# 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 $c$, $x$, $\lambda$ and $\varphi$ 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

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

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 $\varphi_i$, 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 $\Pi$ 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 ($\lambda_i$). 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 $\lambda_i$ try to decrease the bond deformations, the equilibrium between $c_j$ and $\lambda_i$ 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 $\lambda_i$ 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):

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

where $\delta$ is a function variation, $J$ is an action, and $\tau$ 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 $r$; $\vartheta$ 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; $\sigma$ is a differential effective cross-section of particle scattering into the solid angle $d\Omega$; $\vartheta$ 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 $\tau$ 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, $\mu$ 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

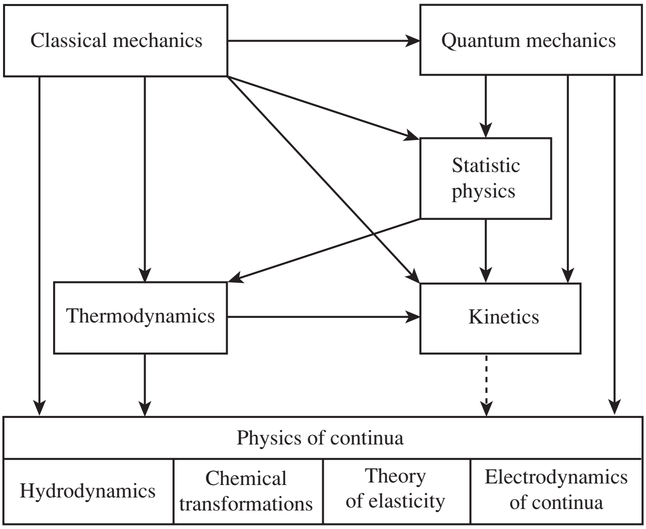

FIGURE 1.1. Relations of thermodynamics to other divisions of theoretical physics.

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):

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

where $G_j$ is molar Gibbs energy of the $j$th 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 $i$th element in a mole of the $j$th component; and $b_i$ is the mole quantity of the $i$th 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 $\nu_j$ 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 $\nu$ 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 $j$th 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 $x_{\text{com}}$ 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 $i$th reagent in the initial state of the system. Based on the positivity of $x_{\text{com}}$ ($x_{\text{com}} > 0$) and negativity of $\nu_j$ 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 $\nu_j$), 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, $\sigma$ 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 $\Delta x$ 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 $\eta$ 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 $\lambda$ 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 $\rho$ 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 $\delta r$ are the pipe radius and its increase due to shock, respectively; $\rho$ and $\delta \rho$ are initial density of the liquid and its increase due to compression, respectively; $\lambda$ is a Lagrange multiplier, here interpreted as a stress in the pipe wall caused by its deformation; and $\varphi$ 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) $\delta r$ 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):

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

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 $\varepsilon_j$.

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 $\varepsilon_j$ can take only discreet values proportional to $Nh\nu$ ($h$ is a Planck constant, $\nu$ 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 $k = \frac{R}{N}$).

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 $\nu^2$ (see, for example, [49]) and integrating by $\nu$, 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 J/mole | State, mole/kg | | |
|---|---|---|---|---|---|
| Name | Formula | | Initial | Equilibrium | Extreme* |
| Benzpyrene | $C_{20} H_{12}$ | 245377 | 0.00 | 0.00 | $4.65\cdot10^{-4}$ |
| Peroxy acetyl nitrate | $CH_3COONO_3$ | −220359 | 0.00 | 0.00 | $3.98\cdot10^{-3}$ |
| Trichlor ethane | $C_2 H_3 Cl_3$ | −240257 | $3.43\cdot10^{-7}$ | 0.00 | $5.30\cdot10^{-7}$ |
| Hydrocarbons | $C_2H_4$ | −12922 | $1.70\cdot10^{-9}$ | 0.00 | — |
| CFC-12 | $CF_2Cl_2$ | −575676 | $1.72\cdot10^{-8}$ | 0.00 | $1.03\cdot10^{-7}$ |
| | $CFCl_3$ | −377308 | $1.72\cdot10^{-7}$ | 0.00 | $2.06\cdot10^{-7}$ |
| Methane | $CH_4$ | −130107 | $5.83\cdot10^{-3}$ | 0.00 | — |
| Carbon monoxide | CO | −169407 | $7.00\cdot10^{-6}$ | 0.00 | — |
| Carbon dioxide | $CO_2$ | −457182 | $1.20\cdot10^{-2}$ | $1.79\cdot10^{-2}$ | $1.79\cdot10^{-2}$ |
| Carbonyl sulfide | COS | −210718 | $5.83\cdot10^{-8}$ | 0.00 | $7.00\cdot10^{-7}$ |
| Chlorine | $Cl_2$ | −66450 | 0.00 | $6.44\cdot10^{-7}$ | — |
| Hydrogen | $H_2$ | −38905 | $1.92\cdot10^{-5}$ | 0.00 | — |
| Water vapor | $H_2O$ | −298051 | 1.04 | 1.05 | 1.05 |
| Hydrogen peroxide | $H_2O_2$ | −205732 | $6.42\cdot10^{-9}$ | 0.00 | — |
| Sulfuric acid | $H_2SO_4$ | −821886 | 0.00 | $7.00\cdot10^{-7}$ | $7.00\cdot10^{-7}$ |
| Hydrochloric acid | HCl | −147978 | $1.17\cdot10^{-8}$ | $3.02\cdot10^{-7}$ | $1.59\cdot10^{-6}$ |
| Hydrogen chloride | HF | −325045 | 0.00 | $2.06\cdot10^{-7}$ | — |
| Nitrous acid | $HNO_2$ | −154133 | $7.70\cdot10^{-13}$ | $1.17\cdot10^{-12}$ | $7.9\cdot10^{-2}$ |
| Nitric acid | $HNO_3$ | −213410 | $5.01\cdot10^{-8}$ | $5.73\cdot10^{-8}$ | $1.38\cdot10^{-1}$ |
| Hydroperoxyl | $HO_2$ | −58563 | $2.30\cdot10^{-12}$ | 0.00 | — |
| Nitrogen | $N_2$ | −57072 | 26.79 | 26.79 | — |
| Nitrogen pentoxide | $N_2O_5$ | −92682 | $2.90\cdot10^{-10}$ | 0.00 | $4.33\cdot10^{-2}$ |
| Nitrogen oxides | NO | 28487 | $5.90\cdot10^{-12}$ | $6.17\cdot10^{-15}$ | $6.55\cdot10^{-2}$ |
| | $NO_2$ | −37345 | $4.19\cdot10^{-9}$ | $4.27\cdot10^{-9}$ | $1.18\cdot10^{-1}$ |
| Oxygen | $O_2$ | −61110 | 7.19 | 7.18 | — |
| Ozone | $O_3$ | 70613 | $1.39\cdot10^{-6}$ | 0.00 | — |
| Sulfur oxides | $SO_2$ | −370743 | $6.42\cdot10^{-7}$ | 0.00 | $7.00\cdot10^{-7}$ |
| | $SO_3$ | −472315 | 0.00 | $2.17\cdot10^{-14}$ | — |

* 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 ($x^{\mathrm{eq}}$). 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 $x^{\mathrm{eq}}$ 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 $x^{\mathrm{eq}}$.

For partial equilibria, as well as for $x^{\mathrm{eq}}$, 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 $x^{\mathrm{eq}}$) monotonically does not increase. Similar to $x^{\mathrm{eq}}$, 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 $y = (0, 0, 1)^T$ (vertex$A_3$). Figure 1.2a shows the point of equilibrium $x^{\mathrm{eq}}$, 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*) $A_1 \rightleftarrows A_2, \quad A_1 \rightleftarrows A_3, \quad A_1 + A_2 \rightleftarrows 2A_3$

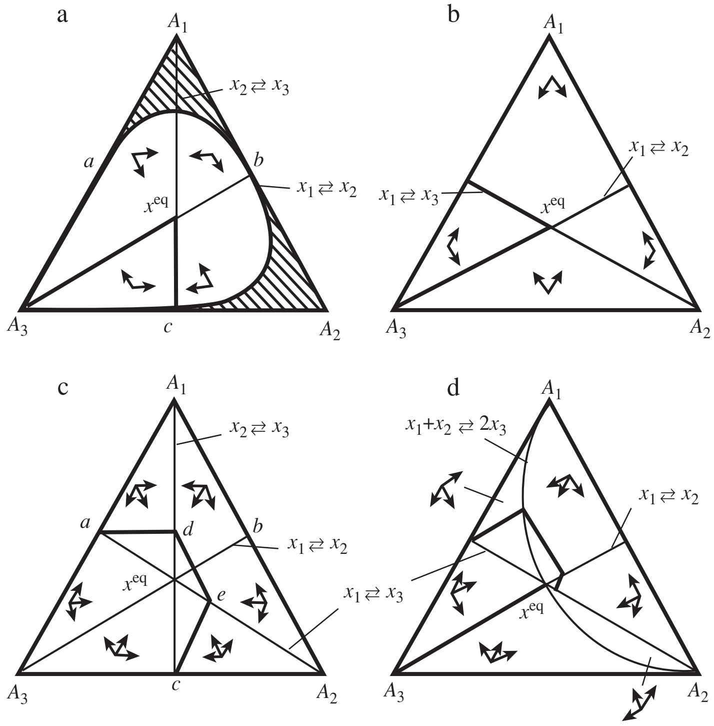

FIGURE 1.2. A graphical interpretation of the algorithm of search for attainable states of a thermodynamic system at a given mechanism of the process.

Let us consider construction of a set of possible equilibria for the mechanism $c$. To determine the possible direction of the reaction near vertex $A_3$set 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; $\alpha_j$, $\beta_j$ 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 ($\alpha_j$) and as a product ($\beta_j$). Both forward and reverse reactions are written in (1.69). For the reverse reaction $\beta_j$ is the number of molecules $A_j$ taking part in one act of reaction as an initial reagent; $\alpha_j$ 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 $\gamma_r$ 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 $j$th 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 $j$th component. Specifically, $c_j$ is the number of species (moles) of the $j$th 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 $j$th 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 non-isolated 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 $M_j$ $(j = 1, \dots, n)$, 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:

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

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

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

where $\lambda_i$ are the uncertain Lagrange multipliers. One of the explanations of expression (1.77) consists in the fact that the scalar product $M, \mu\left(M^{\mathrm{eq}}\right) = \sum\limits_j M_j, \mu_j\left(M^{\mathrm{eq}}\right)$ 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 $\rho$, 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 $\lambda$: $f(kM) = k^\lambda f(M)$ 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 $\lambda$, 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 $j$th coordinate in this basis.

The mechanism is the list of elementary processes each set by its stoichiometric equation of the form (1.69), the $r$th elementary process is assigned its stoichiometric vector $\gamma_r$ 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 $\tau$ 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

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

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 $\gamma_r$ 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 $\tau$ 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 $\mu_j$ 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 $\lambda$. 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 $\varphi_r$, 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 $\alpha_{rj}$ 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, $\gamma_s$ 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 $\varphi_s$ 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 $\mu^p$ *thermodynamically admissible* if for any stoichiometric vector $\gamma_s$,

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

The vector of pseudopotentials $\mu^p$ 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 $\chi$ 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 $\mu^p$.

The physical sense of the orthogonality conditions of the vectors $\gamma_s$ and $\chi$, 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 $\mu^p$. The thermodynamic admissibility $\mu^p$ 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; $\lambda$ 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; $\varphi_t$ 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 $\varphi_t$ 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:

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

The thermodynamic Lyapunov function $G(x, U, U_T, V, V_T)$ is constructed again as $-\frac{S_\Sigma}{R}$, where $S_\Sigma$ 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 $\mu$ we can write the necessary conditions of extremum in the problems with linear constraints

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

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):

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

where $\lambda_i$ 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 $\mu$.

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 $M = (M_1, \ldots, M_m)$ 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 $\mu_{M_j} = \dfrac{\partial H(M)}{\partial M_j}$. $\mu_M$ is a vector with coordinates $\mu_{M_j}$. 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 $\mu_M$ find vector $\mu$ 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 $\mu\,(\mu_M)$ and $x\,(\mu\,(\mu_M))$ (see (1.119)–(1.121)). As a result, we obtain

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

where $\mu_M l$ is the product of the vector of line $\mu_M$ 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 $\mu_M$. To set them as functions of $M$, we have to make the Legendre transformation, find the function $H(M)$ through $G\,(\mu_M)$ 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 $\mu$, that is,

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

then equations (1.124) acquire a particularly simple form:

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

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

$$H(M) = (\mu_M, l\Psi\,(\mu_M l)) = (\mu_M l, \Psi\,(\mu_M l)) \leq 0,$$

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

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 $\mu_M$ or $x$ and $\mu$.

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 $\Phi$ is represented as a sum by stages $\sum\limits_s \Phi_s$

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

where $V$ and $\varphi_s$ 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 $\Phi$ 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 $\tau$ 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 $\upsilon$ is flow rate; $c$ is concentration; $\varphi$ 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

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

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 $s$, $z$, $\sigma$ 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 $RT_{\text{ent}}$ 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

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

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

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

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:

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

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

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 $\upsilon_{\text{ent}}$ and $\upsilon_{\text{out}}$ 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,

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

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

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

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 $T^0$, $c_{\text{ent}}$, $\nu_{\text{ent}}$ and $\nu_{\text{out}}$, 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 $c^{\text{eq}}$ 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 $\gamma$ for which $\sum\limits_j a_{ij}\gamma_j=0$. 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 $c^{\text{eq}}$ 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 $c^{\text{eq}}$. 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 $T^0$, $c_{\text{ent}}$, $\upsilon_{\text{ent}}$, $\upsilon_{\text{out}}$ 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 $\dfrac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}}c_{\text{ent}}$. 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 $\dfrac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}}c_{\text{ent}}$. 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

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

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 $\upsilon_{\text{ent}}$, $\upsilon_{\text{out}}$ 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 $c^{\text{eq}}$ and the vector $\dfrac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}}$. 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 $c^{\text{eq}}$ at high rates of chemical reactions and near $\dfrac{\upsilon_{\text{ent}}}{\upsilon_{\text{out}}} c_{j\text{ent}}$, 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

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

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 $\sigma$, 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 $\mu_{x1}$, $\mu_{x2}$ are vectors of chemical potentials of substances of the first and second groups, respectively. In the assumption that $\mu_{x1}$ 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 $\delta_\sigma$.

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 $\sigma, z$. 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 $\gamma$ 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,

$$\sum_{\sigma} \lambda_\sigma \gamma_{\sigma 2}^{12} \operatorname{sign}(w_\sigma^{12}) + \sum_{z} \lambda_z \gamma_z^{2} \operatorname{sign}(w_z^{2}) = 0. \tag{1.155}$$

This statement allows inversion: if, for the given point $c^{02}$ there are positive numbers $\lambda_\sigma$, $\lambda_z$ such that conditions (1.155) are met, then there are such rate functions $w_\sigma$ 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 $\mu_{x2}$ 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

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

For each arrangement of signs in (1.156) we can answer the question if a set of positive numbers $\lambda_\sigma$, $\lambda_z$ 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 $\varepsilon_\sigma$, $\varepsilon_z$ such that for any $\sigma$, $z$ there will be $\varepsilon_\sigma, \varepsilon_z = 1, -1$, or 0. Each signature $\varepsilon$ is bound to a set of those $\mu_{x2}$ for which at all $\sigma$, $z$

$$\operatorname{sign}\left(\delta_\sigma + \left(\gamma_{\sigma 2}^{12}, \mu_{x2}\right)\right) = -\varepsilon_\sigma, \ \ \operatorname{sign}\left(\gamma_z^{2}, \mu_{x2}\right) = -\varepsilon_z. \tag{1.157}$$

Denote this set as $M_\varepsilon$.

For each signature $\varepsilon$ we can find out if there positive numbers $\lambda_\sigma$, $\lambda_z$ 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 $\varepsilon$ for which such combinations of $\lambda_\sigma$ and $\lambda_z$ exist. The set of all possible values of chemical potentials $\mu_{x2}$ 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 $M_\varepsilon$.

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 $\mu_{x2}$, 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 $c^0$can 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 $\mu_x$.

Compare with each signature $\varepsilon_s$ a “compartment,” the set $M_\varepsilon$ specified in the coordinates $\mu_x$ by a linear system of equations and inequalities

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

In the compartment $M_\varepsilon$ we have $\operatorname{sign}(w_s) = \varepsilon_s$ for all $s$. For some $\varepsilon$ the system (1.162) may turn out to be incompatible and the set $M_\varepsilon$ may appear to be empty. Each signature $\varepsilon$ is corresponds to a convex set $Q_\varepsilon$ 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 $\lambda_s$ such that $q = \sum_s \lambda_s \gamma_s \varepsilon_s$. We describe $Q_\varepsilon$ by linear equations and inequalities for all $\varepsilon$ such that $M_\varepsilon \neq \emptyset$. If the point $c^0$ belongs to $M_\varepsilon$, 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 $Q_\varepsilon$.

At a given $c_{\text{ent}}$ for each $\varepsilon$ 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 $M_\varepsilon$ is linear in coordinates $\mu_x$; the second one that expresses the belonging of $c^0 - c_{\text{ent}}$ to the set $Q_\varepsilon$ 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 $M_\varepsilon$ 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 $M_\varepsilon$. Among them 6 are two-dimensional, 6 are one-dimensional

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*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 $\varepsilon$ corresponds to the set $Q_\varepsilon$, an aggregate of linear combination with positive coefficients of vectors $\gamma_s \varepsilon_s$. The compartments $M_\varepsilon$ and sets $Q_\varepsilon$ are shown in Fig. 1.3. For $\varepsilon = (0, 0, 0)$ obviously

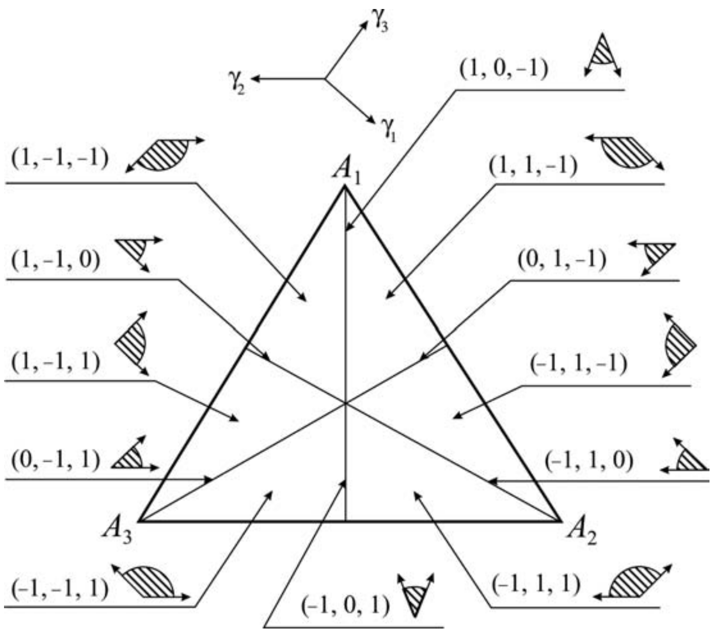

FIGURE 1.3. Compartments $M_\varepsilon$, sets $Q_\varepsilon$ (inside the dashed angles).

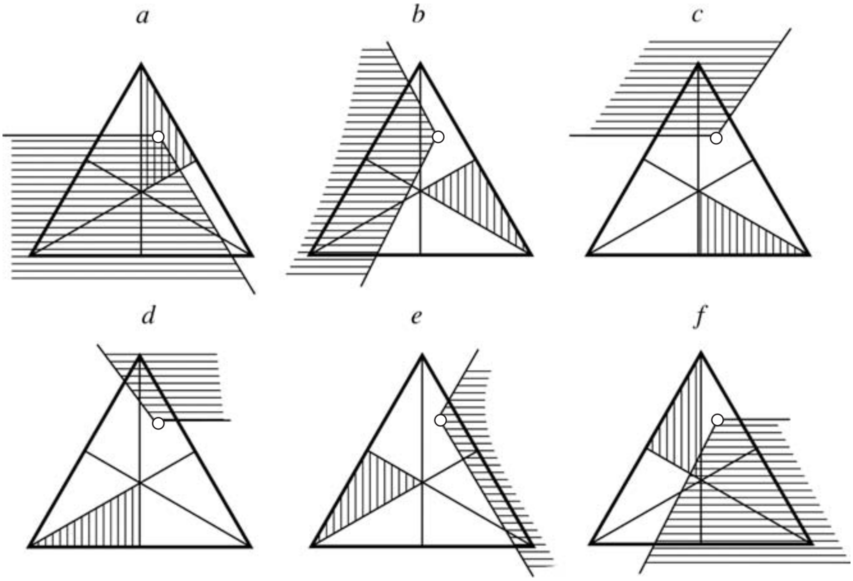

FIGURE 1.4. The sets $c_{\text{ent}} + Q_\varepsilon$ (horizontal dashing) and compartment $M_\varepsilon$ (vertical dashing) for signatures. a. (1, 1, –1), b. (–1, 1, –1), c. (–1, 1, 1), d. (–1, –1, 1), e. (1, –1, 1), f. (1, –1, –1).

$Q_\varepsilon = \{0\}$. For the remaining $\varepsilon$ the sets $Q_\varepsilon$ 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 $M_\varepsilon$ 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 $M_\varepsilon$ consider the set $c_{\text{ent}} + Q_\varepsilon$. Combination for all $\varepsilon$ 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 $M_\varepsilon$ 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 $c_{\text{ent}}$ 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 $M_\varepsilon$ at four more different $\varepsilon$. 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 $\varepsilon$ except for the above $\varepsilon = (1, 1, -1)$. The regions of possible stationary states in the three described cases are shown in

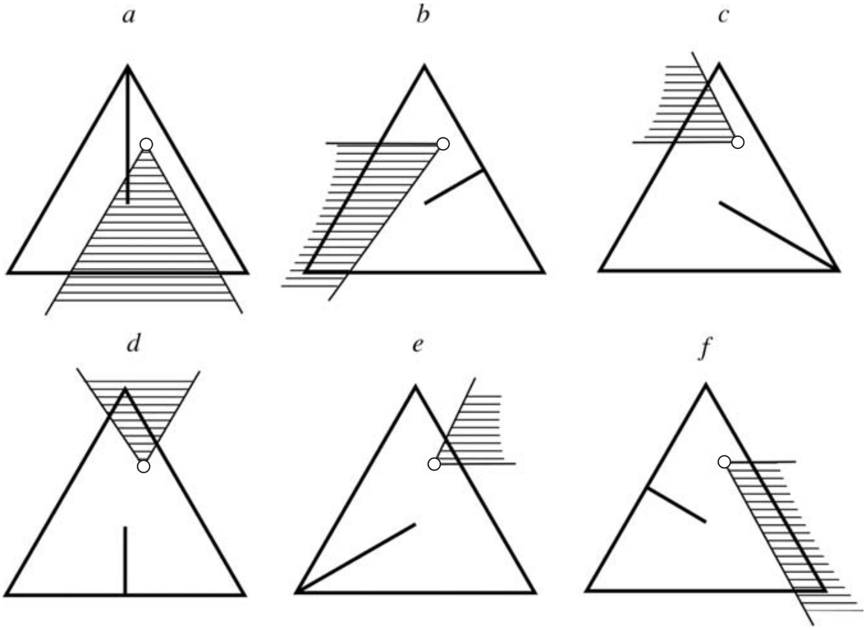

FIGURE 1.5. Sets $c_{\mathrm{ent}} + Q_{\varepsilon}$ (horizontal dashing) and compartments $M_{\varepsilon}$ (bold sections) for signatures. *a.* (1, 0, –1), *b.* (0, 1, –1), *c.* (–1, 1, 0), *d.* (–1, 0, 1), *e.* (0, –1, 1), *f.* (1, –1, 0).

Figs. 1.6*a–c*. These regions are open and not always convex (Fig. 1.6*a*, *b*). The input mixture $c_{\mathrm{ent}}$ 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.

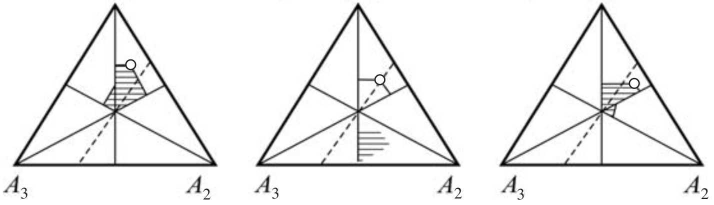

FIGURE 1.6. Sets of possible stationary states $M^0$ for the homogenous CSFR (dashed). *a.* $c_{2\mathrm{ent}} < c^{\mathrm{eq}}$; *b.* $c_{2\mathrm{ent}} = c^{\mathrm{eq}}$; *c.* $c_{2\mathrm{ent}} > c^{\mathrm{eq}}$; dashed line is set by the equality $c_2 = c^{\mathrm{eq}}\,(c_{1\mathrm{ent}} > c_{2\mathrm{ent}}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

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.