = 800$ K)

	Mole ratio H_2O:C = 2		Mole ratio H_2O:C = 3	
Mole ratio O_2:C	x^{eq}	$x_{CH_4}^{ext}$	x^{eq}	$x_{CH_4}^{ext}$
0	0.46	0.51	0.45	0.52
0.1	0.42	0.51	0.40	0.52
0.2	0.37	0.51	0.35	0.52
0.3	0.32	0.51	0.30	0.52
0.4	0.27	0.51	0.25	0.52
0.5	0.22	0.51	0.20	0.52

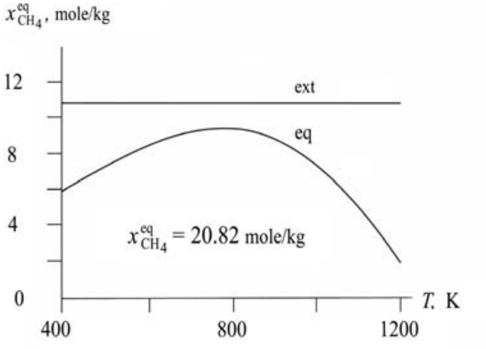


FIGURE 5.23. The equilibrium and extreme concentrations of methane versus temperature at steam conversion. $P = 5$ MPa; y, mole: 1 C, 2 H_2O.

thermodynamics in this area is an excellent illustration of the "omnipotence" of equilibrium distribution.

The use of low-temperature plasma in chemical and energy technology is attractive because an introduction of active particles (ions and free radicals) in the reaction mixture accelerates target transformations. The high-temperature jet present in the plasma reactor makes one suppose improved conditions for heat and mass exchange. Therefore, in plasma processes substantial improvements are possible for such important characteristics of chemical transformations as extent of conversion initial substances, volumetric rate of raw material supply, and selectivity. Eventually, all these factors should increase capacity of technological units, and reduce their dimensions, weight, and cost.

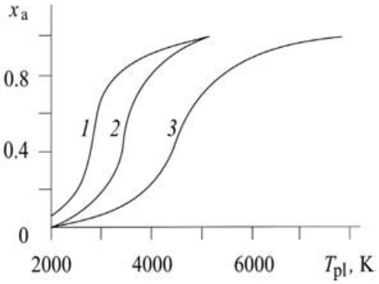
As an energy carrier, electricity applied in plasma generators (plasmatrons) provides high performance in plasma-chemical reactors, allowing for simplicity of start-up and load control, and high maneuverability.

Plasma processes can find possible applications in fuel gasification to produce *syngas* (a mixture of CO and H_2), gasification in the system of fuel preparation and the integrated gasification combined cycle at power plants, and ignition and lightening of the pulverized-coal torch in boiler furnaces. The latter option has already been implemented in the Russian power sector [95, 149].

Perfection limits for plasma technologies, in particular plasma gasification of coal, can be estimated using thermodynamics based on the assumptions that the intensity of exchange processes in the plasma reactor favors quick leveling of the flow temperatures, and that reactions proceed along the equilibrium trajectories.

In the first MEIS-based calculations of plasma gasifiers the authors included the *electric neutrality equation* (2.78) in the system of constraints. However, comparison of the calculation results with the data of pilot installation operation showed that the composition of final products of plasma gasification corresponded to the final equilibrium state (x^{eq}) of the ordinary gasification processes (with production of energy that was needed for the endothermal process supplied by burning an additional amount of fuel). The difference between plasma and traditional technologies is that in the latter the point x^{eq} is not reached. Therefore, condition (2.78) in thermodynamic calculations of plasma gasifiers was unnecessary.

FIGURE 5.24. The share of active species x (atoms, ions, etc.) in the plasma-forming gas versus its temperature T_{pl}. 1–CO_2 ; 2– H_2O; 3–H_2 or O_2.



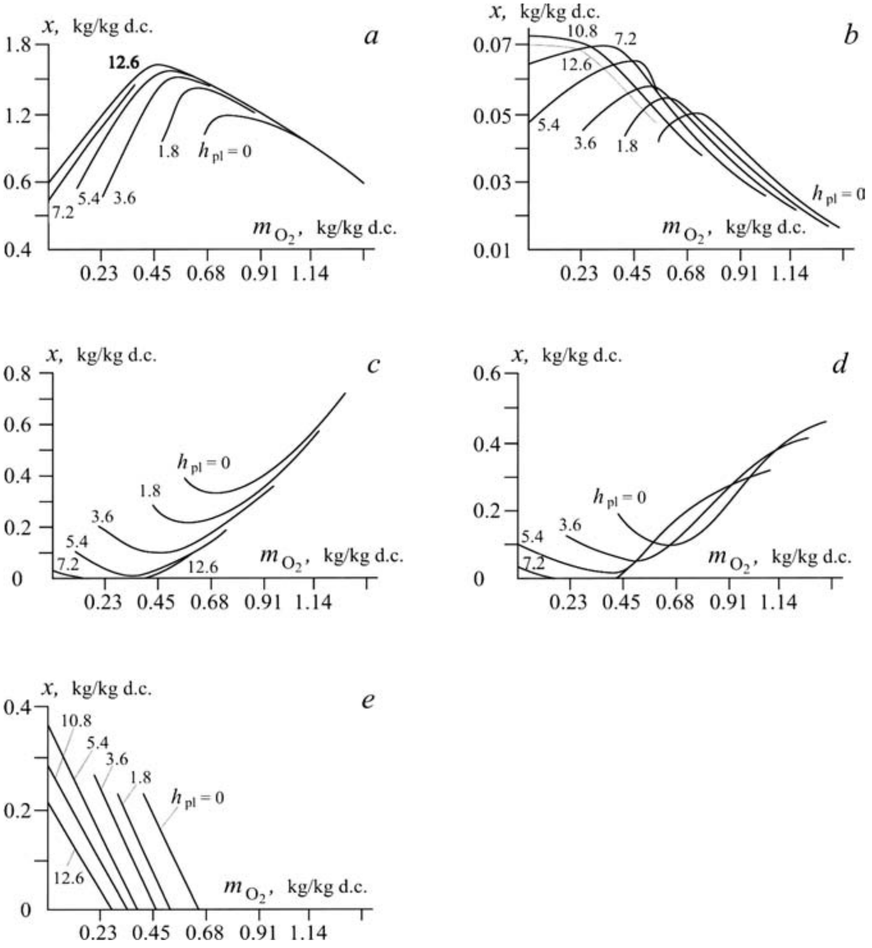


FIGURE 5.25. Plasma gasification of coal. Specific yields of (*a*) carbon oxide x_{CO}, (*b*) hydrogen x_{H_2}, (*c*) carbon dioxide x_{CO_2}, (*d*) water vapor x_{H_2O}, and (*e*) condensed carbon x_{C_c} as functions of oxygen consumption m_{O_2} at different plasma energy values h_{pl}, MJ/kg d.c. ($m_{H_2O} = 0.114$kg/kg dry coal).

This electric neutrality equation should obviously be included in the system of MEIS constraints at modeling the processes in plasmatrons and when choosing the plasma-forming gases.

The main plasma-forming gases in technologies of fossil fuel processing and burning may be H_2O, CO_2, and O_2 (in some cases H_2). MEIS was applied to study their ability to ionize in the range of operation temperatures (2500–8000 K) of plasmatrons [82]. The calculation results are given in Fig. 5.24, which shows that CO_2 is ionized the most easily, H_2O is ionized with considerably more difficulty, and O_2 and H_2 are ionized most poorly. At $T = 3500$ K the quantity of active species in CO_2 plasma is 47% higher than in plasma of H_2O and 88% higher than in plasma of O_2 and H_2; for $T = 4500$ K these ratios make up 14% and 59%, respectively. Hence, CO_2 and H_2O are the most adequate for use as plasma-forming gases.

As in the previous examples of combustion and gasification, the perfection limits of plasma technology were calculated as applied to Kansk–Achinsk coal. In calculations the values of specific (per 1 kg of dry coal (d.c.)) consumption of water vapor, oxygen and plasma energy were varied over wide ranges. The calculations resulted in determination of dependences of process equilibrium temperature and the product specific yields (CO, H_2, CO_2, H_2O, etc.), as well as the dependences of efficiency on the indicated varied quantities. Some calculation results are presented in Fig. 5.25.

The thermodynamic analysis of competing coal gasification processes showed that the plasma processes are characterized by higher yields of the target products CO and H_2 and lower yields of the ballast constituents. Application of the results of thermodynamic modeling in broader technical and economic studies on plasma gasification proved that this process can be competitive when electricity consumption for plasmatrons is no more than 6–7% of the total energy (chemical and electric) consumption [82]. The current progress in plasma technologies allows us to take these figures as attainable [95, 149].

Conclusion

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

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

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

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

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

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

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

Afterword

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

Supplement

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

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

Introductory Remarks

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

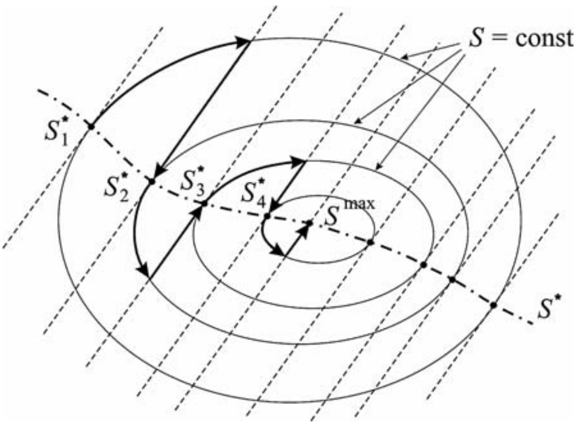


FIGURE S.1. Entropy-conserving dynamics with periodic coarse graining.

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

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

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

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

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

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

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

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

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

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

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

Find

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

subject to

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

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

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

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

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

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

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

Examples of Equilibrium Description Application

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

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

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

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

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

Find

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

subject to

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

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

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

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

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

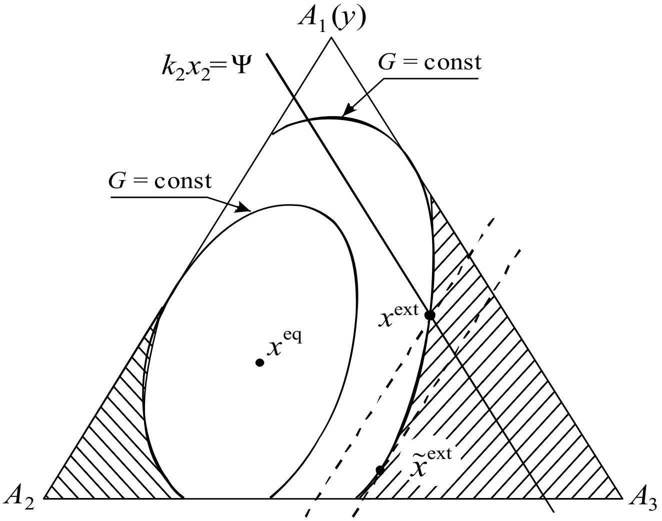


FIGURE S.2. Graphical interpretation of isomerization process.

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

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

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

(see Section 2.2).

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

(S.10) the following reactions are considered:

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

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

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

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

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

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

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

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

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

$$x_{NO} \le K x_O^{ext}. \tag{S.17}$$

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

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

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

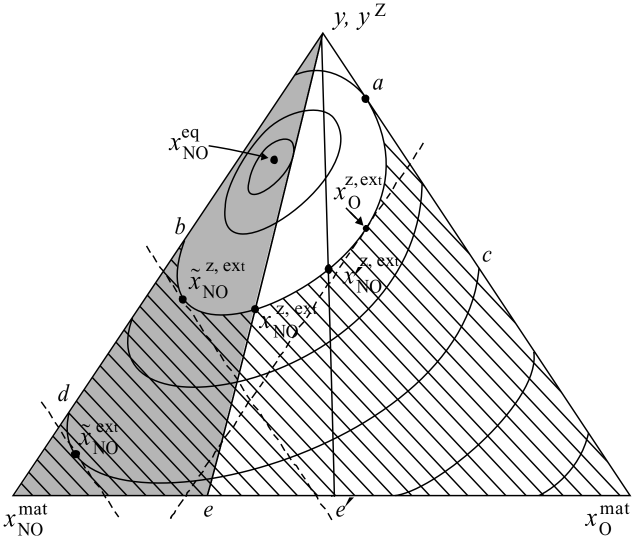


FIGURE S.3. Graphical interpretation of the nitrogen oxide formation.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Find

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

subject to

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

$$\sum_{i=1}^{n} \left|P_i^{\text{br.k}}\right| \left(\gamma_i^{\text{br}} P_i^{\text{br.k}} - \gamma_i^{\text{fr}} x_i^{k2}\right) \geq 0, \tag{S.22}$$

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

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

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

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

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

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

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

Conclusion

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

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

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

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

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