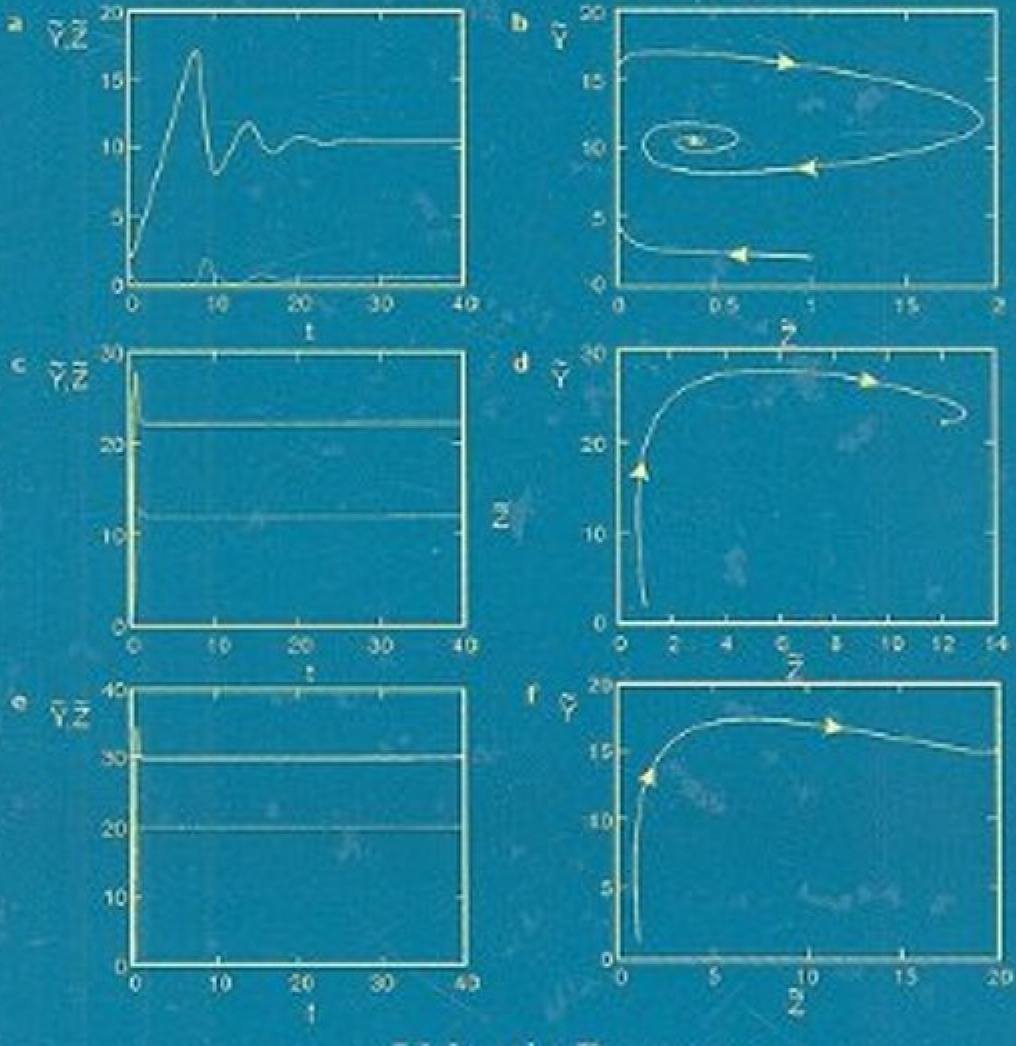
Thermodynamics of Non-Equilibrium Processes for Chemists with a Particular Application to Catalysis



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To my scientific parents, Kirill Zamaraev and Georgij Zhidomirov

PREFACE

Thermodynamics of nonequilibrium and irreversible processes is a comparatively new area of thermodynamics that goes back to the 1950s. This area is traditionally considered very complex and inapplicable for routine chemical investigations. Therefore, the traditional version of this discipline usually is taught to only those chemical students who have a very strong background in physics.

For this book, the author has adapted the thermodynamics of nonequilibrium processes course that has been taught since 1995 at the Department of Natural Sciences of the Novosibirsk State University. It was determined that the subject can be taught in such a way that anyone who has formal physicochemical education in the fields of classical thermodynamics of equilibrium processes and traditional chemical kinetics should be able to understand the topic.

Moreover, the discipline combines thermodynamics and chemical kinetics and thus may be helpful to researchers who are engaged in studying complex chemical transformations—in particular, catalytic transformations. For example, some of the important concepts in this subject are the conditions of kinetic irreversibility of complex stepwise stoichiometric reactions and rate determining and rate limiting stages. The lecturers in traditional chemical kinetics recognize that these concepts are not simple ones and tend to "conceal" them in their courses. Fortunately, these concepts appear to be consistently and properly defined in terms of thermodynamics of nonequilibrium processes.

Traditionally, the introduction to thermodynamics of nonequilibrium processes is introduced at the end of a course on classical equilibrium thermodynamics. However, it has become evident that for successful learning, thermodynamics of nonequilibrium processes should be presented only after a formal course of chemical kinetics. For this reason, it was decided in the Novosibirsk State University to offer thermodynamics of nonequilibrium processes as a separate course to finalize and generalize the common semestrial courses of classical thermodynamics and chemical kinetics at the Department of Natural Sciences. Since 1999, the course has been offered to all four year students at the department and updated constantly because of progress in the field. As a result, the scope and sequence of this course differ considerably from other versions.

This book is a synopsis of lectures on thermodynamics of nonequilibrium processes and from a course on thermodynamics of operating catalysts, both from Novosibirsk State University. The content of this book mostly reflects the author's particular scientific interests. Therefore, the author apologizes to those who expected to find information on irreversible processes like diffusion in synthesis materials. It is hoped that the author's approach to teaching nonequilibrium thermodynamics will be adopted by others.

The author would like to express his cordial gratitude to Mrs. Natalia Chistyakova and Elena Nikiforova, who patiently assisted him during the preparation of the lectures for Russian speaking students, as well as with translations and preparation of the English version.

Valentin Parmon
March 2009, Novosibirsk, Russia

LIST OF MAIN SYMBOLS

A, B, C, etc.	substances
$\tilde{A}$	thermodynamic rush (absolute activity) of substance A
A_r	affinity of chemical reaction
c	molar concentration
CF	rate controlling factor
G	the thermodynamic Gibbs potential
H	enthalpy
h	the Planck constant
i,j	indices of reaction groups
J	flux of a thermodynamic parameter
k	traditional constant of the reaction rate
k_B	the Boltzmann constant
L_{ij}	the Onsager reciprocity coefficient
$\tilde{n}$	thermodynamic rush (of a reaction group or substance)
$\boldsymbol{P}$	rate of energy dissipation
p	pressure
Q	quantity of heat
R	universal gas constant
r	size of a particle
S	entropy
s	local density of entropy
T	thermodynamic temperature
U	internal energy
V	volume
v	rate of a reaction
X	thermodynamic force
α	index of substance A_α
γ	coefficient of activity or fugasity
ε	"truncated" constant of the reaction rate
Λ_{ij}	reciprocity coefficient in the Horiuti Boreskov Onsager relations

μ	chemical potential
ξ	the chemical variable
σ	rate of entropy production
Σ	index of a stepwise transformation
Φ	Lyapunov function

AN INTRODUCTION TO THE PROBLEMS UNDER DISCUSSION

The main aim of thermodynamics as a particular science is to predict the final state a system must reach under given ambient conditions and to describe some important properties of this state. The transition to the state is a consequence of a chain of successive spontaneous transformations that occur in the course of the *spontaneous evolution* of the system.

In the traditional (*classical*) thermodynamics, one of the principal conclusions is that the final state of *closed* systems is the *full thermodynamic equilibrium*. This equilibrium is stable and characterized by the minimum of a related thermodynamic potential F:

$$dF = 0;\ d^2F > 0.$$

Depending on the additional external conditions imposed on the system evolution, thermodynamic Gibbs (G), Helmholtz (A), etc. potentials are minimized.

The reason for the spontaneous evolution with minimizing thermodynamic potentials is the Second Law of Thermodynamics that needs an inevitable increase in entropy, S, of any isolated system with irreversible processes occurring in it. Unfortunately, the classical equilibrium thermodynamics is incapable of predicting the *path of this evolution*. Moreover, classical thermodynamics does not take into consideration at all the time factor, which is the principal parameter of any evolution.

In *open* systems, which are characterized by an exchange of matter with the surrounding medium, the evolution towards stable thermodynamic equilibrium may appear to be impossible in principle. However, the spontaneous evolution of such systems leads also to some state with its properties being dependent on the boundary conditions for the system. We shall consider, in general, that the system exists in a *dynamic equilibrium* if the imposed boundary conditions are *compatible* with such equilibrium. The latter means that, for example, the system may achieve a *stationary* state implying no change in the matter concentration and/or temperature field distribution in time. The typical and limit example of the dynamic equilibrium is indeed the stable thermodynamic equilibrium.

In the absence of an external force field, the system at stable thermodynamic equilibrium must be fully uniform (isotropic) in respect of such parameters as temperature, pressure and chemical potentials of all the involved components. In other words, there are zero gradients of these parameters through the inner space of the system at the thermodynamic equilibrium. As a result, any matter or energy flows are not observed in these systems.

When the system is out of full thermodynamic equilibrium, its *non-equilibrium* state may be characteristic of it with gradients of some parameters and, therefore, with matter and/or energy flows. The description of the spontaneous evolution of the system via non equilibrium states and prediction of the properties of the system at, e.g., dynamic equilibrium is the subject of *thermodynamics of irreversible (non-equilibrium) processes*. The typical purposes here are to predict the presence of solitary or multiple local *stationary* states of the system, to analyze their properties and, in particular, stability. It is important that the potential instability of the open system far from thermodynamic equilibrium, in its dynamic equilibrium may result sometimes in the formation of specific rather organized *dissipative structures* as the final point of the evolution, while traditional classical thermodynamics does not describe such structures at all. The highly organized entities of this type are living organisms.

The problem of spontaneous evolution of chemically reactive systems has a close relation to the topics of chemical kinetics. Hence, thermodynamics of irreversible processes allows, among others, some important interrelations to be established between kinetics of particular chemical processes and thermodynamic parameters of the reactants involved.

Thermodynamics of irreversible processes as a consistent science was created in the late 1940's, its creation is to a great extent associated with the names of R. Onsager, I. Prigogine, L. Glansdorf, V. De Groot and other eminent scientists. Two of them – R. Onsager and I. Prigogine – were awarded the Nobel Prize in 1968 and 1977, respectively. At present, this field of science is progressing.

Thermodynamics of non equilibrium processes relates directly to any chemical transformations. In the course of a complex multistep chemical transformation, any, even a spatially homogeneous but reactive, system may be considered indeed as an open system with respect to the concentrations of *reaction intermediates* because their concentrations always depend on the externally given concentrations of initial reactants and often on the concentrations of final products of the transformation.

Moreover, many dynamic chemical systems, for example catalytic and biological, stop *operating* at the state of full thermodynamic equilibrium.

Operation of such systems is only possible when they have *exchange of matter with the environment*, i.e. when they are *open* with respect to the initial reactants and final products; i.e. the systems exist in a thermodynamically non equilibrium state. Evidently, the non equilibrium state of open systems can only be maintained due to the occurrence of *thermodynamic driving forces* which are responsible for generation of matter and/or energy flows.

A particular contribution of thermodynamics of non equilibrium processes is the possibility of describing an *interference* of various processes that proceed simultaneously in non equilibrium systems. A spectacular example of the interference is interdependence of the rates of various stoichiometric *stepwise chemical processes* (i.e. transformations with a set of intermediate steps) with the common reaction intermediates.

Traditionally, direct kinetic methods are used to describe and analyze an operating reactive system by writing and solving a system of kinetic differential equations. The evident advantages of such an approach are thoroughly adapted algorithms for deriving and solving the kinetic equations, convenient criteria for analysis of the kinetic scheme stability, as well as possibility of describing some specific dynamic effects like existence of multiple stationary states, potential oscillations in the rate of complex chemical reactions, "limit cycles", bifurcations, chaotic reaction modes, etc. However, the necessary condition for obtaining adequate results of such analysis is the validity of the *a priori* insight into the scheme of chemical transformations under study and exact enough knowledge on the rate constants of individual elementary steps.

Chemical kinetics resembles (in some sense) classical mechanics, which allows the final state of the dynamic systems to be accurately predicted when dynamic equations are known for describing the time behavior of the system and exact starting conditions are given. On the other hand, in complex kinetic schemes, the final result of the transformations under consideration is expected to change considerably depending on the particular assumptions about elementary steps of the process and the choice of the kinetic scheme, as well as on the assumptions, rather arbitrary sometimes, about reversibility of each of these steps. This makes it difficult to describe the time evolution of the systems with poorly understood or complex mechanisms of chemical transformations.

Some of the above enumerated problems can be resolved when taking into consideration that chemical transformations are initiated everywhere by thermodynamic driving forces, which exist in the system and change along with the transformations. Analysis of the influence of these forces is the challenge of thermodynamics of non equilibrium processes. The present book demonstrates the possibility of the useful application of tools of thermodynamics of non equilibrium processes for analyzing the state of operating chemically reactive systems, in particular for predicting the path of the evolution of these systems and rate of some stepwise processes, even though the intimate mechanism of the analyzed processes is not fully understood.

As applied in the analysis of heterogeneous phenomena, a well known serious limitation of the purely kinetic approach is the extremely difficult description, in terms of kinetics, of phase equilibria of individual phases in the reaction system at its operation. In a system at full equilibrium, the traditional instrument for studying these phenomena is classical thermodynamics, while thermodynamics of non equilibrium processes can help in analyzing evolving systems.

Essential advantages of the thermodynamics of non equilibrium processes are: the possibility of correct quantitative explanation of important concepts of rate limiting and rate determining steps at complex chemical transformations; the possibility of the use of one effective transformation instead of a series of the reaction intermediate transformations, without the loss of the correctness when analyzing a specific influence of this transformation series on the total course of the complex process; as well as the possibility of analyzing the influence of thermodynamic parameters of both external reactants and of reaction intermediates on some important parameters of complex reactions like apparent activation energy, etc.

Again, a considerable generalization in treating very large ensembles of interacting objects opens the transfer from classical mechanics to statistical physics. By analogy, thermodynamics of non equilibrium processes plays the role of statistical physics in the analysis of large ensembles of chemical transformations. The identification of driving forces of these transformations allows general conclusions to be made on the path of evolutionary changes in a complex chemically reactive system, as well as on its final state, irrespective of the specific mechanisms of the elementary processes involved.

Thus, the tools of thermodynamic of non equilibrium processes make it possible to have a combined kinetic and thermodynamic analysis of many complex chemical processes that is hardly possible using other methods. It is of importance that in thermodynamics of non equilibrium processes, the time factor becomes as significant as the traditional thermodynamic parameters.

CHAPTER 1

Systems in Thermodynamics of Nonequilibrium Processes

Contents

1.1. DEFINITIONS

Thermodynamics of nonequilibrium (irreversible) processes is an extension of classical thermodynamics, mainly to open systems. Unfortunately, the Second Law of classical thermodynamics cannot be applied directly to systems where nonequilibrium (i.e., thermodynamically irreversible) processes occur. For this reason, thermodynamics of nonequilibrium processes has used several principal concepts that are supplementary to the classical thermodynamics postulates. In contrast to the postulates, many of the concepts in thermodynamics of nonequilibrium processes can be mathematically substantiated by considering, for example, the time hierarchy of the processes involved.

The following are the basic propositions as supplementary concepts of this topic:

1. In any system under study, the processes can be classified into *external* (induced by outside forces) and *internal* ("spontaneous"), and, as a consequence, the changes in the system state caused by the external and internal thermodynamic forces can be examined separately in the overall entropy changes.
2. The variety of "spontaneous" simultaneously occurring thermodynamic processes can be considered as *conjugated* (interdependent) inside the system.
3. Of principal importance is the concept of *stability* of a nonequilibrium state of the system.

The evolution of thermodynamically nonequilibrium systems (including the systems with complex stepwise chemical transformations, among them catalytic and biological reactions) occurs with respective changes in thermodynamic parameters of the whole system or of its parts. Hence, nonequilibrium states are inherent in the nonequilibrium systems (both open and closed), while the relevant parameters and features of those states can be functions of time and/or space. For example, when a system is temperature and pressure isotropic, the Gibbs potential, G, of the entire system may be a function of not only temperature (T) and pressure (p) but also of *time* (t):

$$G = G(T, p, t) = U(T, p, t) + p(t) \cdot V(T, p, t) - T(t) \cdot S(T, p, t).$$

Here, U is internal energy of the system, V is its volume, and S is the entropy of the system.

Universal quantities T and p related to the whole system are not always appropriate for description of a nonequilibrium system due to its probable spatial inhomogeneity. In general, the nonequilibrium system needs to be characterized using *local* extensive parameters—for example, the Gibbs potential $g(T(\vec{r},t),p(\vec{r},t))$ per unit mass of the system matter. In this case,

$$G(t)=\int\limits_V \rho(\vec{r},t)g(T(\vec{r},t),p(\vec{r},t))dv,$$

where $\rho(\vec{r},t), T(\vec{r},t), p(\vec{r},t)$ are density, temperature, and pressure, respectively, of the matter in a given point $\vec{r}$ of the system at a time t, and the integration is made on all the system volume V. The function $g(T(\vec{r},t),p(\vec{r},t))$ and the other functions that are mathematically similar to it indicate the *distribution density* of the parameter of interest.

Time scales, which are characteristic of various types of physical and chemical processes, are significantly different. This makes it possible to categorize thermodynamic processes in the system into internal and external processes. Therefore, the first step in considering nonequilibrium thermodynamic processes is to establish the hierarchy of the processes along the time scale.

In this book, we shall always imply that the nonequilibrium state occurs at the *macroscopic* level. However, at the microscopic level, fast processes of thermal relaxation run into each microscopic (physically small) part of the system. These processes bring this physically small part of the system to a state that is thermodynamically stable, the relaxation being much faster than the other nonequilibrium processes under consideration.

The physically small parts of the system are those with characteristic size λ, for which the internal nonuniformities of all intrinsic macroscopic thermodynamic parameters α_i are small in comparison to the magnitudes of these parameters. While a considerable change in parameter α_i along coordinate x occurs at distance

$$L_i \approx \alpha_i \bigg/ \left(\frac{\partial \alpha_i}{\partial x}\right),$$

the said statement is equivalent to inequality

$$v^{1/3} \ll \lambda \ll L_i.$$

Here, v is the volume occupied by one particle (molecule) of the matter, and $\partial\alpha_i/\partial x$ is the gradient of parameter α_i along space coordinate x.

The putative time hierarchy means that characteristic time τ of a change of relevant thermodynamic parameters of the physically small parts under discussion is much longer than time τ_λ of the thermal relaxation in these parts but much shorter than time τ_L needed to establish the equilibrium in the entire system:

$$\tau_\lambda \ll \tau \ll \tau_L.$$

The typical τ_λ in condensed phases is no longer than 10^{8} s. This is much longer than characteristic times of oscillation periods of atoms and molecules ($\sim 10^{12}$ to 10^{13} s) but, on the other hand, much shorter than characteristic times that are necessary to detect stepwise chemical transformations (see following) in chemical synthesis, catalysis, and so on.

In these approximations, local thermodynamic quantities (e.g., pressure, temperature, concentration, etc.) may obviously be addressed to each physically small part, even at the spatial inhomogeneity of the system. This also means that in these approximations molecules of chemical compounds are "thermalized" in each physically small part of the system—that is they are in the Maxwell Boltzmann thermal equilibrium with this part of the system, and their properties can be described using the chemical potential of the compound, which would correspond to the temperature and local concentration of the compound (compounds) in the given point of the system.

While studying *stationary* (see following) states of chemically reactive systems, we shall presume, as is done in traditional courses of chemical kinetics, that the relaxation of the concentrations of intermediates of chemical transformations to some "quasi stationary" state is much faster than the change of the concentrations of initial reactants (see Section 2.1). Therefore, for example, the concentration of reactive intermediates may be considered as an "internal" parameter in contrast to the "external" parameters that are the concentrations of initial reactants and final products that change considerably more slowly.

This book treats a substance of interest in the same way as the classical "equilibrium" thermodynamics—that is, as a continuous object. For this reason, we will not discuss emergence and evolution of spontaneous fluctuations at the microscopic level that can appear due to both the atomic and molecular nature of the substance and the limited number of molecules in a finite volume. Phenomena related to the atomic and molecular nature of substances and thus involving the finiteness of the number of the substance particles in local processes are the subject of statistical thermodynamics of nonequilibrium processes that fall outside the scope of this treatment.

In the consideration of chemical transformations, we shall distinguish *elementary* and *combined (stepwise) stoichiometric* transformations. The elementary chemical transformations are those that run through the formation of only one transition state. The transition state is not thermalized, or at least not thermalized at the "reaction coordinate." The stepwise transformations comprise the formation of some intermediate products, which we shall always consider as thermalized.

To describe chemical transformations, it is very helpful to use the concept of the *reaction group*: an ensemble of thermalized compounds (molecules) that which are involved (as initial reactants or final products) directly in the chemical transformations. In describing the transformations, we shall label a Greek index—for example, α ($\alpha = 1, \ldots, k$)—to each thermalized compound A_α while labeling the reaction groups using a Latin index (e.g., i). Therefore, all stoichiometric transformations will be characterized with two Latin indices—for example, ij[*] to indicate the transformation of reaction group i into reaction group j where thermalized compounds A_α are present with stoichiometric coefficients $\nu_{i\alpha}$ and $\nu_{j\alpha}$:

$$\sum_\alpha \nu_{i\alpha} A_\alpha \rightleftarrows \sum_\alpha \nu_{j\alpha} A_\alpha .$$

A major principle in classical thermodynamics is the principle of intimate equilibrium. It means that the thermodynamic reversibility of any chemical transformations—that is, any ij transformation—must, in principle, allow for the possibility of both direct and reverse (backward) transformations. The direct and reverse transformations of elementary reactions pass through identical transition states.

We shall treat the total rate v_{ij} of a chemical transformation ij as the rate of changing the chemical variable (chemical transformation depth) ξ_{ij}—the quantity characterizing this transformation—expressed in moles

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[*] In simple cases, the transformations may be numbered with a single Latin index unless it might cause a misunderstanding.

as the number of events of resultant transformations of a given type in unit time and in unit volume:

$$v_{ij} = \frac{d\xi_{ij}}{dt}. \tag{1.1}$$

Chemical ij transformations of thermalized components in the reaction groups are described also in terms of a change in the current values of the Gibbs potentials, $\Delta_r G_{ij}$, or the value of current *affinity,* A_{rij}, of the respective transformations. These parameters relate unambiguously (by definition) to one another as:

$$A_{rij} \equiv -\Delta_r G_{ij} = -\frac{\partial G}{\partial \xi_{ij}} = \sum_{\alpha} \nu_{i\alpha}\mu_{\alpha} - \sum_{\alpha} \nu_{j\alpha}\mu_{\alpha}. \tag{1.2}$$

Here μ_α is the current chemical potential of thermalized entity A_α, and G is the Gibbs potential of the entire system under consideration.

For convenience, we shall refer to the sum of chemical potentials of the reaction group $\mu_i \equiv \sum_{\alpha} \nu_{i\alpha}\mu_\alpha$ as the *chemical potential of reaction group* i. Hence,

$$A_{rij} \equiv \mu_i - \mu_j. \tag{1.3}$$

To distinguish the affinities and rates of stepwise processes from those of elementary processes, we shall typically use symbol Σ for the former transformations—for example, $A_{r\Sigma}, v_\Sigma$, and so on.

Note that a stepwise reaction can only be considered stoichiometric when the description of resultant transformations does not need the consideration of intermediates. In other words, the stoichiometric stepwise reaction is always stationary with respect to its intermediates.

Let us recall the analytic formulation of the value of chemical potential μ_α of a chemical component A_α in media with a different phase state. By definition,

$$\mu_\alpha = \mu_\alpha^o + RT \ln a_\alpha,$$

where μ_α^o is the standard quantity of the chemical potential—usually at the given thermodynamic temperature *T* and pressure of the component $p_\alpha = 1$ bar, a_α is the activity of substance A_α, and R is the gas constant. The value of activity a_α is expressed via activity coefficient γ_α and either the component partial pressure p_α or its molar concentration c_α: $a_\alpha = \gamma_\alpha \cdot p_\alpha$ or $a_\alpha = \gamma_\alpha \cdot c_\alpha$.

In a thermodynamically ideal system $\gamma_\alpha = 1$ and thus,

$$\mu_\alpha = \mu_\alpha^o + RT \ln c_\alpha, \tag{1.4}$$

or in the gas phase system,

$$\mu_\alpha = \mu_\alpha^o + RT \ln p_\alpha. \tag{1.5}$$

For nonideal liquid and solid solutions, two identical equations of chemical potential can be used:

$$\mu_\alpha = \mu_\alpha^o + RT \ln(\gamma_\alpha c_\alpha), \tag{1.6}$$

or

$$\mu_\alpha = \mu_\alpha^{o'} + RT \ln\left(\gamma_\alpha' x_\alpha\right), \tag{1.7}$$

where c_α and x_α are the concentration and molar fraction of component A_α, respectively, and γ_α and γ_α' are the respective activity coefficients. Notice that in equation (1.6), the value of the standard chemical potential μ_α^o corresponds to the concentration $c_\alpha = 1M$ (1 mol/l), while in equation (1.7), it corresponds to the molar fraction $x_\alpha = 1$—in other words, to the pure substance A_α. If equations (1.6) and (1.7) relate to the same substance, the values of coefficient γ_α in these two cases are, indeed, different.

Both equations (1.6) and (1.7) are thermodynamically identical, but equation (1.6) correlates better with the classical kinetics and, therefore, is more appropriate for writing kinetic equations in terms of thermodynamics (see following).

Standard values μ_α^o and $\mu_\alpha^{o'}$ depend on the total pressure, p, in the system. In particular, for an incompressible condense substance

$$\mu_\alpha^{o'} = \mu_\alpha^{oo'} + V_\alpha(p - 1), \tag{1.8}$$

where $\mu_\alpha^{oo'}$ is the standard chemical potential of the pure component A_α at $p = 1$ bar, V_α is the molar volume of the component.

In recent years, much attention has been paid to "nanosystems" with a highly dispersed substance. When the properties of such a substance are as yet independent of the quantum size effects, in the first approximation one can consider that

$$\mu_\alpha^{o'} = \mu_\alpha^{oo'} + V_\alpha\left(p_{Lapl} - 1\right), \tag{1.9}$$

where for spherical particles of radius r, $p_{Lapl} \approx \frac{2\sigma_\alpha}{r}$ is the so called Laplace pressure inside the particle induced by the surface tension forces; here, σ_α is the surface tension at the "disperse particle–surrounding medium" interface.

The chemical potential of a surface adsorbed substance that forms a "two dimensional gas" can be defined in a similar way. For example, for the thermodynamically ideal case of the Langmuir monolayer adsorption of substance A_α,

$$\mu_\alpha = \mu_\alpha^o + RT \ln \theta_\alpha, \tag{1.10}$$

where θ_α is the coefficient of the surface coverage with substance $A_\alpha(0 \le \theta_\alpha \le 1), \mu_\alpha^o$, is the standard chemical potential of this substance in the adsorbed form at $\theta_\alpha = 1$.

For a nonideal surface, the activity coefficient γ_α, like that in the bulk systems, can be used, so

$$\mu_\alpha = \mu_\alpha^o + RT \ln(\gamma_\alpha \theta_\alpha). \tag{1.11}$$

The chemical potential μ_K of the free (unoccupied) active adsorption centers K on the surface can be defined in a similar way:

$$\mu_K = \mu_K^o + RT\ \mathrm{In}(\gamma_K \theta_K) \equiv \mu_K^o + RT \ln\left[\gamma_K\left(1 - \sum_\alpha \theta_\alpha\right)\right], \tag{1.12}$$

where standard potential μ_K^o refers to the chemical potential of the centers on the fully unoccupied surface $\left(\sum_\alpha \theta_\alpha = 0\right)$.

In the ideal case:

$$\mu_K = \mu_K^o + RT \ln\left(1 - \sum_\alpha \theta_\alpha\right).$$

1.2. THE SECOND LAW OF THERMODYNAMICS AS APPLIED TO OPEN SYSTEMS

1.2.1. Entropy Changes in an Open System

In an open system, the entropy may change due to either increases caused by spontaneous thermodynamically irreversible internal processes in the system, d_iS, or exchanges between the system and the surrounding, d_eS. In chemically reactive systems, d_iS may change as a result, for example, of spontaneous reactions inside the system, while d_eS may change as a result of supply or extraction of heat and/or some reactants.

The terms d_iS and d_eS are postulated in thermodynamics of irreversible processes as independent, and a total of the entropy change, dS, in the open system is expressed as the sum:

$$dS = d_iS + d_eS. \tag{1.13}$$

When only thermodynamically reversible changes occur inside the system, they are not followed by the entropy increase and $d_iS = 0$. Otherwise, in the case of existence of irreversible processes $d_iS > 0$. Obviously, in the isolated systems $d_eS \equiv 0$, and the equation is reduced to

$$dS = d_iS \geq 0.$$

This equation matches the classical formulation of the Second Law of thermodynamics for isolated systems.

In a general case of an open system, at a given point with space coordinate $\vec{r}$ a set of different irreversible processes can occur simultaneously with a total of entropy increment density $d_is(\vec{r}, t) > 0$. In this situation, the overall entropy increment due to internal processes in the entire system is expressed by integral

$$d_iS = \int_V \rho(\vec{r}, t) d_is(\vec{r}, t) dv > 0.$$

While the relationship in equation (1.13) must be met at any time, the following relationship also is met:

$$dS/dt = d_iS/dt + d_eS/dt.$$

This means that the rate of overall changes in the system entropy, dS/dt, is equal to the sum of the rate of emergence (production) of entropy inside the system (d_iS/dt) and of the rate of entropy exchange between the sys tem and the environment (d_eS/dt). Further, we shall use, along with the rate of entropy production in the system $\sigma \equiv d_iS/dt$, the quantity $\boldsymbol{P}$ of the rate of dissipation (scattering) of energy in the form of heat. In the temperature isotropic system:

$$\boldsymbol{P} = Td_iS/dt \equiv T\sigma.$$

Obviously, in the presence of any irreversible internal processes in the sys tem, $\sigma > 0$ and $\boldsymbol{P} > 0$.

Unlike d_iS, d_eS may be of any sign. The positive value d_eS/dt relates to an increase in the system entropy due to the matter and/or energy exchange with the surroundings. The negative value of d_eS/dt relates to the case when the positive entropy outflow from the system to the sur roundings (for example, due to heat or matter outflow) is greater than the positive entropy inflow.

The partition of the entropy change in the open system into two constitu ents, d_iS and d_eS, makes it obvious that the thermodynamic properties of open and isolated systems are principally different. Even though the inequality $d_iS/dt > 0$ is satisfied, the total entropy of the open system can both increase and decrease because the value d_eS/dt can be both positive and negative due to the exchange with the surroundings. The following probable situations of a total of entropy changes in the system illustrate the conclusion:

1. $dS/dt > 0$, if $d_eS/dt > 0$ or $d_eS/dt < 0$, but $|d_eS/dt| < d_iS/dt$
2. $dS/dt < 0$, if $d_eS/dt < 0$ and $|d_eS/dt| > d_iS/dt$
3. $dS/dt = 0$, if $d_eS/dt < 0$ and $|d_eS/dt| = d_iS/dt$

The third case relates to establishing of a stationary state in the system when the entropy production d_iS/dt in the system is compensated by the entropy outflow to the surroundings to brought the total entropy change to zero:

$$dS = d_iS + d_eS = 0;$$
$$dS/dt = d_iS/dt + d_eS/dt = 0.$$

The preceding equations demonstrate that the well known conflict between the fact of existence and evolution of living species and the impera tive of the Second Law of classical thermodynamics on the necessity of the entropy increase is easily solved when taking into account that the living species are the open systems. Indeed, for living species, despite the existence of internal irreversible processes with $d_iS/dt > 0$, the total entropy of the species is either constant or may even decrease via the inflow of negative entropy due to some matter or energy exchange with the surroundings.

The evolution of living species is concomitant indeed, with obvious ordering of the substance consisted therein. In terms of the classical thermodynamics, this seems like a spontaneous decrease in the entropy of living systems and, obviously, interferes with the Second Law of thermodynamics. However, this is only an apparent contradiction; the entropy increase determines the routes of spontaneous processes in isolated systems but not in open systems that are the living species. In real conditions, the total entropy of the living organisms in their evolution decreases on the condition that

$$d_eS/dt < 0, \quad |d_eS/dt| \geq d_iS/dt$$

due to the fact that conjugated processes occur in the environment to increase entropy of the latter.

In most nonphotosynthesizing living species, the overall cycle of the matter and energy exchange can indeed be presented in a simplified form as the antecedent (and initiating the cycle) formation of energy rich "food" ("fuel") molecules such as carbohydrates from CO_2 and water (with the concomitant release of molecular oxygen) in the case of plant photosynthesis followed by degradation of these photosynthesis products again to CO_2 and water via metabolic cycles. Examples of such degradation processes are the breathing processes (oxidation of carbohydrates with molecular oxygen) in most of living organisms (see Figure 1.1).

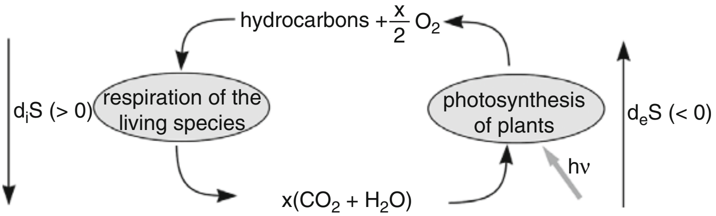


Figure 1.1 A simplified diagram of entropy changes in a living system coupled with the formation of products of plant photosynthesis. hν is light quanta initiating the photosynthetic processes with an entropy decrease.

It is clear that the negative entropy is brought in only at the instant of the electron excitation of chlorophyll molecules in the photosynthesizing organisms through the absorption of "free energy" carriers (solar light photons) by these molecules. This primary photophysical act enables some primary photosynthesis reactions to form energy rich substances. All of the subsequent biochemical processes in the organisms are spontaneous and, thus, irreversible, which results only in an entropy increase.

Note, however, that the decrease in entropy in a living photosynthesiz ing species due to primary photophysical acts is fully compensated by the increase in entropy during the light quanta generation in the course of thermonuclear reactions in the sun. Hence, the Second Law of thermody namics has to be considered as satisfying the life phenomena as well, in case the entire solar system is involved in the consideration.

The entropy of living systems decreases upon assimilation of energy saturated food and/or solar energy along with an increase in the Gibbs poten tial of these systems. When the "negative" entropy inflow from outside is consumed, it makes the living systems more organized compared to the less statistically "organized" and assimilated nutrient materials. We will see in Section 2.6 that the basis of the vital activity in living species is indeed the dynamic dissipation of energy upon degradation of nutrient materials to pro vide the release of the free energy needed to maintain the life of the organism.

In *abiogenic* chemically reactive systems, the entropy may decrease—for example, by means of the generation of energy rich species through an electrolysis inside the system (owing to the "free" electric energy), photolysis, as well as by means of rather intensive matter or heat exchange with the surroundings.

1.2.2. Nonequilibrium Systems with Uniform and Time-Constant Temperature and Pressure

The simplest case of a genuine nonequilibrium system is one with uniform and time constant temperature and pressure. Examples include open or closed systems that consist of low intensive ("sluggish") chemical processes where molecules of the initial reactants, final products, and intermediates may all be considered thermalized.

Let us find d_iS in such an open system where certain processes cause changes in the chemical composition of the system. If uniformity and equilibrium in temperature and pressure distribution (but not the chemical composition) are achieved inside the system, and the exchange processes with the surrounding medium proceed in an equilibrium manner, then the total of entropy changes in such a system is described, as postulated before, by the equation

$$dS = d_iS + d_eS.$$

Under the conditions of the closed system (i.e., in the absence of the matter exchange), d_eS describes a change in the entropy of the open system as resulting from the heat δQ exchange with the environment—that is, $d_eS = \delta Q/T$; thus,

$$d_iS = dS - d_eS = dS - \delta Q/T. \tag{1.14}$$

The d_iS quantity pertains to a spontaneous increase in the entropy inside the system due to chemical transformations of initially nonequilibrated substances and due to possible work done at that site.

We shall suppose that only the mechanical expansion work, $\delta W = pdV$, is done by the system. In accordance with the First Law of thermodynamics, the heat transferred to the system is consumed for changing the internal energy of the system and for the expansion work:

$$\delta Q = dU + pdV. \tag{1.15}$$

Here, dU is a change in the internal energy of the system. Substituting (1.15) to equation (1.4) gives

$$d_iS = (1/T)\,(TdS - dU - pdV) \tag{1.16}$$

or, at constant temperature and pressure:

$$d_iS = -(1/T)\,d(U + pV - TS).$$

The parenthesized equation matches the definition of the Gibbs potential, G, of the system:

$$G = U - TS + pV.$$

Note that variables p and T, which are standard for potential G at considering a thermodynamic equilibrium, are not used for describing differentials in equation (1.16). Hence, at constant temperature and pressure

$$d(U + pV - TS) = dG$$

and

$$d_iS = -dG/T > 0. \tag{1.17}$$

Equation (1.17) is valid for the case of an open system, too—that is, when its Gibbs potential can be additionally varied throughout the flow or during the inflow of matter. Therefore, the rate of entropy production due to irreversible internal processes is

$$\sigma \equiv d_iS/dt = -(1/T)\,(dG/dt) > 0, \tag{1.18}$$

or, what is the same,

$$\boldsymbol{P} \equiv T\sigma = -\frac{dG}{dt} > 0.$$

At the same time,

$$dG/dt < 0.$$

In other words, as expected, at a spontaneous evolution of the system at fixed p and T, its Gibbs potential decreases, $dG < 0$. Thus, the rate of entropy pro duction and energy dissipation in an open system at constant temperature and pressure is proportional to the rate of decreasing its Gibbs potential due to occurrence of irreversible spontaneous processes inside the system.

If the system is nonuniform in temperature and pressure, the derived equations pertain to processes in an elementary volume—that is, to the density of distribution of corresponding quantities. Therefore, determining the system total rates of entropy production and energy dissipation must be done with the integration over the volume.

1.2.3. Fluxes of Thermodynamic Parameters

In general cases, the local rate (per unit volume) of entropy production through internal transformations in the system is determined from the equation

$$\sigma = \frac{d_i(\rho s)}{dt} = \sum_i \frac{\partial(\rho s)}{\partial a_i}\frac{da_i}{dt},$$

where s is the local entropy per unit mass (entropy distribution density), ρ is the density of matter in a given point of the system, and a_i is the local value of thermodynamic parameter a_i. By definition, the rate of changing the parameter a_i

$$\frac{da_i}{dt} \equiv J_i$$

is referred to as a *flux of thermodynamic parameter a_i* (of the process characterized by parameters a_i), while the quantity

$$T\frac{\partial(\rho s)}{\partial a_i} \equiv X_i -$$

is called the *thermodynamic force* (affinity) conjugated with the flux of parameter a_i. Quantities X_i and J_i can be either scalars or vectors depending on the nature of parameter a_i. (In cases of anisotropic solids, these can be even tensors—that is, two dimensional matrixes.)

If $\boldsymbol{P} = T\sigma$ is the local rate of energy dissipation (per unit volume), then, obviously,

$$\boldsymbol{P} = T\sigma = \sum_i X_i J_i > 0. \tag{1.19}$$

Sometimes thermodynamic forces are related directly to σ: $\tilde{X}_i = \frac{\partial\sigma}{\partial a_i}$. When this is the case, $X_i = T\tilde{X}_i$.

In all cases, the rate of entropy production per isothermal unit volume at temperature T is described by the relationship

$$\sigma = \frac{d_iS}{dt} = \sum_i \tilde{X}_i J_i = (1/T)\sum_i X_i J_i > 0.$$

The thermodynamic force (affinity) X_i is a pivotal concept in thermodynamics of nonequilibrium processes because of its relationship to the concept of driving force of a particular irreversible process. Evidently, thermodynamic forces arise in spatially inhomogeneous systems with, for example, temperature , concentration , or pressure inhomogeneity. In spatially uniform homogeneous systems, such forces arise either in the presence of chemically reactive components that have not reached thermodynamic equilibrium via respective chemical transformations or at the thermodynamic possibility of some phase transformations.

Indeed, in a partial by equilibrium (in respect to T and p) system, the irreversibility and, as a result, a decrease in its Gibbs potential ($dG < 0$) and an increase in the entropy owing to internal processes ($d_iS > 0$) may be caused by either spontaneous phase or chemical transformations.

Let us say a stoichiometric chemical transformation ij is described by a reaction between thermalized reactants A_α

$$\sum_\alpha \nu_{i\alpha} A_\alpha \rightleftarrows \sum_\alpha \nu_{j\alpha} A_\alpha$$

and characterized by affinity A_{rij} and rate v_{ij}. The equation (1.18) changes according to equations (1.1) and (1.2) to

$$d_iS/dt = -\left(\frac{1}{T}\right)\left(\frac{dG}{dt}\right) = \left(\frac{1}{T}\right)\left(-\frac{\partial G}{\partial \xi_{ij}} \cdot \frac{\partial \xi_{ij}}{\partial t}\right) = (1/T)A_{rij}v_{ij} > 0. \qquad (1.20)$$

Here, $A_{rij} = \quad \Delta_r G_{ij} = \quad \frac{\partial G}{\partial \xi_{ij}}$ is a current value of chemical affinity—that is, of the driving force of this chemical reaction.

Thus, the rate of entropy production in a chemical stoichiometric trans formation is proportional to the product of the process driving force (chemical affinity of the reactions) and the reaction rate. At the same time, it is obvious that the rate of an elementary process ij is, by definition, the flux of the parameter "chemical variable ξ_{ij}":

$$v_{ij} \equiv \frac{d\xi_{ij}}{dt} = J_{ij},$$

while affinity A_{rij} of this process is the thermodynamic force:

$$A_{rij} = X_{ij}.$$

The inequality equation (1.20) is necessary for all thermally initiated elementary processes, and it means that the direction of the spontaneous elementary chemical transformation coincides with the sign of the current affinity of this transformation. If several simultaneous elementary transfor mations occur in the system, it is evident that

$$d_iS/dt = \frac{1}{2T}\sum_i \sum_j A_{rij} v_{ij} > 0, \qquad (1.21)$$

where the summation is over all reaction groups i, j. The coefficient 1/2 is used to avoid repeated accounting of the involved reactions during the summation over two indices.

1.2.4. The Thermodynamic Conjugation of Processes

Let two stoichiometric stepwise reactions, which involve some combination of elementary chemical reactions, be concurrent in the system. Indicate these stepwise reactions by indices Σ1 and Σ2. It is evident that for stoichiometric stepwise transformations, the elementary reactions can be omitted in the equation for d_iS/dt:

$$\frac{d_iS}{dt} = A_{r\Sigma1}v_{\Sigma1} + A_{r\Sigma2}v_{\Sigma2} > 0. \tag{1.22}$$

Note that the thermodynamically necessary inequality equation (1.22) can be satisfied not only at

$$A_{r\Sigma1}v_{\Sigma1} > 0 \quad \text{and} \quad A_{r\Sigma2}v_{\Sigma2} > 0,$$

but in general also at

$$A_{r\Sigma1}v_{\Sigma1} > 0 \quad \text{but} \quad A_{r\Sigma2}v_{\Sigma2} < 0$$

The latter inequality contradicts the condition of the spontaneous mode of stepwise reaction Σ2. Therefore, in this case the two stepwise reactions under consideration must be interdependent, or conjugate. The former reaction, which is thermodynamically allowed to be spontaneous, is referred to as conjugating, while the latter reaction is referred to as conjugated to the former one. Chapter 2 will demonstrate that the conjugation occurs only in cases when the stepwise processes encompass elementary stages with common (for the stepwise reactions) intermediates omitted in the equation to describe these stoichiometric stepwise transformations.

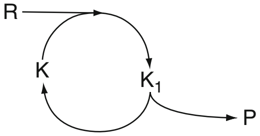
This is namely a thermodynamic conjugation of two processes that allows the conjugated stepwise reaction Σ2 to proceed in a forbidden direction when $A_{r\Sigma2}$ and $v_{\Sigma2}$ are of opposite signs, and thus, the stepwise reaction Σ2 leads, formally, to a decrease in the entropy. Typical examples of the conjugating and conjugated reactions are, respectively, a reaction catalyzed by some catalyst and the closed chain of chemical transformations of the catalyst active center. The simplest combination of such reactions is the catalyzed stepwise reaction

$$\mathrm{R} \rightleftarrows \mathrm{P} \tag{1.23}$$

which can be depicted using the Michaelis Menten scheme

$$\begin{aligned} &\mathrm{R} + \mathrm{K} \rightleftarrows \mathrm{K}_1, \\ &\mathrm{K}_1 \rightleftarrows \mathrm{K} + \mathrm{P} \end{aligned} \tag{1.24}$$

with a respective graphic illustration of cyclic transformations of the catalyst active center:



Here, R and P are the initial reactant and the product of the catalytic reaction, respectively, while K and K_1 are the "free" form of the catalyst active center and the catalytic intermediate. The conjugating reaction is a catalytic reaction (1.23) with affinity $A_{r\Sigma 1} = \mu_R - \mu_P$, while the conjugated reaction proceeds through cyclic transformations (1.24) with the participation of the catalyst active center. The process conjugation happens because of the presence of common intermediates K and K_1, the resulting affinity of the transformation cycle being $A_{r\Sigma 2} = 0$ in the case under the consideration owing to the cyclic mode of the catalytic transformations.

Actual catalytic processes are described in a much more complex way than the reaction sequence (1.24) (see, e.g., Chapter 4). Yet, a more complex example of conjugation of chemical reactions is, indeed, the vital activity of living species based on the metabolic cycles driven by transformations of an energy rich food.

When the conjunctive "thermodynamically forbidden" reaction (in a system with two stoichiometric stepwise reactions) results in a decrease in the system entropy, condition (1.22) determines the top limit rate of the conjugated reaction:

$$|v_{\Sigma 2}| \leq |v_{\Sigma 1}| \cdot \left| \frac{A_{r\Sigma 1}}{A_{r\Sigma 2}} \right|.$$

This helps to establish a relationship between a purely thermodynamic parameter of the conjugate process—its chemical affinity—and the most important kinetic characteristic of the process—the reaction rate. The magnitude of ratio $|v_{\Sigma 2} A_{r\Sigma 2} / v_{\Sigma 1} A_{r\Sigma 1}|$ can be treated as the energetic efficiency of the conjugation that indicates the portion of the Gibbs potential of the conjugating reaction “consumed” by the thermodynamically unfavorable conjugated reaction.

The thermodynamic conjugation may occur not only in chemical reactions but also in other thermodynamic processes—for example, matter and heat transfer. The existence of the top limit for the energetic efficiency of the conjunction is, naturally, not evidence that the conjunction actually takes place. As just mentioned, a necessary condition of the conjunction of stepwise chemical reactions is the existence of at least one common intermediate in these reactions. To find the true value of the conjunction is a particular and, usually, very specific problem (see Section 2.3).

In biology, the thermodynamic conjugation is necessary to make it possible for living species to use the energy released by spontaneous reactions of the cell metabolism. Irreversible chemical transformations in the cell give rise to degradation of the Gibbs energy of the system to heat and result in the irreversible energy dissipation. At the same time, the conjugation of these chemical transformations with the reactions of the food assimilation makes up the compensation of the energy loss to provide evolution or vital activity of the living species and even storage of energy released by the spontaneous metabolic reactions, the energy being stored in the form of chemical bonds of complex biological compounds and cell structures inside the living organism. Indeed, the rate of total entropy production d_iS/dt remains positive for the in-cell conjugated metabolic processes.

1.3. FLUXES AND THERMODYNAMIC FORCES IN SPATIALLY HOMOGENEOUS CHEMICALLY REACTIVE SYSTEMS

A typical example of nonequilibrium spatially homogeneous systems is an isotropic system where a chemical reaction occurs. The application of nonequilibrium thermodynamics for the consideration of chemically reactive systems has a few peculiarities. Indeed, heat and mass transfer processes are characterized usually by continuous variations in temperature and concentration (see Section 1.5). On the other hand, the chemical transformations imply transitions between the discrete states that pertain to the individual reaction groups.

A thermodynamic parameter to describe a stoichiometric reaction ij is, usually, chemical variable ξ_{ij}. If so,

$$J_{\xi_{ij}} = \frac{d\xi_{ij}}{dt} \equiv v_{ij}$$

and as shown in Section 1.2.3,

$$X_{\xi_{ij}} = T\frac{\partial(\rho s)}{\partial \xi_{ij}} = -\Delta_r G_{ij} = A_{rij}.$$

Hence, in stoichiometric chemical transformations, the thermodynamic flux of parameter ξ_{ij} is the rate v_{ij} of this reaction, while the thermodynamic force associated with this flux is the current value of affinity A_{rij} of the reaction.

Hereafter, we shall relate the rate of a chemical reaction to the number of transformation events in unit volume. This is common practice in chemical kinetics. If necessary, it is easy to change to parameters that characterize the rate in the entire system.

1.3.1. The "Thermodynamic" Form of Kinetic Equations

It was just shown that fluxes of thermodynamic parameters that describe transformations in chemically reactive systems are in direct relationships with the rate of chemical reactions. The relationship between the rate of a chemical reaction and physicochemical parameters (reactant concentrations, temperature, etc.) of the system is the subject of a special branch of physical chemistry called chemical kinetics.

In chemical kinetics, the key parameters are traditionally the rate constants and the concentrations of reactants. At the same time for thermodynamic analysis, the parameters such as chemical potential appear to be the most useful. That is why the most convenient way to consider chemical transformations in terms of thermodynamics of nonequilibrium processes is a "thermodynamic" form of kinetic equations. The main elements of the application of this form are given following.

Let us consider a spontaneous (thermally initiated) elementary chemical reaction ij

$$\sum_{\alpha} \nu_{i\alpha} A_{\alpha} \rightarrow \sum_{\alpha} \nu_{j\alpha} A_{\alpha},$$

where A_{α} means the reaction components with their concentration c_{α} ($\alpha = 1, 2, \ldots, k$), and $\nu_{i\alpha}$ is the stoichiometric coefficient for these components to enter reaction group i.

In chemical kinetics, when a reaction proceeds at a given temperature and pressure with the maintenance of the Maxwell Bolztmann distribution in the occupation of the energy levels of the transition state (activated com plex) for the reaction, the rate $\vec{v}_{ij}$ of the reaction under consideration—the number of transformations of reaction group i into reaction group j "from left to right" in unit volume and for unit time—is described in terms of the mass action law

$$\vec{v}_{ij} = \vec{k}_{ij} \prod_{\alpha} c_{\alpha}^{\nu_{i\alpha}},$$

where $\vec{k}_{ij}$ is the traditional rate constant of the i to j transformation.

As previously mentioned (see Section 1.1), in a general case $\mu_{\alpha} = \mu_{\alpha}^{o} + RT \ln(\gamma_{\alpha} c_{\alpha})$, where γ_{α} is the activity coefficient for substance A_{α}. Therefore,

$$c_{\alpha} = \frac{1}{\gamma_{\alpha}} \exp\left(\frac{\mu_{\alpha} - \mu_{\alpha}^{o}}{RT}\right)$$

and the rate of an elementary chemical reaction of any order can be expressed as

$$\begin{aligned} \vec{v}_{ij} &= \vec{k}_{ij} \frac{1}{\prod_{\alpha} \gamma_{\alpha}^{\nu_{i\alpha}}} \exp\left\{\frac{\sum_{\alpha} \nu_{i\alpha}(\mu_{\alpha} - \mu_{\alpha}^{o})}{RT}\right\} \\ &= \left\{\vec{k}_{ij} \frac{1}{\prod_{\alpha} \gamma_{\alpha}^{\nu_{i\alpha}}} \exp\left(-\frac{\mu_{i}^{o}}{RT}\right)\right\} \exp\left(\frac{\mu_{i}}{RT}\right). \end{aligned} \tag{1.25}$$

Here, $\mu_{i}^{o} \equiv \sum_{\alpha} \nu_{i\alpha} \mu_{\alpha}^{o}$ and $\mu_{i} \equiv \sum_{\alpha} \nu_{i\alpha} \mu_{\alpha}$ correspond, respectively, to the standard and current values of the *chemical potential* of the reaction group i in whole.

Let us look at the notations:

$$\begin{aligned} \varepsilon_{ij} &= \vec{k}_{ij} \exp\left(-\sum_{\alpha} \nu_{i\alpha} \mu_{\alpha}^{o}/RT\right) \Big/ \prod_{\alpha} \gamma_{\alpha}^{\nu_{i\alpha}} \\ &\equiv \vec{k}_{ij} \exp\left(-\mu_{i}^{o}/RT\right) \Big/ \prod_{\alpha} \gamma_{\alpha}^{\nu_{i\alpha}} \end{aligned} \tag{1.26}$$

and

$$\tilde{n}_i \equiv \exp(\mu_i/RT) \equiv \exp\left(\sum_{\alpha=1}^{k} \nu_{i\alpha}\mu_\alpha/RT\right)$$
$$= \prod_{\alpha=1}^{k} \exp(\nu_{i\alpha}\mu_\alpha/RT) = \prod_{\alpha=1}^{k} \tilde{n}_\alpha^{\nu_{i\alpha}}. \qquad (1.27)$$

So it is evident that

$$\vec{v}_{ij} = \varepsilon_{ij}\tilde{n}_i.$$

Notice that the dimension of parameter ε_{ij} is s ^{1}, while the parameter $\tilde{n}_i$ is dimensionless irrespective of the actual molecularity of the reaction under consideration. The concomitance of equation (1.25) and the other equations that follow to the necessary dimensions is made, as is common in thermodynamics, by choosing the respective standard states of the reactants.

A more detailed form for writing the equation for parameter ε_{ij} can be based on the activated complex theory. The said theory predicts the following dependence for the rate of elementary chemical reaction i ⟶ j:

$$\vec{v}_{ij} = \chi_{ij}\frac{k_B T}{h\gamma_{ij}^{\#}} \exp\left(-\Delta G_{ij}^{\#o}/RT\right) \prod_{\alpha=1}^{k} (\gamma_\alpha c_\alpha)^{\nu_{i\alpha}}, \qquad (1.28)$$

where k_B and h are the Boltzmann and Plank constants, respectively; $\gamma_{ij}^{\#}$ is the transition state activity (fugacity) coefficient, χ_{ij} is the dimensionless coefficient of *permeability* of the activation barrier, and $\Delta G_{ij}^{\#o}$ is the difference of standard Gibbs potential (i.e., of formation) for a nonthermalized transition state (e.g., of the activated complex) and those of the initial reactants:

$$\Delta G_{ij}^{\#o} = G_{ij}^{\#o} - \sum_{\alpha=1}^{k} \nu_{i\alpha} G_\alpha^{o} \equiv \mu_{ij}^{\#o} - \sum_{\alpha=1}^{k} \nu_{i\alpha}\mu_\alpha^{o} \equiv \mu_{ij}^{\#o} - G_i^{o} = \mu_{ij}^{\neq o} - \mu_i^{o}.$$

Equation (1.28) can be rewritten in the form

$$\vec{v}_{ij} = \frac{k_B T}{h} \exp\left(-\mu_{ij}^{\#}/RT\right) \exp\left(\sum_{\alpha=1}^{k} \nu_{i\alpha}\mu_\alpha/RT\right) = \frac{k_B T}{h} \exp\left(-\mu_{ij}^{\#}/RT\right) \cdot \tilde{n}_i,$$

where $\mu_{ij}^{\#} = \mu_{ij}^{\#o} + RT\ln\left(\gamma_{ij}^{\#}/\chi_{ij}\right)$ is the "standard chemical potential" of the activated complex that allows the consideration of even a nonideal medium. If so, then

$$\varepsilon_{ij} = \frac{k_B T}{h}\exp\left(-\mu_{ij}^{\#}/RT\right). \tag{1.29}$$

Hence, the first approximation of parameter ε_{ij} is independent of the standard thermodynamic characteristics of thermalized reactants but depends only on thermodynamic characteristics of the nonthermalized transition state.

For this reason, we shall further refer to quantities ε_{ij} as the *truncated* rate constant of the elementary process ij. Parameters ε_{ij} involve dynamic characteristics of the system, which depend only on the properties of the transition state (*activated complex*) of the individual elementary reaction ij. As just mentioned, only one transition state is postulated to be characteristic of the true elementary process.

By definition, ε_{ij} must be symmetrical about rearrangement of indices i and j because the same transition state is characteristic of both the direct and the reverse reactions.

The conclusion on the symmetry of ε_{ij} can be independently deduced based on the necessary principle of detailed equilibrium which is a necessary attribute of the classical thermodynamics. Indeed, let us consider an arbitrary elementary reaction ij that is necessarily reversible:

$$\sum_{\alpha=1}^{k} \nu_{i\alpha} A_\alpha \underset{\vec{k}_{ji}}{\overset{\vec{k}_{ij}}{\rightleftarrows}} \sum_{\alpha=1}^{k} \nu_{j\alpha} A_\alpha. \tag{1.30}$$

The overall rate of the reaction is defined as the rate of change in the chemical variable ξ_{ij} that involves both the direct and reverse channels of the transformation. This is identical to the difference between the number of acts of direct and reverse chemical transformations in unit volume in unit time:

$$v_{ij} = \frac{d\xi_{ij}}{dt} = \vec{v}_{ij} - \overleftarrow{v}_{ij} = \varepsilon_{ij}\tilde{n}_i - \varepsilon_{ji}\tilde{n}_j.$$

Any elementary reactions follow the rules of detailed reversibility. Their detailed equilibrium, or $v_{ij} = 0$ occurs at $\mu_i = \mu_j$ (or that is the same as $\tilde{n}_i = \tilde{n}_j$). Thus, it is necessary that $\varepsilon_{ij} = \varepsilon_{ji}$. As a consequence,

$$J_{ij} = v_{ij} = \varepsilon_{ij}\left(\tilde{n}_i - \tilde{n}_j\right). \tag{1.31}$$

Equation (1.31) is of obvious physical sense and indicates tacitly that the direction of the chemical process i $\rightleftarrows$ j depends on the relationship between quantities $\tilde{n}_i$ and $\tilde{n}_j$. When $\tilde{n}_i > \tilde{n}_j$, the process goes from right to left and vice versa. The condition $\tilde{n}_i > \tilde{n}_j$ is equivalent to the occurrence of the positive affinity of the reaction at the given direction of spontaneous chemical transformations.

In *the IUPAC Compendium of Terminology*, parameter $\tilde{n}_\alpha \equiv \exp(\mu_\alpha/RT) \equiv c_\alpha \gamma_\alpha \exp\left(\mu^o_\alpha/RT\right)$ is called the absolute activity of component A_α. However, in virtue of the preceding simple physical analogy, the parameter $\tilde{n}_i$ of a several component reaction group is called a thermodynamic rush of the reaction group i.

Obviously, quantities $\tilde{n}_\alpha$ and $\tilde{n}_i$ are always symbate to the respective chemical potentials μ_α and μ_i. It is important that the difference between the logarithms of rushes $\tilde{n}_i$ and $\tilde{n}_j$ be proportional to the current thermodynamic affinity A_{rij} of the reaction between reaction groups i and j—in other words, to the thermodynamic force X_{ij} related to flux J_{ij}:

$$\begin{aligned} X_{ij} = A_{rij} = -\Delta_r G_{ij} = \sum_{\alpha=1}^{k} \nu_{i\alpha}\mu_\alpha - \sum_{\alpha=1}^{k} \nu_{j\alpha}\mu_\alpha \\ = \mu_i - \mu_j = RT\left(\ln \tilde{n}_i - \ln \tilde{n}_j\right) = RT \ln\left(\tilde{n}_i/\tilde{n}_j\right). \end{aligned} \tag{1.32}$$

When the thermodynamic rushes of the reaction groups are equal to one another, $\tilde{n}_i = \tilde{n}_j$, for all feasible reactions ij in the system, the system is in the stable thermodynamic equilibrium ($A_{rij} \equiv 0$), and, therefore, changes in chemical variables and overall rates of all the reactions are naturally equal to zero.

Figure 1.2 gives the comparative graphical interpretations of an elementary chemical reaction in commonly accepted *energetic* coordinates and in the *thermodynamic* coordinates under the discussion. Note that the traditional *energetic* coordinates are always related to the fixed (typically, unit) reactant concentrations and, therefore, identify the behavior of standard values of the plotted parameters. As for the *thermodynamic* coordinates, they illustrate the process that proceeds under real conditions and are not restricted by the standard values of chemical potentials or thermodynamic rushes of the reactants. The thermodynamic (canonical) form of kinetic equations is convenient for a combined kinetic thermodynamic analysis of reversible chemical processes, especially for those that proceed in the stationary mode.

We must emphasize that

$$v_{ij} = \varepsilon_{ij}\tilde{n}_i\left\{1 - \exp\left[(\mu_j - \mu_i)/RT\right]\right\} = \varepsilon_{ij}\tilde{n}_i\left\{1 - \exp\left(-A_{rij}/RT\right)\right\}.$$

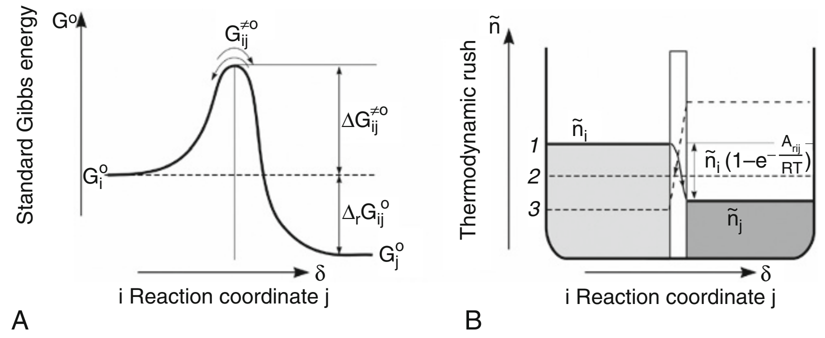


Figure 1.2 Schematic representation of the pathway of elementary reaction ij in the traditional energetic coordinates with the activation barrier (a) and in the coordinates of thermodynamic rushes $\tilde{n}_i$ of reactants (b). In the latter case, the reaction can be represented as a flow of a fluid between two basins separated by a membrane with permeability ε_{ij}; the examples are given for the left-to-right and right-to-left reactions (cases 1 and 3, respectively); case 2 illustrates the thermodynamically equilibrium system.

Thus, at $A_{rij} > RT$, the reaction rate relates only to the direct reaction channel (from i to j) and is independent of the reverse channel (from j to i). In the other words, the inequality $A_{rij} > RT$ is a strict condition of kinetic irreversibility of process ij.

Obviously, the rate of entropy production through a spontaneous elementary reaction ij in unit volume of the system under consideration equals

$$\sigma_{ij} = \frac{v_{ij}A_{rij}}{T} = \frac{v_{ij}(\mu_i - \mu_j)}{T} = R\varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j)(\ln \tilde{n}_i - \ln \tilde{n}_j) \geq 0,$$

where $\sigma_{ij} = 0$ corresponds to the situation of $\tilde{n}_i = \tilde{n}_j$—that is, to the partial equilibrium between reaction groups i and j.

When many thermally initiated elementary reactions are in a system, the total rate of entropy production in unit volume is

$$\sigma = \frac{R}{2}\sum_i \sum_j \varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j)(\ln \tilde{n}_i - \ln \tilde{n}_j) \geq 0. \qquad (1.33)$$

Both chemical variables ξ_{ij} and concentrations c_α of components A_α may be treated as thermodynamic parameters. If the flux of the concentration of chemical component A_α is being considered rather than the flux of chemical variable ξ_{ij}, then the elementary reaction ij defines only one of the constituents of its concentration flux:

$$\begin{aligned}J_{ij}(\alpha) &\equiv \left(\frac{dc_\alpha}{dt}\right)_{ij} = v_{ij}(\alpha) = (\nu_{j\alpha} - \nu_{i\alpha})\frac{d\xi_{ij}}{dt}\\ &= \varepsilon_{ij}(\nu_{j\alpha} - \nu_{i\alpha})(\tilde{n}_i - \tilde{n}_j) \equiv \varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j)\frac{\partial(\ln\tilde{n}_j - \ln\tilde{n}_i)}{\partial \ln\tilde{n}_\alpha}.\end{aligned}$$

The total concentration flux of component A_α (the reaction rate with respect to component A_α) is the sum of all available component A_α trans formation channels, which equals

$$\begin{aligned}J(\alpha) &\equiv \frac{dc_\alpha}{dt} = v_\alpha = \frac{1}{2}\sum_i\sum_j J_{ij}(\alpha) = \frac{1}{2}\sum_j\sum_j(\nu_{j\alpha} - \nu_{i\alpha})\frac{d\xi_{ij}}{dt}\\ &= \frac{1}{2}\sum_i\sum_j(\nu_{j\alpha} - \nu_{i\alpha})\varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j) \equiv \frac{1}{2}\sum_i\sum_j\varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j)\frac{\partial(\ln\tilde{n}_j - \ln\tilde{n}_i)}{\partial(\ln\tilde{n}_\alpha)}\\ &= \frac{1}{2RT}\sum_i\sum_j\varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j)\frac{\partial X_{ji}}{\partial(\ln\tilde{n}_\alpha)}.\end{aligned}$$

As before, coefficient 1/2 is introduced to avoid repeated accounting of all of the available reactions channels, while partial derivatives with respect to In $\tilde{n}_\alpha$ are used instead of stoichiometric coefficients $\nu_{i\alpha}$ in accordance with the definition of parameter $\tilde{n}_i$ (see equation (1.27)) that gives

$$\frac{\partial(\ln\tilde{n}_i)}{\partial(\ln\tilde{n}_\alpha)} = \frac{\partial\left(\sum_\beta \nu_{i\beta}\ln\tilde{n}_\beta\right)}{\partial(\ln\tilde{n}_\alpha)} = \nu_{i\alpha}.$$

When several reactions occur in the system simultaneously, the flux of the component concentrations generally depends on the many thermo dynamic forces $X_{ij} \equiv A_{rij}$—in other words, on the affinities of various elementary reactions.

While keeping in mind a certain scheme of chemical transformations and applying the preceding relationships, one can easily consider the dynamics of chemical transformations in any reactive system and analyze the process in combined terms of both kinetics and thermodynamics.

1.3.2. The Relationship between the Stationary Rate and the Thermodynamic Forces of a Stepwise Stoichiometric Process

We have already demonstrated that the behavior of an arbitrary combination of elementary chemical processes cannot be described in terms of only one thermodynamic force. Nevertheless, sometimes it is possible describe a stationary stepwise stoichiometric process using only one thermodynamic force.

The simplest example is a stepwise process that proceeds via an arbitrary combination of elementary monomolecular transformations of intermediates that all exist in their stationary states. When this is the case, the stationary rate of the stepwise process appears to be proportional to the difference between thermodynamic rushes of the initial and final reaction groups—in other words, the stepwise process can be considered from the viewpoint of both kinetics and thermodynamics as a single effective elementary reaction.

Let us demonstrate the validity of this serious statement with an example of the simplest stepwise reaction:

$$\mathrm{R} \rightleftarrows \mathrm{P},$$

where R and P are the initial reactant and final product, respectively. Let Y be the only intermediate of the process:

$$\mathrm{R} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{Y} \overset{\varepsilon_2}{\rightleftarrows} \mathrm{P}.$$

Indeed, in the stationary state with respect to intermediate Y,

$$\frac{\mathrm{d[Y]}}{\mathrm{dt}} = \varepsilon_1(\tilde{\mathrm{R}} - \tilde{\mathrm{Y}}) - \varepsilon_2(\tilde{\mathrm{Y}} - \tilde{\mathrm{P}}) = 0.$$

Thus,

$$\tilde{\mathrm{Y}} = \frac{\varepsilon_1\tilde{\mathrm{R}} + \varepsilon_2\tilde{\mathrm{P}}}{\varepsilon_1 + \varepsilon_2}$$

and

$$\mathrm{v}_\Sigma = \frac{\mathrm{d[P]}}{\mathrm{dt}} = \varepsilon_2(\tilde{\mathrm{Y}} - \tilde{\mathrm{P}}) = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}(\tilde{\mathrm{R}} - \tilde{\mathrm{P}}) \equiv \varepsilon_\Sigma(\tilde{\mathrm{R}} - \tilde{\mathrm{P}}).$$

Here and elsewhere, [A] and $\tilde{A}$ mean the concentration and the thermodynamic rush of reactant A, respectively.

This statement on the relationship between the stationary rate of the stepwise process and the thermodynamic force that initiates it can be easily generalized for the case of an arbitrary combination of monomolecular transformations of intermediates. The simplest and most visual way to do that is to use the perfect analogy between equation (1.31) of the rate of elementary chemical reaction v_{ij} and the Ohm's law for electric current I_{ij} between two points, i and j, of an electric circuit with electric potentials U_i and U_j, respectively:

$$l_{ij} = \frac{U_i - U_j}{R_{ij}} \equiv \sigma_{ij}(U_i - U_j).$$

Here, R_{ij} and σ_{ij} are the active resistance and the corresponding electric conductance of the circuit fragment between points i and j. Note that in kinetic equation (1.31), thermodynamic rushes $\tilde{n}_i$ of the reactant groups behave as electric potentials in the points, while parameter ε_{ij} is equivalent to electric conductance σ_{ij}.

For monomolecular processes of any complexity, this electrotechnic analogy makes it possible to determine the stationary rate of chemical reactions with respect to the reactive species. To do this, one has to consider the Kirchhoff equation for the balance of current inflow and outflow at all points of the electric circuit contacts.

Let us consider a stationary stepwise process where the transformations of a reactant (reactant group) R into the final product (product group) P

$$R \rightleftarrows P$$

are provided due to the formation of an arbitrary set of intermediate compounds Y_i that participate in an arbitrary combination of monomolecular transformations:

$$R \overset{\{\varepsilon_{Ri}\}}{\rightleftarrows} \{Y_i \overset{\{\varepsilon_{ij}\}}{\rightleftarrows} Y_j\} \overset{\{\varepsilon_{jP}\}}{\rightleftarrows} P. \tag{1.34}$$

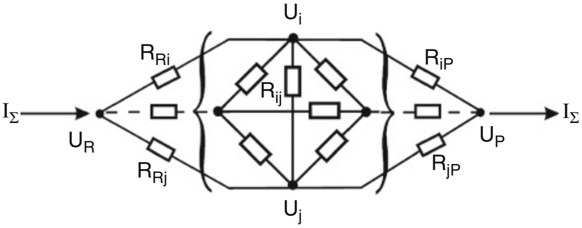
Here, $\{Y_i \overset{\{\varepsilon_{ij}\}}{\rightleftarrows} Y_j\}$ symbolizes the preceding arbitrary combination of the intermediate transformations (i,j = 1, . . . , m), while ε_{Ri} and ε_{jP} are the truncated rate constants of the transformations between reactant groups R and Y_i, and P and Y_j, respectively.

In the stationary mode with respect to all intermediates Y_i,

$$v_{Y_i} \equiv \frac{d[Y_i]}{dt} = 0,$$

that means the equality of the rates of the formation and consumption of component Y_i.

While comparing the stationary kinetic equations (in their thermodynamic form) for the intermediate concentrations of system (1.34) to the Kirchhoff equation for the electric current inflow and outflow at all junction points of an equivalent electric circuit, one can easily ascertain that the combination of reactions (1.34) will be described by the equivalent electric diagram



(1.35)

Indeed, while the electric charge is not accumulated at the junction points of the resistors in the circuit, the reactive intermediates are not additionally accumulated or consumed in time at the stationary mode in respect to intermediates (see Figure 1.3).

Each resistor junction point in diagram (1.35) is characterized by its own potential U_i, all of the points being linked by resistors R_{ij}. The resistivity of some of these resistors may be of infinite quantities that correspond to the absence of any chemical transformations via these routes.

We know from basic physics that a total of electric current I_Σ that passes between points R and P in an electric circuit of a type (1.35) is proportional to the difference of electric potentials between terminal points of the circuit and equals

$$I_\Sigma = \sigma_\Sigma(U_R - U_P),$$

where σ_Σ is an effective electric conductance of the entire circuit. The value of σ_Σ is calculated by the Kirchhoff equations and is equal to a certain algebraic combination of those resistances that are arranged between points R and P.

As for chemical process (1.34), these speculations imply that its overall rate v_Σ in the mode that is stationary in respect to the intermediates is also

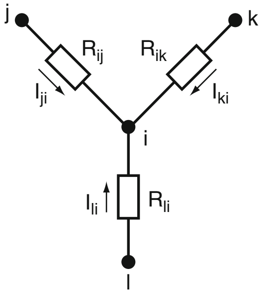


Figure 1.3 Illustration of the application of the Kirchhoff equations for the balance of electric charge inflowing to and outflowing from point i: $I_{ji} + I_{ki} + I_{li} = 0$.

proportional to the difference of thermodynamic rushes of the initial and final reaction groups:

$$v_\Sigma \equiv \frac{d[P]}{dt} = \varepsilon_\Sigma(\tilde{R} - \tilde{P}), \tag{1.36}$$

where $\tilde{R}$ and $\tilde{P}$ are thermodynamic rushes of the initial reactant and final product of the stepwise reaction, respectively; ε_Σ is an algebraic combination of parameters $\{\varepsilon_{Ri}, \varepsilon_{jP}, \varepsilon_{ij}\}$ only.

Hence, the stationary rate of the stationary chemical stepwise transformation under consideration is related with a single thermodynamic force, $A_{r\Sigma} = \mu_R \quad \mu_P$. This means that the consideration of a stationary stepwise stoichiometric process can be reduced to the consideration of an effective elementary reaction.

The conclusion is valid for any processes that can be reduced to monomolecular processes—that is, those nonmonomolecular processes whose reactant group $\tilde{n}_i$ is characterized by strictly constant combinations of parameters $\tilde{n}_\alpha$, where given $\tilde{n}_\alpha$ is involved in no more than one parameter $\tilde{n}_i$. Thus, in this situation, the parameter $\tilde{n}_i$ can be considered as a fully independent parameter even though it is, in accordance to equation (1.27), a combination of parameters $\tilde{n}_\alpha$ for several A_α or relates to a nonmonomolecular process with respect to given A_α. For example, a stepwise process

$$R \rightleftarrows P,$$

that follows the pathway with two intermediates Y_1 and Y_2:

$$R \rightleftarrows Y_1 + Y_2 \rightleftarrows P$$

is reduced formally to the preceding monomolecular process $R \rightleftarrows Y \rightleftarrows P$, where Y symbolizes the constant combination $Y = Y_1 + Y_2$.

If the transformation pathway cannot be reduced to monomolecular reactions, nonunit stoichiometric coefficients may appear at some junction points of the kinetic resistors. In terms of electric circuits, this means that the absence of the balance of the current inflow and outflow at this junction point may cause nonlinearity and deviations from the canonical form of the Kirchhoff equation.

Equation (1.36) conforms to the relationship deduced by Horiuti and Boreskov in the 1940s for a particular case of stationary single route catalytic reactions [1–4]. This relationship states that the overall rate of such a stepwise catalytic process can be expressed as the difference between the rates of the direct (v^+) and reverse (v) routes of this stepwise process:

$$v_\Sigma = v^+ - v \quad = v^+\left(1 - \frac{v}{v^+}\right) = v^+\left\{1 - \left(\frac{\varphi(c_\alpha)}{K_p}\right)^M\right\},$$

where in the case under consideration, $v^+ = \varepsilon_\Sigma\tilde{R}$, a $v \quad = \varepsilon_\Sigma\tilde{P}$; $\varphi(c_\alpha)$ is a function that coincides formally with the mass action low for the stepwise reaction in the direction "from right to left," M is a formal molecularity of the stepwise process that is equal to the number of molecules of reactants constituting the reactive complex transforming at the rate limiting step, and K_p is the equilibrium constant for the stepwise reaction. In this case, $M = 1$.

The commonly known consequence of the Kirchhoff equation is that the electric potential in each intermediate junction point i is described by the equation

$$U_i = U_R + (U_P - U_R)\delta_i,$$

where δ_i is an algebraic combination of quantities R_{ij} or σ_{ij} compatible with the relationship $0 \le \delta_i \le 1$. Hence, the stationary values of thermodynamic rushes of the intermediates of the chemical stepwise reaction under consideration are also of the intermediate magnitudes between the values of thermodynamic rushes of the initial and final reaction groups:

$$\tilde{Y}_i = \tilde{R} + \left(\tilde{P} - \tilde{R}\right)\delta_i. \tag{1.37}$$

Here, δ_i is an algebraic combination of ε_{Ri}, ε_{jP}, ε_{ij} for the given intermediate, while $0 \le \delta_i \le 1$. Thus, if chemical processes occur under stationary conditions, the values of chemical potentials of the intermediates (which are the internal parameters) must be between the values of chemical potentials of the initial reactant and final product.

In some cases, coefficients ε_Σ and δ_i may be written as simple algebraic expressions. For example, let the stepwise process under consideration involve a series of consecutive monomolecular transformations of intermediates Y_i:

$$R \overset{\varepsilon_1}{\rightleftarrows} Y_1 \overset{\varepsilon_2}{\rightleftarrows} Y_2 \overset{\varepsilon_3}{\rightleftarrows} \ldots \overset{\varepsilon_m}{\rightleftarrows} Y_m \overset{\varepsilon_{m+1}}{\rightleftarrows} P.$$

In the electrotechnical analogy, this series is like a chain of consecutively linked resistors. Therefore, it is evident that the total resistance of the chain is

$$R_\Sigma = \sum_{i=1}^{m+1} R_i,$$

that gives

$$\frac{1}{\varepsilon_\Sigma} = \sum_{i=1}^{m+1} \frac{1}{\varepsilon_i}$$

and

$$\delta_i = \varepsilon_\Sigma \cdot \sum_{j=1}^{i} \frac{1}{\varepsilon_j}.$$

These equations match the statement of classical chemical kinetics that upon consecutive chemical transformations, one should summarize the kinetic resistances of each consecutive transformation.

Apparently, thermodynamic rushes for the series of transformations under consideration and, as a result, chemical potentials of the intermediates in their stationary states must decrease progressively while passing from one intermediate to another. When the stepwise transformation may follow several parallel pathways of consecutive elementary transformations, the said relationship between the stationary chemical potentials of the intermediates must be met for each of the possible pathways of the stepwise reaction.

These speculations are of extreme importance because they lead to the conclusion that the analysis of any stationary stepwise process involving an arbitrary series of monomolecular (or reduced to monomolecular) transformations can be substituted for by an analysis of only one effective monomolecular reaction. It also is important that this conclusion is general and valid for the system irrespectively of how close it is to its thermodynamic equilibrium.

The similar features of stationary processes are characteristic of some step wise reactions with nonmonomolecular transformations of the intermediate as well. For example, the stationary rate of a stepwise process is proportional to the difference of thermodynamic rushes of the initial and final reaction groups for any schemes of stepwise processes with the transformations linear to the intermediates. However, the value of ε_Σ may depend in such cases not only on ε_{ij} but also on thermodynamic rushes of some initial or final reactants.

Let us look at an example of a simple scheme of transformations that are linear with respect to their intermediates. First, we will consider a stoi chiometric stepwise process:

$$R_1 + R_2 \rightleftarrows P \tag{1.38}$$

that follows the one intermediate (Y) route:

$$\begin{gathered} R_1 \overset{\varepsilon_1}{\rightleftarrows} Y, \\ Y + R_2 \overset{\varepsilon_2}{\rightleftarrows} P. \end{gathered} \tag{1.39}$$

The rate of this stepwise process is

$$v_\Sigma = \frac{d[P]}{dt} \equiv \frac{-d[R_1]}{dt} \equiv \frac{-d[R_2]}{dt} = \varepsilon_2(\tilde{Y}\cdot\tilde{R}_2 - \tilde{P}).$$

If the process is stationary with respect to the intermediate,

$$\begin{gathered} \frac{d[Y]}{dt} = \varepsilon_1(\tilde{R}_1 - \tilde{Y}) - \varepsilon_2(\tilde{Y}\cdot\tilde{R}_2 - \tilde{P}) = 0, \\ \tilde{Y} = \frac{\varepsilon_1\tilde{R}_1 + \varepsilon_2\tilde{P}}{\varepsilon_1 + \varepsilon_2\tilde{R}_2}. \end{gathered}$$

Hence,

$$v_\Sigma = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2\tilde{R}_2}(\tilde{R}_1 \cdot \tilde{R}_2 - \tilde{P}) \equiv \varepsilon_\Sigma(\tilde{R}_1 \cdot \tilde{R}_2 - \tilde{P}) \tag{1.40}$$

where

$$\varepsilon_\Sigma = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2\tilde{R}_2}.$$

In a more general case, when a stepwise stoichiometric process

$$R_1 + R_2 \leftrightarrows P$$

follows the scheme

$$\begin{gathered} R_1 \leftrightarrows \{Y_{li}\}, \\ Y_{li} + R_2 \leftrightarrows \{Y_{2j}\}, \\ Y_{2j} \rightleftarrows P, \end{gathered}$$

which is linear with respect to intermediates Y_{1i} ($i = 1, \ldots$) and Y_{2j} ($j \quad 1$, ...), the both intermediates being involved in arbitrary monomolecular transformations $\{Y_{1i}\}$ and $\{Y_{2j}\}$, the overall stationary rate of the stepwise process is

$$v_\Sigma \equiv \frac{d[P]}{dt} \equiv \frac{-d[R_1]}{dt} \equiv \frac{-d[R_2]}{dt} = \varepsilon_\Sigma\left(\tilde{R}_1 \cdot \tilde{R}_2 - \tilde{P}\right).$$

Here, ε_Σ is again a combination of parameters ε_{ij} and $\tilde{R}_2$. Thus, this is also the case of comparing the obtained expression for v_Σ with the Horiuti Boreskov relationship

$$v_\Sigma = v^{+} - v \quad ,$$

where $v^{+} = \varepsilon_\Sigma\tilde{R}_1\tilde{R}_2$ and $v \quad = \varepsilon_\Sigma\tilde{P}$.

In the traditional kinetic form, this expression can be written as

$$v_\Sigma = \vec{k}_\Sigma \prod_\alpha c_\alpha^{\nu_{R\alpha}} - \overleftarrow{k}_\Sigma \prod_\alpha c_\alpha^{\nu_{P\alpha}} = \vec{k}_\Sigma\left(\prod_\alpha c_\alpha^{\nu_{R\alpha}} - \frac{1}{K_{p\Sigma}}\prod_\alpha c_\alpha^{\nu_{P\alpha}}\right).$$

For elementary reactions, the term *molecularity* is commonly used, ν_{ij}, of the elementary transformation, which means the number of molecules that are involved directly in the elementary act: $\vec{\nu}_{ij} = \sum\nu_{i\alpha}$ и $\overleftarrow{\nu}_{ij} = \sum\nu_{j\alpha}$. Evidently, this term cannot be applied directly to the stepwise processes, but the expression for v_Σ may be associated with the term *formal molecularity* v_Σ *of the stepwise reaction*, which equals

$$\vec{\nu}_\Sigma \equiv \sum_\alpha \nu_{R\alpha}$$

for the left to right reaction and

$$\overleftarrow{\nu}_{\Sigma} \equiv \sum_{\alpha} \nu_{P\alpha}$$

for the reverse reaction.

It is important to remember that if the Horiuti Boreskov relationship is valid at any concentrations of "external" reactants, then both of the formal molecularities of the stepwise reaction remain constant as well. Note also that in most cases, the Horiuti Boreskov relationship may not be valid for the stationary occurrence of stepwise reactions with transformations that are nonlinear in respect to the intermediates. The formal molecularities of the entire stepwise process in such cases may change upon variations in the concentrations of the "external" reactants.

1.3.2.1. Transformations that are Nonlinear in Respect to their Intermediates

The failure of the Horiuti Boreskov relationship and the possibility of changing the formal molecularities of a stepwise reaction can be demonstrated in the following simple example. Let us consider a stepwise process

$$2\mathrm{R} \rightleftarrows \mathrm{P}, \tag{1.41}$$

that follows a simple scheme that is nonlinear in respect to intermediate Y:

$$\mathrm{R} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{Y}, \tag{1.42}$$

$$\mathrm{Y} + \mathrm{Y} \overset{\varepsilon_2}{\rightleftarrows} \mathrm{P}.$$

When the stepwise reaction is written in the form (1.41), its formal molecularity is evidently $\vec{\nu}_{\Sigma} = 2$ for the direction from left to right and $\overleftarrow{\nu}_{\Sigma} = 1$ for the direction from right to left. The rate of the stepwise process in the stationary mode is

$$v_{\Sigma} \equiv \frac{d[P]}{dt} \equiv -\frac{1}{2}\frac{d[R]}{dt} = \varepsilon_2(\tilde{Y}^2 - \tilde{P}) = \frac{\varepsilon_1}{2}(\tilde{R} - \tilde{Y}).$$

The following relationship is valid for the stationary state with respect to the intermediate:

$$\frac{d[Y]}{dt} = \varepsilon_1(\tilde{R} - \tilde{Y}) - 2\varepsilon_2(\tilde{Y}^2 - \tilde{P}) = 0.$$

Now let us introduce a new variable

$$\delta \equiv \tilde{R} - \tilde{Y}$$

that gives

$$\tilde{Y} = \tilde{R} - \delta.$$

From the condition of the stationary mode it gives

$$\varepsilon_1\delta - 2\varepsilon_2(\tilde{R}^2 - 2\tilde{R}\delta + \delta^2 - \tilde{P}) = 0, \tag{1.43}$$

or

$$\delta^2 - \left(2\tilde{R} + \frac{\varepsilon_1}{2\varepsilon_2}\right)\delta + (\tilde{R}^2 - \tilde{P}) = 0. \tag{1.44}$$

This equation is quadratic in respect to δ. Its solution gives

$$\delta_{1,2} = \left(\tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2}\right) \pm \sqrt{\left(\tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2}\right)^2 - \left(\tilde{R}^2 - \tilde{P}\right)}. \tag{1.45}$$

Both of the solutions with respect to variable δ relate to real and positive quantities. However, if the stepwise reaction goes, say, from left to right, then in the stationary state, two inequalities must be fulfilled: $\tilde{R} > \tilde{Y}$ и $\tilde{Y}^2 > \tilde{P}$. As a consequence, $0 < \delta < \tilde{R}$. While $\delta_1 < \tilde{R}$, only the solution $\delta = \delta_2 < \tilde{R}$ has physical sense.

Although

$$v_\Sigma = \frac{\varepsilon_1}{2}\delta,$$

it is evident that the stationary rate of the stepwise process is in general not proportional to $\left(\tilde{R}^2 \quad \tilde{P}\right)$; in other words, not proportional to the difference between thermodynamic rushes of the initial and final reaction species. This proves that for stepwise chemical transformations that are nonlinear in respect to intermediates, the Horiuti Boreskov relationship can indeed be invalid.

It is important to consider, however, that for the stepwise process under consideration, the Horiuti Boreskov relationship is obviously fulfilled in the case when the process occurs close to the equilibrium, which means $\tilde{R}^2 \approx \tilde{P}$ or, more specifically,

$$\tilde{R}^2 - \tilde{P} \ll \left(\tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2}\right)^2.$$

In this case, it follows from equation (1.45) that

$$\delta = \delta_2 \approx \tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2} - \left(\tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2}\right)\left\{1 - \frac{1}{2}\frac{\tilde{R}^2 - \tilde{P}}{\left(\tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2}\right)^2}\right\} = \frac{2\varepsilon_2\left(\tilde{R}^2 - \tilde{P}\right)}{\varepsilon_1 + 4\varepsilon_2\tilde{R}},$$

and thus

$$v_\Sigma = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + 4\varepsilon_2\tilde{R}}(\tilde{R}^2 - \tilde{P}). \qquad (1.46)$$

Hence, the Horiuti Boreskov relationships are always met close to the equilibrium. In terms of the kinetic thermodynamic analysis, it means that close to the equilibrium the stepwise process can be considered as one effective elementary reaction between the initial and final reaction groups. Relationship (1.46) is valid, too, for the reverse process (from right to left) that occurs near the equilibrium point.

At the same time, this means that near the equilibrium of the stepwise process under consideration, actually $\vec{\nu}_\Sigma = 2$ and $\overleftarrow{\nu}_\Sigma = 1$. More difficulties arise at the analysis of the stationary rate of the stepwise process in the sys tem that is far away from the equilibrium. For example, for a left to right direction of the process, equation (1.44) is simplified at $\tilde{R}^2 \gg \tilde{P}$:

$$\delta^2 - \left(2\tilde{R} + \frac{\varepsilon_1}{2\varepsilon_2}\right)\delta + \tilde{R}^2 = 0.$$

One can see that at $\tilde{R} \gg \frac{\varepsilon_1}{4\varepsilon_2}$,

$$\delta \approx \tilde{R}$$

and

$$v_\Sigma \approx \frac{\varepsilon_1}{2}\tilde{R}.$$

Formally, this corresponds to the rate of a kinetically irreversible mono molecular reaction

$$R \rightarrow \frac{P}{2};$$

that is, to $\vec{\nu}_\Sigma = 1$. It means a sufficient change in the value of the formal molecularity in comparison with what we had close to the equilibrium.

At the same time, at $\tilde{R} \ll \frac{\varepsilon_1}{4\varepsilon_2}$,

$$\delta \approx \frac{2\varepsilon_2}{\varepsilon_1}\tilde{R}^2$$

and

$$v_\Sigma \approx \varepsilon_2\tilde{R}^2,$$

that corresponds, formally, to the rate of a kinetically irreversible bimolecular reaction

$$R + R \rightarrow P;$$

that is, $\vec{\nu}_\Sigma = 2$.

When the stepwise reaction goes in the right to left direction far from its equilibrium,

$$\tilde{R}^2 \ll \tilde{P}$$

and the following solution is physically meaningful:

$$\delta = \delta_2 < 0.$$

It is obvious that if

$$\tilde{P} \gg \left(\tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2}\right)^2,$$

then

$$\delta \approx -\sqrt{\tilde{P}}$$

and consequently,

$$v_\Sigma \approx -\frac{\varepsilon_1}{2}\sqrt{\tilde{P}}.$$

Formally, the resulting expression relates to the impact of the driving force of a hypothetical kinetically irreversible stoichiometric reaction

$$\frac{1}{2}P \rightarrow R;$$

that is, $\overleftarrow{\nu}_\Sigma = 1/2$.

It is interesting that at $R_1 = R_2$ the preceding stepwise reaction (1.38) is identical to stepwise reaction (1.41). Nevertheless, the formal molecularity of stepwise process (1.38) remains constant at any concentrations of external reactants, this being a direct consequence of the scheme (1.38) linearity with respect to intermediate Y.

1.3.3. Chemical Potentials of Intermediates

In a stationary process, the direction of changes in actual values of μ_i and $\tilde{Y}_i$ for intermediates Y_i is always strongly determined. For example, in the course of consecutive monomolecular transformations, the values of μ_i (and, correspondingly, of $\tilde{Y}_i$) always decrease along the pathway from the initial reactant to the final product (Figures 1.4 and 1.5).

In the stationary state, the actual current values of chemical potentials of the intermediate reactive species must decrease in the stepwise fashion toward the final products, the values being only those between the "external" initial reactants and the final products. Hence, any chemical transformations of the intermediates are described only by the transformations between the said stationary values of chemical potentials. Figuratively speaking, the intermediates in their stationary state accumulate the Gibbs

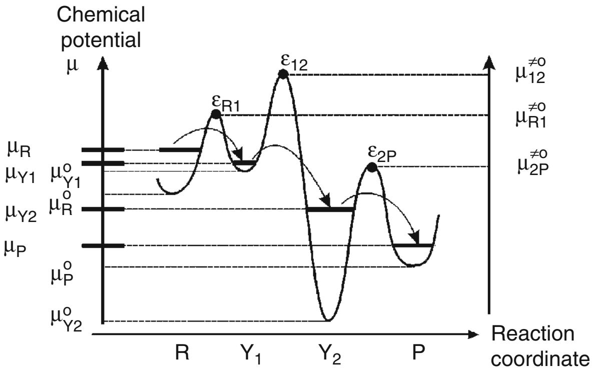


Figure 1.4 A schematic diagram of chemical potential changes at the stationary occurrence of a stepwise reaction $R \rightleftarrows Y_1 \rightleftarrows Y_2 \rightleftarrows P$, where R and P are the initial reactant and final product of the reaction, while Y_1 and Y_2 are thermalized intermediates. The minimums in the traditional potential energy profile relate to the standard chemical potentials of thermalized external reactants and intermediates. However, actual chemical transformations of the intermediates occur at stationary values μ_{Y1} and μ_{Y2} (bold lines), the rates of these transformations being dependent on the difference of the corresponding thermodynamic rushes and the values of truncated rate constants ε_{ij} (the latter are functions of standard chemical potentials $\mu_{ij}^{/ \circ}$ of the transition states only).

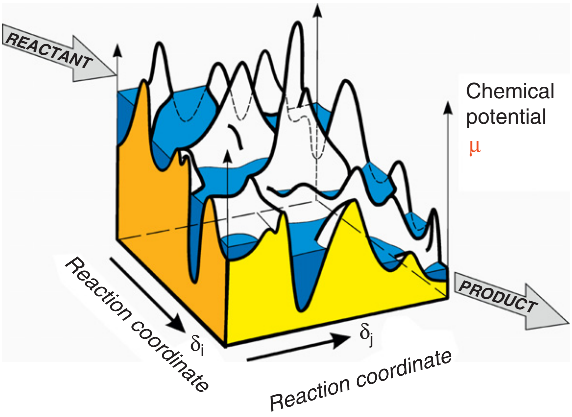


Figure 1.5 The world of *mountains* of actual chemical potentials of transition states and *lakes* of stationary chemical potentials of intermediates in the systems with a plurality of the allowed monomolecular transformation of initial reactant R into final product P. The surface levels of the stationary lakes are gradually decreasing from the reactant to the product.

energy of the initial reactant group to raise their stationary chemical potentials (for example, due to an increase in the intermediate concentration) above the level of the final reactant group potential to the level that is determined by truncated rate constants ε_{ij} of the chemical reactions—in other words, by the standard characteristics of corresponding transition states.

1.4. THE KINETIC-THERMODYNAMIC ANALYSIS OF THE STATIONARY MODE OF NONCATALYTIC STEPWISE REACTIONS

The thermodynamic form of kinetic equations is helpful for providing the kinetic thermodynamic analysis of the effect of various thermodynamic parameters on the stationary rate of complex stepwise processes. Following are a few examples of such analyses in application to the noncatalytic reactions. The analysis of the occurrence of catalytic transformations is more specific because the concentrations and, therefore, the chemical potentials and thermodynamic rushes of the intermediates are usually related to one another in the total concentrations of the catalytically active centers. (Catalytic reactions are discussed in more detail in Chapter 4.)

1.4.1. Independence of the Stationary Rate of the Standard Thermodynamic Parameters of the Reaction Intermediates*

We just saw that for a stepwise reaction

$$\mathrm{R} \rightleftarrows \mathrm{P},$$

that is linear in respect to intermediates, in its stationary mode

$$\mathrm{v}_\Sigma = \varepsilon_\Sigma\left(\tilde{\mathrm{R}} - \tilde{\mathrm{P}}\right).$$

In this case, ε_Σ is determined by the standard thermodynamic parameters of both the transition states and the initial and final reactants but not of the thermalized intermediates. Therefore, equations (1.36) and (1.40) conclude that the stationary rate of a complex stepwise reaction comprising an arbitrary combination of intermediate linear transformations is independent of the standard values of thermodynamic parameters of the intermediates. It is determined only by the difference of thermodynamic rushes of the initial reactant and the product, as well as by the standard thermodynamic parameters of the transition states between various intertransforming reaction groups.

This specific feature of the stationary state of chemical systems that undergo their evolution via an arbitrary combination of only monomolecular (or reduced to monomolecular) transformations, as well as transformations that are linear in respect to the intermediates, is of practical importance to simplify the analysis of complex stepwise chemical processes with the use of methods of nonequilibrium thermodynamics.

1.4.2. Criteria of Kinetic Irreversibility of Chemical Reactions

Sometimes partial thermodynamic equilibria between some reaction groups may happen at the stationary occurrence of complicated stepwise processes. Unlike true (full) equilibria, the partial equilibria occur with the boundary conditions that contain the values of the chemical potentials of intermediates (i.e., the concentrations of intermediates) that are determined by the stationary states.

An important consideration is the variations in thermodynamic rushes of the reaction groups in elementary reactions that are not in the partial

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*Generally, the conclusion may be invalid for catalytic transformations (see Section 4.2.2).

equilibrium. Evidently, at $\mu_i - \mu_j \geq RT$ the actual values of $\tilde{n}_i$ and $\tilde{n}_j$ differ a great deal. At the same time, at a large (against RT) difference between μ_i and μ_j, the rate of the backward reaction is negligible compared to the reaction in the forward direction. It means that this individual reaction can be considered kinetically irreversible.

Let us find the correct thermodynamic criteria of kinetic irreversibility of chemical reactions. It is evident for an elementary reaction ij that the statement

$$v_{ij} = \varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j) \approx \varepsilon_{ij}\tilde{n}_i$$

is identical to the statement of $\tilde{n}_i \gg \tilde{n}_j$. While $\mu_j = \mu_i - A_{rij}$, then

$$v_{ij} = \varepsilon_{ij}\left[\exp\left(\frac{\mu_i}{RT}\right) - \exp\left(\frac{\mu_j}{RT}\right)\right] = \varepsilon_{ij}\tilde{n}_i\left[1 - \exp\left(-\frac{A_{rij}}{RT}\right)\right]. \tag{1.47}$$

Hence, the correct thermodynamic criterion of the kinetic irreversibility at any step in the chemical transformation chain is a considerable (against quantity RT) change in the chemical potential of the reaction groups related to this step—that is, $A_{rij} > RT$. Note that the criterion is valid for both elementary and stepwise reaction, although in the latter case, one must consider the affinity for the stepwise transformation: $A_{r\Sigma} > RT$.

In kinetic diagrams, the kinetic irreversibility is usually indicated with a single arrow (→), while the potential kinetic reversibility is shown by a double arrow (⇄). In any complex pathway with the known drops of chemical potentials at individual stages, the transformation chain can be broken down into kinetically reversible and kinetically irreversible steps (Figure 1.6). A priori consideration of some elementary steps of a stepwise reaction as kinetically irreversible may cause some serious mistakes in making conclusions via classical kinetic analysis of the scheme of chemical transformations.

An important consequence of the preceding consideration is the evident occurrence of the limitation (which is typically not taken into account) for the maximum allowed number of kinetically irreversible steps in the real stationary chemical reactions. Indeed, when the consecutive elementary chemical reactions proceed in the stationary mode, a total of affinity $A_{r\Sigma}$ of the stepwise reaction equals the sum of affinities of all the elementary steps

$$A_{r\Sigma} = \Sigma A_{rij},$$

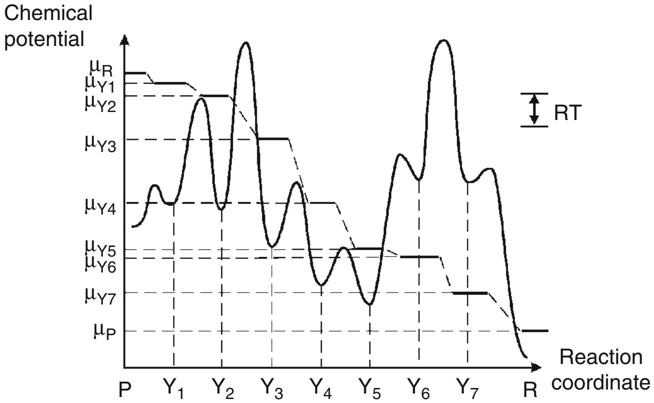


Figure 1.6 Partition of the transformation sequence into groups with the kinetic "irreversibility" between them. When the reaction goes left to right, transformations $Y_2 \rightarrow Y_3$, $Y_3 \rightarrow Y_4$, $Y_4 \rightarrow Y_5$, $Y_5 \rightarrow Y_6$, $Y_6 \rightarrow Y_7$, and $Y_7 \rightarrow P$ can be considered as kinetically irreversible, whereas the kinetic reversibility must be taken into consideration for transformations $R \rightleftarrows Y_1$, $Y_1 \rightleftarrows Y_2$, and $Y_5 \rightleftarrows Y_6$. The differences of stationary chemical potentials of intermediates are greater than RT for the former groups but smaller than RT for the latter groups (the scale is shown at the top right).

so that the maximum number of kinetically irreversible steps cannot exceed the value more than $m = (\mu_R \quad \mu_P)/RT = A_{r\Sigma}/RT$. Although this limitation seems rather obvious, it can hardly be deduced in terms of a "pure" kinetic approach.

1.4.3. Rate-Limiting, Rate-Determining and Rate-Controlling Steps

The concept of the rate limiting step in a sequence of chemical transformations is conventionally associated with a "bottleneck." It is hardly possible to provide a consistent mathematical definition of a bottleneck in terms of classical chemical kinetics, but the concept of the rate controlling step can be defined easily.

According to the IUPAC *Compendium of Terms in Physical Chemistry,* the rate controlling (rate determining) step of a stepwise reaction is an elementary reaction of which rate constant has the greatest (greater than the other rate constants) influence on the resulting rate of the stepwise reaction. Formally, the rate controlling step can be identified by comparing the magnitudes of the rate controlling factor CF_i of individual steps of the stepwise process:

$$CF_i = (\partial \ln v_\Sigma / \partial \ln k_i)_{K_j, k_l,\ j \neq i,\ l \neq i}, \qquad (1.48)$$

where v_Σ is the resulting rate of the stepwise reaction; k_i is the rate constant of elementary reaction i; and K_j is the equilibrium constant of elementary reaction j. The rate controlling step is that with the largest value of CF_i.

Notice, however, that in a general case, equation (1.48) has a mathematical dilemma: While the reaction groups are identical for the direct and backward reactions, the rate constant of any elementary "forward" reaction i is rigidly bound with that of its backward reaction:

$$\overrightarrow{k}_i = \overleftarrow{k}_i K_i = \overleftarrow{k}_i \exp\left(-\Delta_r G_i^o/RT\right) = \overleftarrow{k}_i \exp\left(A_{ri}^o/RT\right).$$

Here, $\Delta_r G_i^o$ is the change of the standard Gibbs energy for the reaction i in the forward direction. As a result, $\overrightarrow{k}_i$ derivative is mathematically invalid at fixed $\overleftarrow{k}_i$ in equation (1.48). Thus, equation (1.48) cannot be applied directly for finding the rate determining steps, since the preceding thermodynamic relationships of some rate constants are necessary to consider for mathematical reasons.

The classical chemical kinetics allows resolution of the problem by classifying all of the steps of the stepwise process into two categories: fast (i.e., those resulting in partial dynamic equilibria of some of elementary reactions) and slow (those that are far from their dynamic equilibria). In this case, the overall reaction rate v_Σ appears to be a function of parameters k_i of the direct reaction only for the slow stages and of parameters K_i for the fast stages. Thus, the slow elementary reactions are considered as kinetically irreversible—that is, only a forward reaction i but not its backward reaction can be considered.

If the latter condition is met, two independent equations can be derived from equation (1.48):

$$CF_{kin,i} = (\partial \ln v_\Sigma / \partial \ln k_i)_{k_j, K_l,\ j \neq i,\ l \neq i} \tag{1.49}$$

and

$$CF_{eq,i} = (\partial \ln v_\Sigma / \partial \ln K_i)_{k_j, K_l,\ j \neq i,\ l \neq i}. \tag{1.50}$$

Here, symbol CF_{kin} is used for designating the influence of true kinetic parameters—the rate constants k_i—that control the rate of the stepwise reaction. Symbol CF_{eq} means the influence of equilibrium fast stages that control the stepwise reaction rate through thermodynamic parameters such as equilibrium constants K_i rather than kinetic ones.

In a general case, a priori classification of elementary reactions into "fast" and "slow" is hardly possible. Hence, the problem of how to identify the rate controlling steps of an ad hoc stepwise process remains obscure. The thermodynamic form of kinetic equations allows a consistent approach to identification of the rate determining parameters by separating the influence of standard thermodynamic parameters of the transition states of the reactions (via parameters ε_{ij}) and of thermodynamic parameters of thermalized intermediates (via parameters $\tilde{n}_{\alpha}$). This means of analysis may be of particular importance for finding the solutions to many urgent problems because the specialization of the question "Which parameters are determining the process rate?" changes to "Which is more important: energetic parameters of the transition states or energetic parameters of thermalized reactants?"

In fact, when the reaction rate is expressed using parameters ε_{ij} and $\tilde{n}_{i}$, it is easy to separate the influence of standard thermodynamic parameters of the transition states from the influence of thermodynamic parameters of thermalized reactants (these may be both initial reactants and intermediates). If so, it is reasonable to discuss two types of rate controlling factors CF:

1. The rate controlling factors that are dependent on the parameters of the transition states of elementary reactions ij:

$$\mathrm{CF}_{\mathrm{tr}ij} = \left(\partial \ln v_{\Sigma} / \partial \ln \varepsilon_{ij}\right)_{\varepsilon_{kl},\mu_{\beta},kl\neq ij(k,l,\beta=1,2,\ldots)} \tag{1.51}$$

2. The rate controlling factors that are dependent on standard parameters of thermalized reactants A_{α}:

$$\mathrm{CF}_{\alpha} = \left(\partial \ln v_{\Sigma} / \partial \ln \tilde{A}_{\alpha}^{o}\right)_{\varepsilon_{ij},\mu_{\beta}(\beta=1,2,\ldots,\beta\neq\alpha)}, \tag{1.52}$$

where $\tilde{A}_{\alpha}^{o} \equiv \exp\left(\mu_{\alpha}^{o}/RT\right)$.

It is essential that the equations for CF in this form have no "mathematical" contradictions related to the previously mentioned relationships between the rate constants of the forward and backward reactions.

Following are a few examples of such identification of the rate controlling parameters that are demonstrated at the consideration of stepwise reactions with simple schemes of the transformations. Included are the stationary modes of the reaction occurrences.

1.4.4. Rate-Determining Parameters of a Sequence of Monomolecular Reactions

Let us consider the simplest stepwise reaction

$$\mathrm{R} \rightleftarrows \mathrm{P},$$

where R and P are the initial reactant and final product, respectively, and the reaction is mediated by one intermediate Y:

$$\mathrm{R} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{Y},$$

$$\mathrm{R} \overset{\varepsilon_2}{\rightleftarrows} \mathrm{P}.$$

The preceding shows that stationary rate v_Σ of this stepwise reaction is

$$v_\Sigma = \frac{d[P]}{dt} = -\frac{d[R]}{dt} = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\left(\tilde{R} - \tilde{P}\right). \tag{1.53}$$

One can see from this equation that when $\varepsilon_1 \ll \varepsilon_2$,

$$v_\Sigma \approx \varepsilon_1\left(\tilde{R} - \tilde{P}\right);$$

that is, the first step is the rate determining one. The second step is the rate determining one at $\varepsilon_1 \gg \varepsilon_2$:

$$v_\Sigma \approx \varepsilon_2\left(\tilde{R} - \tilde{P}\right).$$

Indeed, this means that the criterium for choosing the rate determining step is the minimum of ε_i.

In a more general case, when the stepwise process includes a set of consecutive monomolecular transformations:

$$\mathrm{R} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{Y}_1 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{Y}_2 \overset{\varepsilon_3}{\rightleftarrows} \ldots \overset{\varepsilon_n}{\rightleftarrows} \mathrm{Y}_n \overset{\varepsilon_{n+1}}{\rightleftarrows} \mathrm{P}. \tag{1.54}$$

where Y_i are thermalized intermediates, the stationary rate of the overall process is expressed as

$$v_\Sigma \equiv \frac{d[P]}{dt} = -\frac{d[R]}{dt} = \varepsilon_\Sigma\left(\tilde{R} - \tilde{P}\right), \tag{1.55}$$

where

$$\frac{1}{\varepsilon_\Sigma}=\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}+\frac{1}{\varepsilon_3}+\ldots+\frac{1}{\varepsilon_n}+\frac{1}{\varepsilon_{n+1}}. \tag{1.56}$$

The first important consequence of relationships (1.55)–(1.56) is the preceding conclusion that the stationary rate of sequential monomolecular transformations is fully independent of the standard thermodynamic parameters of thermalized intermediates. The only thermodynamic parameters that affect the stationary rate of the stepwise process are chemical potentials of the initial and final products as constituents of parameters $\tilde{R}$ and $\tilde{P}$, as well as standard chemical potentials of the transition states as constituents of parameters ε_i.

One can also see from equation (1.56) that in the scheme under consideration, the step with minimum ε_i is the rate determining one, too. In fact, equation (1.56) gives CF_{tri} as equal to

$$\begin{aligned} CF_{tri} &= \partial \ln \varepsilon_\Sigma / \partial \ln \varepsilon_i = \partial \ln(1/\varepsilon_\Sigma)/\partial \ln(1/\varepsilon_i) \\ &= \frac{\varepsilon_\Sigma}{\varepsilon_i}\cdot\frac{\partial(1/\varepsilon_\Sigma)}{\partial(1/\varepsilon_i)} = \frac{\varepsilon_\Sigma}{\varepsilon_i} = 1 \Bigg/ \left(\frac{\varepsilon_i}{\varepsilon_1}+\frac{\varepsilon_i}{\varepsilon_2}+\ldots+\frac{\varepsilon_i}{\varepsilon_{n+1}}\right). \end{aligned} \tag{1.57}$$

Hence, the maximum CF_{tri} quantity is determined by the minimum value of ε_i.

At the same time, the rate determining step features the maximum difference of thermodynamic rushes (or the maximum difference of chemical potentials) between the reacting partners in the process under consideration. Indeed, in the consecutive transformations, the stationary rates are identical through all of the reaction channels:

$$v_\Sigma \equiv \frac{d[P]}{dt} = v_1 = v_2 = \ldots = v_{n+1} = v_i = \varepsilon_i(\tilde{Y}_{i\ \ 1} - \tilde{Y}_i).$$

(Here and later, $\tilde{Y}_o$ means $\tilde{R}$, while $\tilde{Y}_{n+1}$ means $\tilde{P}$.)

Therefore, the difference of thermodynamic rushes at elementary step i is equal to

$$\tilde{Y}_{i\ \ 1} - \tilde{Y}_i \equiv \exp(\mu_{i\ \ 1}/RT) - \exp(\mu_i/RT) = \frac{v_\Sigma}{\varepsilon_i}.$$

And thus, the difference $\left(\tilde{Y}_i \quad \tilde{Y}_{i+1}\right)$ is maximum indeed at the minimum ε_i value.

The maximum difference of thermodynamic rushes is, obviously, correspondent to the occurrence of the bottleneck in the stepwise reaction. Therefore, the rate limiting step in a sequence of chemical transformations is naturally to define as some elementary step with the maximum difference of thermodynamic rushes (or that has nearly the same chemical potentials) of the reaction groups involved in the transformation. Horiuti first mentioned this specificity of the stepwise reaction bottleneck.

In our example, the rate limiting and rate determining steps coincide, but this may not happen. Some examples of when there is no coincidence in the rate limiting and rate determining steps are discussed in the case of catalytic stepwise reactions (see Section 4.3).

Among the thermodynamic parameters of thermalized reactants, only parameters of *external* reactants R and P influence the rate v_Σ in this example. The most considerable is the influence of the reactant with the greatest thermodynamic rush—for example, $\tilde{R}$. This also means that reactant R is the initial reactant in the stepwise transformation (i.e., the reaction goes from R toward P). This statement is illustrated diagrammatically in Figure 1.7.

When the transformation chain has only one pronounced limiting step, $Y_{j\ 1} \rightleftarrows Yj$, inequality $\varepsilon_{\text{lim}} \equiv \varepsilon_j \ll \varepsilon_i$, where $i \neq j$, is obviously satisfied:

$$\tilde{Y}_{j\ 1} - \tilde{Y}_j \approx \frac{\varepsilon_\Sigma}{\varepsilon_j}\left(\tilde{R} - \tilde{P}\right) \approx \tilde{R} - \tilde{P}.$$

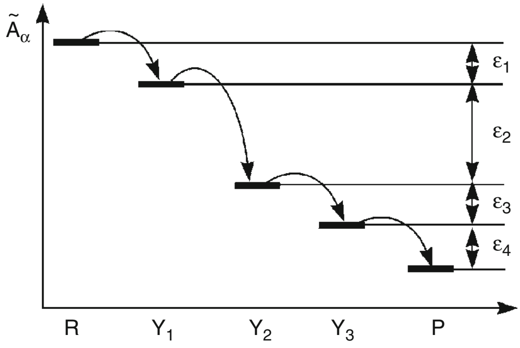


Figure 1.7 An example of the interrelation of the bottleneck created by the rate-limiting step of a consecutive set of monomolecular transformations with the decrease in thermodynamic rushes of consecutive thermalized in intermediates Y_i. The stationary rate of the overall stepwise reaction here should be $v_\Sigma = \varepsilon_2(\tilde{R}\quad \tilde{P})$. Thus, the rate-controlling parameters here are truncated rate constant ε_2 and, consequently, the energy of the transition state for elementary reaction $Y_1 \rightleftarrows Y_2$, as well as thermodynamic rushes of initial reactant R and final product P.

Hence, practically all the difference of thermodynamic rushes in the transformation chain falls on only one rate limiting step. When the stepwise reaction is kinetically irreversible (i.e., $\tilde{R} \gg \tilde{P}$),

$$\tilde{Y}_{j\ \ 1} - \tilde{Y}_j \approx \tilde{R}.$$

Thus, all of the steps prior to the rate limiting one may be treated, formally, as being in partial equilibrium.

An important a priori assumption of the kinetic irreversibility of any step of a stepwise process is that it may result in considerable errors in identifying both the rate limiting and the rate determining steps. Let us illustrate this statement with the preceding sequence of monomolecular reactions. If the "kinetic irreversibility" of all of the elementary reactions is a priori assumed, then the direct consequence of this statement is the following relationship:

$$v_{\Sigma} = \varepsilon_1 \tilde{R} \approx \varepsilon_2 \tilde{Y}_1 \approx \ldots \approx \varepsilon_{n+1} \tilde{Y}_n.$$

At the same time, by definition,

$$v_{\Sigma} = \varepsilon_{\Sigma} \tilde{R}.$$

This means that $\varepsilon_{\Sigma} = \varepsilon_{1,}$ and, as a result, the first elementary reaction, which is a priori considered kinetically irreversible, appears to be the rate determining or even rate limiting step of the entire transformation. This conclusion may differ from the result of analysis obtained without any a priori assumptions on the kinetic irreversibility of individual steps. In conclusion, any a priori assumption on the kinetic irreversibility of, for example, all steps of the stepwise process is evidently too crude in general cases. In our example, the objective requirement of the rate limiting nature of the first step is the inequality $\varepsilon_1 \ll \varepsilon_i$ at $i \neq 1$.

1.4.5. Apparent Activation Energy of a Stepwise Process

The thermodynamic form of kinetic equations allows us to easily find the apparent activation energy, $E_{a\Sigma}$, for the stationary occurrence of stepwise processes, especially in the case of their kinetic irreversibility. For instance, if stepwise process (1.54) goes from left to right and is kinetically irreversible in whole—that is, $\tilde{R} \gg \tilde{P}$—and if ε_{lim} is the smallest quantity of all ε_i in the transformation chain, then

$$v_{\Sigma} \equiv \frac{d[P]}{dt} = \varepsilon_{\text{lim}} \tilde{R}. \tag{1.58}$$

By definition, the apparent activation energy of a process is determined by the equation

$$E_{a\Sigma} = RT^2 \frac{d \ln v_\Sigma}{dT},$$

with T being the temperature for which the value of $E_{a\Sigma}$ is defined. Evidently, if the temperature dependencies of $\varepsilon_{\lim}$ and $\tilde{R}$ are given by equations (1.26)–(1.29), in our example,

$$E_{a\Sigma} = \Delta_f H^{\neq o}_{\lim} - \Delta_f H^o_R + RT. \tag{1.59}$$

Here, $\Delta_f H^o_R$ and $\Delta_f H^{/o}_{\lim}$ are the standard enthalpies of formation of initial "external" reactant R and of the transition state of the rate determining elementary reaction, respectively. In other words, the resulting activation energy of this stepwise process is determined by the difference between the standard enthalpy of the transition state (from the transformation chain) with the "highest" Gibbs energy and the standard enthalpy of the initial reactant (Figure 1.8). The appearance of an additional RT term in equation (1.59) is a result of the presence of a preexponential factor $\frac{k_B T}{h}$ in equation (1.29).

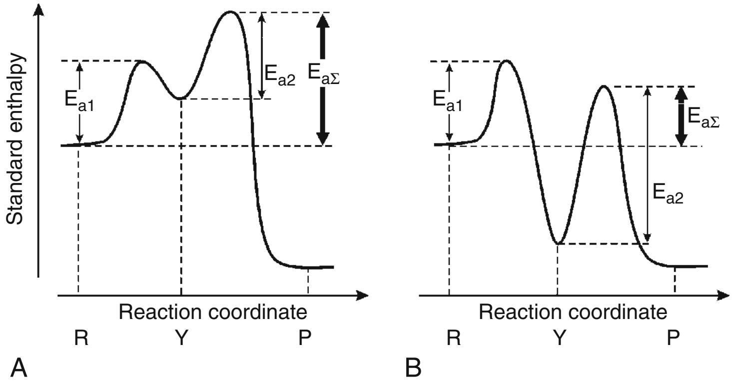


Figure 1.8 A graphical interpretation of determination of the apparent activation energy $E_{a\Sigma}$ of a simple stepwise process $R \rightleftarrows P$ with one intermediate $Y(R \overset{\varepsilon_1}{\rightleftarrows} Y \overset{\varepsilon_2}{\rightleftarrows} P)$ in the case of a left-to-right process with the elementary reaction $Y \rightleftarrows P$ as the rate-limiting stage. Cases a and b relate to different enthalpies of the transition state formation.

Notice that equation (1.59) meets the commonly known rule that the apparent activation energy of a consecutive process equals the activation energy of the rate limiting step minus the sum of the heats (or plus sum of standard enthalpies, $\sum_i \Delta_r H_i^o$) of the preceding stages, which are treated as being in equilibrium.

In fact, activation energy of a kinetically irreversible reaction i equals

$$E_{ai} \equiv \Delta_f H_i^{\neq o} - \Delta_f H_i^o + RT,$$

where $\Delta_f H_i^o$ is the standard enthalpy of formation of the starting reagent for this reaction.

If this reaction is the rate limiting step, then

$$E_{ai} \equiv E_{a\,\mathrm{lim}}.$$

Then equation (1.59) gives

$$E_{a\Sigma} = E_{a\,\mathrm{lim}} + \Delta_f H_i^o - \Delta_f H_R^o \equiv E_{a\,\mathrm{lim}} + \sum_i \Delta_r H_i^o.$$

The same conclusion can be made with the help of classical kinetics: Since all of the steps that precede the rate limiting step can be considered as being in equilibrium (see Section 1.4.4), the apparent "classical" rate constant for the stepwise transformation is expressed as

$$\vec{k}_\Sigma = \prod_i K_i \vec{k}_{\mathrm{lim}},$$

where $\vec{k}_{\mathrm{lim}}$ means the "classical" rate constant of the rate limiting step, while $\prod_i K_i$ means the product of the equilibrium constants for all of the preceding steps. Note that the apparent activation energy of a stepwise process can be lower than activation energies of elementary steps comprised in this stepwise process (see Figure 1.8B).

1.4.6. Rate-Limiting Steps, Rate-Determining Parameters, and Apparent Activation Energy of Simple Schemes of Chemical Transformations

Following are several simple examples of finding the rate limiting steps in consecutive transformations, both linear and nonlinear, in respect to intermediates.

Example 1 The Chain of Linear Transformations in Respect to Intermediates

Let us find the rate-determining parameters for a simple stepwise bimolecular reaction just discussed (see equations (1.38) (1.39)):

$$R_1 + R_2 \rightleftarrows P,$$

where R_1 and R_2 are the initial reactants and P is the final product for the case when the stepwise mechanism is described by a simple scheme with one thermalized intermediate Y:

$$R_1 \overset{\varepsilon_1}{\rightleftarrows} Y,$$
$$R_2 + Y \overset{\varepsilon_2}{\rightleftarrows} P.$$

According to the equation (1.40), the stationary rate of this stepwise reaction is expressed as

$$v_{\Sigma} \equiv \frac{d[P]}{dt} = \quad \frac{d[R_1]}{dt} = \quad \frac{d[R_2]}{dt} = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2 \tilde{R}_2} (\tilde{R}_1 \tilde{R}_2 \quad \tilde{P}).$$

Obviously, the rate-determining step is easy to identify by comparing summands in the denominator of this equation.

At $\varepsilon_1 \ll \varepsilon_2 \tilde{R}_2$

$$v_{\Sigma} \approx \frac{\varepsilon_1}{\tilde{R}_2} (\tilde{R}_1 \tilde{R}_2 \quad \tilde{P});$$

that is, the first step is the rate-determining one. The same step appears to be the rate-limiting one.

When $\varepsilon_1 \gg \varepsilon_2 \tilde{R}_2$,

$$v_{\Sigma} \approx \varepsilon_2 \left(\tilde{R}_1 \tilde{R}_2 \quad \tilde{P}\right),$$

and the second step is the rate-determining as well as the rate-limiting one. It is easy to see in this example that the rate-determining steps are the bottlenecks as well and thus coincide with the rate-limiting ones.

Let us find the apparent activation energy of the stepwise reaction in the situation far from the reaction equilibrium: at the condition $A_{r\Sigma} \equiv \mu_{R_1} + \mu_{R_2} \quad \mu_P > RT$. Since this is a left-to-right stepwise reaction, then

$$\tilde{R}_1 \tilde{R}_2 \quad \tilde{P} = \exp\left[(\mu_{R_1} + \mu_{R_2})/RT\right] \quad \exp(\mu_P/RT) \approx \tilde{R}_1 \tilde{R}_2.$$

Therefore, if the first elementary reaction is the rate-determining one, then

$$v_{\Sigma} \approx \varepsilon_1 \tilde{R}_1$$

and

$$E_{a\Sigma} \approx \Delta_f H_1^{/o} \quad \Delta_f H^o_{R_1} + RT.$$

It is evident that the given equation of $E_{a\Sigma}$ is identical to the equation of the activation energy E_{a1} of the first elementary step because

$$E_{a1} = \Delta_f H_1^{/o} \quad \Delta_f H^o_{R_1} + RT.$$

If the second elementary reaction is the rate-determining one, then

$$v_{\Sigma} \approx \varepsilon_2 \tilde{R}_1 \tilde{R}_2$$

and

$$E_{a\Sigma} \approx \Delta_f H_2^{/o} \quad \Delta_f H^o_{R_1} \quad \Delta_r H^o_{R_2} + RT. \tag{1.60}$$

In this case, the apparent activation energy is not equal to the activation energy of the rate-determining step. By definition, the activation energy for elementary step 2 equals

$$E_{a2} = \Delta_f H_2^{/o} \quad \Delta_f H^o_Y \quad \Delta_f H^o_{R_2}, \tag{1.61}$$

that differs from the relationship in equation (1.60).

One can see, however, that

$$E_{a\Sigma} = E_{a2} + \Delta_f H^o_Y \quad \Delta_f H^o_{R_1} \equiv E_{a2} + \Delta_r H^o_{R_1,Y},$$

where $\Delta_r H_{R1,Y} \equiv \Delta_f H^o_Y \quad \Delta_f H^o_{R1}$ is the enthalpy of step 1. Thus, the activation energy again equals the sum of the activation energy of the rate-determining step and the enthalpy of the preceding step.

In the case of a right-to-left stepwise reaction that is far from equilibrium,

$$\tilde{R}_1 \tilde{R}_2 \quad \tilde{P} \approx \quad \tilde{P}.$$

Therefore, if step 1 is the rate-determining one, then

$$v_{\Sigma} = \frac{d[P]}{dt} \approx \quad \varepsilon_1 \frac{\tilde{P}}{\tilde{R}_2}.$$

In this case

$$E_{a\Sigma} \approx \Delta_f H_1^{/o} \quad \Delta_f H_P^o + \Delta_f H_{R_2}^o + RT \equiv$$
$$= \left(\Delta_f H_1^{/o} \quad \Delta_f H_Y^o + RT\right) + \left(\Delta_f H_Y^o + \Delta_f H_{R_2}^o \quad \Delta_f H_P^o\right) \equiv E_{\overleftarrow{a}1} + \Delta_r H_{P,R_2Y}^o,$$

where $E_{\overleftarrow{a}1}$ symbolizes the activation energy of elementary reaction 1 that goes right to left that is, from Y to R_1 and $\Delta_r H_{P,R_2Y}^o$ is, as before, the standard enthalpy of the preceding (here) reaction 2 ($P \rightleftarrows R_2 + Y$).

If elementary reaction 2 is rate-determining in the right-to-left stepwise process, then

$$v_\Sigma = \frac{d[P]}{dt} \approx \quad \varepsilon_2 \tilde{P}$$

and

$$E_{a\Sigma} \approx \Delta_f H_2^{/o} \quad \Delta_f H_P^o + RT \equiv E_{\overleftarrow{a}2},$$

where $E_{\overleftarrow{a}2}$ is the activation energy of elementary reaction 1 that goes right to left.

Example 2 The Chain of Transformations with a Step that Is Nonlinear in Respect to Intermediates

Let us identify the rate-determining step of the preceding simple stepwise reaction (1.41) (1.42):

$$2R \rightleftarrows P,$$

that proceeds by the nonlinear mechanism in respect to intermediate Y:

$$R \overset{\varepsilon_1}{\rightleftarrows} Y,$$
$$Y + Y \overset{\varepsilon_2}{\rightleftarrows} P.$$

It follows unambiguously from relationship (1.44) that when

$$\varepsilon_1 \ll 4\varepsilon_2 \tilde{R},$$

step 1 is the rate-determining as well as the rate-limiting step. This inequality is identical to relationship

$$\varepsilon_1 \tilde{R} \ll 4\varepsilon_2 \tilde{R}^2,$$

indicating that at $\delta \approx \tilde{R}$, reaction 1 has a lower potential penetrating "capacity" than reaction 2.

In the left-to-right stepwise process far from equilibrium, $\tilde{R}^2 \gg \tilde{P}$ and, therefore,

$$v_\Sigma \approx \frac{\varepsilon_1}{2}\tilde{R}.$$

In this case

$$E_{a\Sigma} = \Delta_f H_1^{/o} - \Delta_f H_R^o + RT \equiv E_{a1},$$

where E_{a1} is the activation energy of the first, rate-determining, elementary step. If $\varepsilon_1 \gg 4\varepsilon_2\tilde{R}$, then the second reaction is both the rate-determining and the rate-limiting step.

For the left-to-right stepwise reaction far from its thermodynamic equilibrium, relationship (1.45) gives

$$\delta = \delta_2 \approx \left(\tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2}\right)\left\{1 - 1 + \frac{1}{2}\frac{\tilde{R}^2}{\left(\tilde{R} + \frac{\varepsilon_1}{4\varepsilon_2}\right)^2}\right\} \approx \frac{\varepsilon_1}{2\varepsilon_2}\tilde{R}^2$$

and, therefore,

$$v_\Sigma \approx \varepsilon_2\tilde{R}^2.$$

This implies

$$\begin{aligned} E_{a\Sigma} &= \Delta_f H_2^{/o} - 2\Delta_f H_R^o + RT \\ &\equiv \left(\Delta_f H_2^{/o} - 2\Delta_f H_Y^o + RT\right) + \left(2\Delta_f H_Y^o - 2\Delta_f H_R^o\right) = E_{a2} + 2\Delta_r H_{R,Y}^o, \end{aligned}$$

where $E_{a\Sigma} \equiv \Delta_f H_2^{/o} - 2\Delta_f H_Y^o + RT$ is the activation energy of the second elementary step (for the left-to-right pathway), and $\Delta_r H_{R,Y}^o \equiv \Delta_f H_Y^o - \Delta_f H_R^o$ is the standard enthalpy of the reaction $R \rightleftarrows Y$.

Thus, in the case under consideration, the apparent activation energy of the stepwise process is equal to the activation energy of the rate-determining stage plus double enthalpy of the preceding stage. The apparent activation energies of the right-to-left process can be determined the same way. Notice also that the preceding stepwise reaction (1.38) at $R_1 = R_2 = R$ is fully identical to the stepwise reaction (1.41). However, the resulting $E_{a\Sigma}$ for these stepwise reactions appears to be different due to different schemes of the stepwise transformations.

1.4.7. Qualitative Analysis of Some Peculiarities of Stationary States of Stepwise Processes

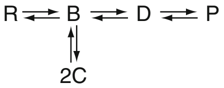
The preceding approaches of the join kinetic thermodynamic analysis of the occurrence of the stepwise processes with the known schemes of the transformations is useful for a qualitative analysis of the state of chemical intermediates in the course of, for example, steady state processes. Let us demonstrate this statement in some examples.

Example 3 The Sequence of the Chemical Potential and Concentration Values for a Stepwise Reaction

Let us consider a gas-phase stepwise reaction

$$\mathrm{R} \rightleftarrows \mathrm{P},$$

with $A_{r\Sigma} = 3$ kJ/mol. It goes left to right and follows the pathway



where B, C, and D are intermediates, and reaction B ⇄ D is known to be the rate-determining one. Find for the stationary state (1) the hierarchy of chemical potentials of the intermediates and (2) the hierarchy of the intermediate concentrations. Is there a kinetically irreversible step in the process under consideration? Consider the cases at temperatures $T_1 = 300$ K and $T_2 = 1000$ K.

Solution

In the left-to-right reaction, the necessity of decreasing thermodynamic rushes as well as the existence of partial equilibrium for transformations B ⇄ 2 C give

$$\mu_R > \mu_B = 2\mu_C > \mu_D > \mu_P.$$

The concentration interrelation can be determined from these inequalities, too. However, one should take into consideration that, for example, in ideal mixtures

$$\mu_\alpha = \mu_\alpha^o + RT \ln c_\alpha.$$

Thus, the hierarchy of the concentration may not follow the preceding inequality.

It is essential that $RT_1 = 2.49$ kJ/mol and $RT_2 = 8.31$ kJ/mol. Hence:

1. at temperature T_1

$$RT_1 \approx A_{r\Sigma},$$
$$\mu_A \geq \mu_B = 2\mu_C \geq \mu_D \geq \mu_E.$$

2. at temperature T_2

$$A_{r\Sigma}/RT \approx 0.3;$$

that is, all of the reactions proceed nearby equilibrium.

While $A_{r\Sigma}/RT \leq 1$ for both cases, there are no steps that are kinetically irreversible for the stepwise reaction under consideration.

Example 4 Conditions for Formation of a Solid

Stepwise reaction R ⇄ P in a liquid solution is accompanied by the formation of a solid by-product E. The reaction pathway is

$$R \overset{\varepsilon_1}{\rightleftarrows} B \overset{\varepsilon_2}{\rightleftarrows} P,$$
$$B + D \overset{\varepsilon_3}{\rightleftarrows} E\downarrow,$$

where B is an intermediate and D is an "external" reactant. At what concentrations of the "external" reactants is the formation of solid product E thermodynamically prohibited at the stationary occurrence of the process?

Solution

For intermediate B in its stationary state

$$\frac{d[B]}{dt} = \varepsilon_1\left(\tilde{R} \quad \tilde{B}\right) \quad \varepsilon_2\left(\tilde{B} \quad \tilde{P}\right) \quad \varepsilon_3\left(\tilde{B}\cdot\tilde{D} \quad \tilde{E}\right) = 0.$$

Simultaneously,

$$\frac{d[E]}{dt} = \varepsilon_3\left(\tilde{B}\cdot\tilde{D} \quad \tilde{E}\right).$$

Product E does not form at $\frac{d[E]}{dt} < 0$.

While E is a solid substance, then $\tilde{E} = \text{const}$.

In the stationary state in respect to intermediate B

$$\tilde{B} = \frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P} + \varepsilon_3\tilde{E}}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3\tilde{D}}.$$

Hence,

$$\frac{d[E]}{dt} = \varepsilon_3\left(\frac{(\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P} + \varepsilon_3\tilde{E})\tilde{D}}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3\tilde{D}} \quad \tilde{E}\right)$$
$$= \frac{\varepsilon_3}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3\tilde{D}}\left\{\varepsilon_1(\tilde{R}\cdot\tilde{D} \quad \tilde{E}) + \varepsilon_2(\tilde{P}\cdot\tilde{D} \quad \tilde{E}\right\}.$$

The sign of this equation depends on the sign of the parenthetical equation. Component E does not form at

$$\varepsilon_1(\tilde{R}\cdot\tilde{D}\quad\tilde{E})+\varepsilon_2(\tilde{P}\cdot\tilde{D}\quad\tilde{E})<0$$

or that is the same as

$$(\varepsilon_1\tilde{R}+\varepsilon_2\tilde{P})\tilde{D}<(\varepsilon_1+\varepsilon_2)\tilde{E}.$$

1.5. THERMODYNAMIC FORCES IN SPATIALLY NONUNIFORM SYSTEMS

Real systems are typically spatially nonuniform even if they are inhomogeneous. Such systems are obviously nonequilibrium, since the nonuniform in respect to temperature, pressure, concentrations, and so on generates the matter and/or heat fluxes. This section considers some mathematical tools for calculating thermodynamic forces and fluxes in such systems, as well as the relation of these quantities with "conventional" thermodynamic parameters.

1.5.1. Calculating the Thermodynamic Forces in Spatially Nonuniform Systems

To calculate the thermodynamic forces in spatially nonuniform systems, mathematical notion of divergence is essential. The divergence of a vectorial field $\vec{a}(M)$ in point (x,y,z) is determined as a scalar quantity

$$\operatorname{div}\vec{a}\equiv\vec{\nabla}\vec{a}\equiv\nabla_i a^i=\frac{\partial P}{\partial x}+\frac{\partial Q}{\partial y}+\frac{\partial R}{\partial z},$$

where P, Q, and R are the spatial components of vector $\vec{a}$. The physical meaning of divergence is the limit ratio of the vectorial field flux through a closed surface surrounding some point at the volume circumscribed by this collapsed surface.

If $\vec{a}(M)$ is the field of the rates in a steady flow of an incompressible fluid, then $\operatorname{div}\vec{a}$ means intensity of a source ($\operatorname{div}\vec{a}>0$) or sink ($\operatorname{div}\vec{a}<0$) arranged at this point. When there is neither source nor sink, then $\operatorname{div}\vec{a}=0$.

The following properties are characteristic of the divergence operator:

$$\operatorname{div}\left(\vec{a}+\vec{b}\right)=\operatorname{div}\vec{a}+\operatorname{div}\vec{b},$$

$$\operatorname{div}(\varphi\vec{a})=\varphi\operatorname{div}\vec{a}+\vec{a}\operatorname{grad}\varphi,$$

where grad $\varphi \equiv \vec{\nabla}\varphi = \vec{e}_i \frac{\partial \varphi}{\partial x_i}$ is operator of the gradient of scalar φ and $\vec{e}$ is unit vector.

Consider an extensive quantity $B = \rho b$, where ρ is the density of the matter and b is the quantity of B per unit mass. According to the Ostrogradsky theorem, the local quantity of any extensive parameter $B(\vec{r}, t) = \rho(\vec{r}, t) b(\vec{r}, t)$ in a macroscopic system obeys the balance equation

$$\rho \frac{db}{dt} = -\mathrm{div}\vec{J}_B + \sigma_B, \tag{1.62}$$

where $\vec{J}_B$ is the density of full flux of B in point $\vec{r}$, while σ_B is the density of sources (or sinks) of parameter B in this point—in other words, the induced and normalized to volume rate of the parameter B variations due to the existence of the sources.

Neither sources nor sinks exist for the extensive parameters characterized by the conservation laws. Therefore, for example, the spatial distribution of a nontransforming chemical component is described (due to necessity of the mass balance) by equation

$$\rho \frac{dc}{dt} = -\mathrm{div}\vec{J}_c,$$

where $c = c(\vec{r}, t)$ is this component concentration (scalar) and $\vec{J}_c$ is the density of its concentration flux (vector).

It is easy to apply the Ostrogradsky theorem for deriving the entropy fluxes and the thermodynamic forces that initiate these fluxes. In fact, the balance of entropy (it also is an extensive parameter, $S = \rho s$) is

$$\rho \frac{ds}{dt} = -\mathrm{div}\vec{J}_s + \sigma_s, \tag{1.63}$$

where $\vec{J}_s$ is the entropy flux density, which is a vector in a nonuniform system and $\sigma_s \equiv \sigma$ is the local rate of emergence (production) of entropy in terms of our consideration.

Since according to equation (1.19),

$$\sigma_s = \frac{1}{T} \sum_i \vec{J}_i \overline{X}_i,$$

the analytical equations for both σ_s and $\vec{J}_i$ make it possible to find $\vec{X}_i$.

1.5.2. Calculating the Thermodynamic Forces in Spatially Inhomogeneous Systems

Explicit values $\vec{J}_s$ and σ_s can be found by comparing expression (1.63) with the expression for $\rho\frac{ds}{dt}$ derived from the principal Gibbs's equation

$$dG = dU + pdV - TdS = \sum_i \mu_i dn_i.$$

It follows from the equation that

$$TdS = dU + pdV - \sum_i \mu_i dn_i.$$

Dividing this equation by system volume V gives

$$Tds = du + pd\tilde{v} - \sum_i \mu_i dc_i,$$

where s is the local density of entropy, u is the local density of internal energy, $\tilde{v} = \rho^{\ 1}$ is the specific volume (ρ is the local mass density of the medium), and μ_i and c_i are the local values of the chemical potential and concentration of component i.

1.5.2.1. Heat Transfer in Solids Due to Heat Conductivity

Let us deduce the balance equation for entropy in a uniform solid body with a nonuniform temperature inside. In doing so, we shall ignore the possible volume variations due to the heat expansion $(d\tilde{v} = 0)$. The flux of matter is also excluded in the solid $(dc_i = 0)$. In this case, therefore,

$$ds = \frac{du}{T},$$

where,

$$\frac{ds}{dt} = \frac{1}{T}\frac{du}{dt}.$$

There are no heat sources in this system. While the energy conservation requires $\sigma_Q = 0$, then

$$\rho\frac{du}{dt} = -\text{div}\vec{J}_Q,$$

where $\vec{J}_Q$ is the density of the heat flux (a vector). These equations give the entropy balance equation

$$\rho\frac{ds}{dt} = -\frac{1}{T}\mathrm{div}\vec{J}_Q. \tag{1.64}$$

The latter equation allows us to find J_S and σ_S. To do this, one has to reduce the balance equation (1.64) to the form of the canonical Ostrogradsky balance equation (1.63)—that is, present the second term in the deduced equation in the form identical to the equation $\left(\ \mathrm{div}\vec{J}_S + \sigma_S\right)$.

While

$$\mathrm{div}\frac{\vec{J}_Q}{T} = \frac{1}{T}\mathrm{div}\vec{J}_Q + \left(\vec{J}_Q, \vec{\nabla}\frac{1}{T}\right) = \frac{1}{T}\mathrm{div}\vec{J}_Q - \frac{1}{T^2}\left(\vec{J}_Q, \vec{\nabla}T\right),$$

equation (1.64) gives

$$\rho\frac{ds}{dt} = -\mathrm{div}\frac{\vec{J}_Q}{T} - \frac{1}{T^2}\left(\vec{J}_Q, \vec{\nabla}T\right).$$

The comparison of this equation with equation (1.63) gives the entropy flux density

$$\vec{J}_s = \frac{\vec{J}_Q}{T},$$

as well as the density of the entropy source—that is, the local rate of entropy production:

$$\sigma_s = -\frac{1}{T^2}\left(\vec{J}_Q, \vec{\nabla}T\right).$$

It follows from the definition of thermodynamic force for the case of a vectorial flux and vectorial thermodynamic force that

$$\sigma \equiv \sigma_s = \frac{1}{T}\vec{J}_Q\vec{X}_Q = \frac{1}{T}\sum_{i=1}^{3} J_{Qi}X_{Qi},$$

Hence,

$$X_{Qi} = -\frac{1}{T}\nabla_i T \equiv -\frac{1}{T}\frac{\partial T}{\partial x_i}. \tag{1.65}$$

It is important to emphasize that thermodynamic force $\vec{X}_Q$ is a vector, whereas X_{Qi} is its Cartesian component corresponding to the Cartesian coordinate i of heat flux $\vec{J}_Q$. The centuries old practice states the well known relationships between heat fluxes and temperature gradients, which are expressed by the Fourier law of heat conduction

$$\vec{J}_Q = -\lambda\vec{\nabla}T,$$

where λ is the heat conduction coefficient.

While the daily experience underlying the Second Law of thermo dynamics tells us that $\lambda \geq 0$ always, then

$$\sigma = \frac{\lambda}{T^2}\left(\vec{\nabla}T, \vec{\nabla}T\right) \geq 0.$$

So we see that $\sigma_s \geq 0$ always, which meets the Second Law of thermo dynamics. Again, for the entire system

$$\frac{d_iS}{dt} = \int_v \sigma dv = \int_v \frac{\lambda}{T^2}\left(\vec{\nabla}T\right)^2 dv \geq 0.$$

1.5.2.2. Diffusion Transfer of Matter

Consider a system that consists of a diffusing matter that is characterized by its local concentration c and, correspondingly, chemical potential $\mu = \mu^o + RT \ln c$. If no changes are made to the internal energy dU and the work pdV produced by the matter diffusion, we have

$$-TdS = \mu dn,$$

wherefrom

$$\rho\frac{ds}{dt} = -\rho\frac{\mu}{T}\frac{dc}{dt}.$$

In accordance with the mass conservation law, the system has neither sources nor sinks of mass and, therefore,

$$\rho\frac{dc}{dt} = -\mathrm{div}\vec{J}_c,$$

where $\vec{J}_c$ is the flux of the diffusing matter (vector). Hence,

$$\rho\frac{ds}{dt} = \frac{\mu}{T}\mathrm{div}\vec{J}_c.$$

By taking into account that

$$\operatorname{div}\left(\frac{\mu}{T}\vec{J}_c\right) = \frac{\mu}{T}\operatorname{div}\vec{J}_c + \left(\vec{J}_c, \vec{\nabla}\frac{\mu}{T}\right),$$

we shall reduce, as before, the equation for $\rho\frac{ds}{dt}$ to the form corresponding to canonical equation (1.63):

$$\rho\frac{ds}{dt} = -\operatorname{div}\left(-\frac{\mu}{T}\vec{J}_c\right) - \left(\vec{J}_c, \vec{\nabla}\frac{\mu}{T}\right). \tag{1.66}$$

Hence, the density of the entropy flux for the case of the matter diffusion is

$$\vec{J}_s = -\frac{\mu}{T}\vec{J}_c.$$

It follows from equation (1.66) that

$$\sigma_s = -\left(\vec{J}_c, \vec{\nabla}\frac{\mu}{T}\right) = \frac{1}{T}\vec{J}_c\vec{X}_c.$$

Therefore, flux $\vec{J}_c$, which is induced by thermodynamic force $\vec{J}_c$, is also a vector that is expressed as

$$\vec{X}_c = -T\vec{\nabla}\frac{\mu}{T}.$$

It is essential that flux $\vec{J}_c$, like the preceding example, is also proportional to the gradient of some quantity, namely μ/T. The same dependence may be found in different ways. In fact, the Fick law of diffusion gives

$$\vec{J}_c = -D\vec{\nabla}c,$$

where $D \geq 0$ is the diffusion coefficient. While $c = \exp\{(\mu \quad \mu^{o})/RT\}$ for thermodynamically ideal systems, an isothermal system with the concentration independent diffusion coefficient D will have

$$\vec{J}_c \propto \vec{\nabla}\exp\{(\mu - \mu^{o})/RT\} = \exp\{(\mu - \mu^{o})/RT\}\vec{\nabla}\frac{\mu}{RT} \propto \vec{\nabla}\frac{\mu}{T}. \tag{1.67}$$

Obviously, the relationship $\sigma_s \geq 0$ is satisfied for diffusion due to $D \geq 0$.

1.5.2.3. Electric Current in a Solid Conductor

Let us say that electric current of density j passes through a solid conductor. The local quantity of the specific power of the heat release dq/dt in unit volume of the conductor is described by the Joule law:

$$\frac{dq}{dt} = -j\cdot\nabla\varphi \equiv \vec{J}\cdot\vec{E}.$$

Here, $\nabla\varphi$ is the gradient of electric field potential φ in the conductor, which is equal by definition to electric field intensity E. Thus,

$$\frac{ds}{dt} = \frac{1}{T}\frac{dq}{dt} = -\frac{1}{T}\vec{j}\vec{E} = \frac{1}{T}\vec{J}_e\vec{X}_e.$$

It is obvious here that the electricity flux (vector) corresponds to the electric current density

$$\vec{J}_e \equiv \vec{j},$$

and the thermodynamic driving force of the electricity transfer is

$$\vec{X}_e = \vec{E} \equiv -\vec{\nabla}\varphi.$$

According to Ohm's law, $j = \gamma E$, where γ is the coefficient of a spectric electroconductivity with $\gamma > 0$. In this case, relationship $\sigma_s \geq 0$ is necessarily satisfied due to nonnegative coefficients γ.

1.6. CHAPTER EXERCISES

1. What are the additional statements to the three laws of classical equilibrium thermodynamics and are applied for constructing the theory of thermodynamics of nonequilibrium processes?
2. When are the approaches of thermodynamics of nonequilibrium processes (i.e., kinetic thermodynamics analysis) preferable in respect to the traditional "pure" kinetic description? Why? How does the remoteness from thermodynamic state display itself in chemical kinetics?
3. Why are chemical processes classified into stepwise processes and elementary steps and reactants are classified into starting reactants, final products, and intermediates?

4. What is the dimension of thermodynamic forces?
5. Why it is desirable to identify the stoichiometric stepwise reactions and intermediate transformations for the combined kinetic thermodynamic analysis of complex processes? How many kinetically irreversible steps are allowed for a stationary stepwise reaction whose affinity equals 10 kJ/mol? The system temperature is 300 K.
6. In what cases is it possible to use the conception of thermodynamic force for a chemical reaction?
7. What is the specificity of the "thermodynamic form" of kinetic equations? What parameters are used for writing these equations? How do they relate to traditional parameters of chemical kinetics? When is this form particularly useful?
8. Demonstrate with a reversible monomolecular reaction

$$\mathrm{A} \overset{k_1}{\underset{k_2}{\leftrightarrows}} \mathrm{B}$$

   as an example, that near equilibrium the overall rate v of the reaction is proportional to the reaction affinity A_r. How is the proximity of the reaction to equilibrium identified?
9. For some complex kinetic schemes, you must calculate the time dependence of the concentrations of reactants that are involved in the chemical transformations. Can the tools of thermodynamics of nonequilibrium processes be helpful in doing this? Why or why not?
10. You need to calculate kinetics of a stepwise reaction A → B that follows the mechanism

$$\mathrm{A} \xrightarrow{1} \mathrm{Y} \xrightarrow{2} \mathrm{B}$$

   with the traditional rate constants $k_1 = 10^8\ s^{\ 1}$ and $k_2 = 10^7\ s^{\ 1}$. When is it a good idea to use the tools of thermodynamics of nonequilibrium processes?
11. You need to calculate kinetics of a stepwise reaction A + B → C that follows the mechanism

$$\mathrm{A} \xrightarrow{1} \mathrm{Y}$$
$$\mathrm{Y} + \mathrm{B} \xrightarrow{2} \mathrm{C}$$

with the traditional rate constants $k_1 = 10^8$ s ^{1} and $k_2 = 10^8$ cm^3·s ^{1}. When is it a good idea to use the tools of thermodynamics of non equilibrium processes?

12. Write the equation for the rate of entropy production of the stepwise reaction

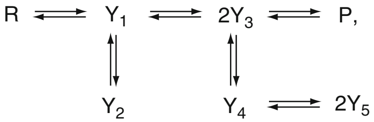
$$R_1 + R_2 \rightleftarrows P,$$

which follows the mechanism

$$R_1 \overset{1}{\rightleftarrows} Y_1 \overset{2}{\rightleftarrows} 2\,Y_2$$
$$R_2 \overset{3}{\rightleftarrows} 2\,Y_2 \overset{4}{\rightleftarrows} Y_3 \overset{5}{\rightleftarrows} P$$

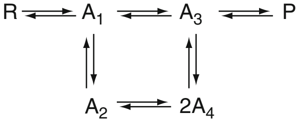
in (1) the stationary and (2) the nonstationary modes in respect to intermediates Y_i.

13. A stepwise process R $\rightleftarrows$ P follows the mechanism



where Y_i are intermediates. Find in the thermodynamic form the equation for the stationary rate of this stepwise process.

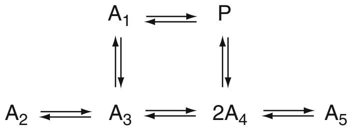
14. Transformation of starting reactant R to product P follows the mechanism



where A_i are the intermediates. Express the relationship between the chemical potentials and the concentrations of the reaction intermediates A_i in the stationary mode of the process. Write the equation for the rate of entropy production.

15. Show the relationship between the chemical potentials and concentrations of the reaction intermediates A_i in the stationary mode of the process of transformation of starting components R_i to product P by the scheme

$$R_1 + R_2 \rightleftarrows A_1$$



Write the equation for the rate of entropy production.

16. Transformation of starting component R to product P follows the scheme

$$R \rightleftarrows + A_1 \rightleftarrows A_2 \rightleftarrows A_3 \rightleftarrows P$$
$$A_1 + H^+ \rightleftarrows A_4 \rightleftarrows A_3 + H^+$$

Here, A_i is intermediate compounds, and H^+ is a proton from the solvent. Show the relationship between the chemical potentials and concentrations of the reaction intermediates in the stationary mode of the process.

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CHAPTER 2

Thermodynamics of Systems Close to Equilibrium

Contents

2.1. THE RELATIONSHIP BETWEEN THE VALUES OF FLUX AND THE THERMODYNAMIC FORCE CLOSE TO THERMODYNAMIC EQUILIBRIUM

Thermodynamic fluxes J are generally functions of thermodynamic forces X that induce the fluxes. Near the thermodynamic equilibrium, both the thermodynamic driving forces and fluxes of the processes are rather small. In such situations, the values of thermodynamic forces X and the conjugate fluxes J are in a simple linear relationship

$$J = LX, \tag{2.1}$$

where L is a coefficient that is independent of thermodynamic force X and proportional, normally, to the gradient of intensive thermodynamic parameters.

Relationship (2.1) is the direct consequence of a series expansion of function J(X) in terms of small parameter X near the equilibrium state that is characterized by $X = 0$ and $J(0) = 0$:

$$J(X) = J(0) + \frac{\partial J}{\partial X} X + \frac{1}{2} \frac{\partial^2 J}{\partial X^2} X^2 + \ldots.$$

Relationship (2.1) is produced from this expansion, provided that small quantities of the second and higher orders with respect to X are neglected:

$$J(X) \approx \frac{\partial J}{\partial X} X.$$

Thus,

$$L = \left. \frac{\partial J}{\partial X} \right|_{X=0}.$$

The validity of linear relationships of type (2.1) is supported, for example, by Ohm's law where the magnitude of current I—that is, the electricity carrier flux J_e—is proportional to the thermodynamic driving force that is the difference (gradient) of electric potentials ΔU between the part of the electric circuit with the electrical resistance R:

$$J_e = I = -\Delta U/R.$$

Thus, in the case under consideration, the proportionality coefficient $L = 1/R$—that is, the electric conductivity—is independent of the respective thermodynamic driving force $X_e = \quad \Delta U$.

Similar linear relationships between the process rate and its driving force are valid for the cases of simple diffusion of matter or heat transfer due to heat conduction. For example, while the Fick Law relates to the matter transfer due to diffusion

$$J_c = dc/dt = -D \nabla c,$$

then, allowing for relationship (1.67), we have

$$\vec{J}_c = -D \exp\left(\frac{\mu - \mu^{\circ}}{RT}\right) \vec{\nabla} \frac{\mu}{T} \sim \vec{X}_c.$$

According to the Fourier Law on the heat transfer due to heat conductivity,

$$J_Q = dQ/dt = -\lambda \, \nabla T.$$

Therefore, with relationship (1.65), we have

$$\vec{J}_Q = -\lambda \vec{\nabla} T = \lambda T \vec{X}_Q.$$

In the above expressions for J_c and J_Q, c and μ are the molar concentration and the corresponding chemical potential of the diffusing matter, Q is the quantity of transferred heat, and coefficients D and λ are independent of the gradients of quantities c and T.

Near thermodynamic equilibrium, similar linear relationships are also valid for elementary chemical processes, as well as for stepwise processes where the rates are proportional to the difference between the thermodynamic rushes of the initial and final reaction groups (see Section 1.4.2). Here, the criterion of proximity to thermodynamic equilibrium is relationship $|A_{rij}| < RT$, where A_{rij} is the affinity for the transformation of reaction group i to reaction group j.

In fact, while

$$A_{rij} = \mu_i - \mu_j = RT(\ln \tilde{n}_i - \ln \tilde{n}_j) = RT \ln(\tilde{n}_i/\tilde{n}_j),$$

then

$$\tilde{n}_j = \tilde{n}_i \exp(-A_{rij}/RT)$$

and

$$v_{ij} = \varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j) = \varepsilon_{ij}\tilde{n}_i[1 - \exp(-A_{rij}/RT)]. \qquad (2.2)$$

At $|A_{rij}| < RT$,

$$v_{ij} \approx \varepsilon_{ij}\tilde{n}_i \frac{A_{rij}}{RT} = L_{ij} \cdot A_{rij}, \qquad (2.3)$$

where L_{ij} is the quantity determined by the properties of the equilibrium state of the system and, for this reason, independent of chemical affinity A_{rij}—that is, of the thermodynamic force of the chemical reaction.

Obviously, the conclusion on proportionality between the rate of a reaction and its chemical affinity is valid, as well as in the cases where an arbitrary complex (not an elementary) stoichiometric stepwise reaction occurs near its equilibrium, the stepwise reaction being characterized by a certain value of chemical affinity (see, e.g., expression (1.36)).

2.2. THE INTERACTION BETWEEN THERMODYNAMIC PROCESSES AND LINEAR ONSAGER RELATIONS

All thermodynamic processes can be characterized by magnitudes of both their rate (flux) and their driving force. However, if several thermodynamic processes are concurrent in a system, they can affect one another. As a result, the rate of each of the processes (the flux of each thermodynamic parameter) depends not only on "its own" thermodynamic force but also on the driving forces of all the other processes that occur in the system. The possibility of thermodynamic processes being interdependent is principally an idea for constructing thermodynamics of nonequilibrium processes. This idea appears to be helpful for treating some complex phenomena and/or the phenomena, which are difficult to interpret otherwise.

L. Onsager was the first person to formulate in 1931 the principle of interacting thermodynamic processes. The underlying idea is that the rate of numerous interacting irreversible processes can be described by linear differential equations with constant coefficients:

$$J_i = \sum_j L_{ij} \nabla a_j,$$

where a_j are intensive thermodynamic parameters (T, p, μ, etc.), and L_{ij} are the coefficients that are independent of the gradients of parameters a_j—that is, of the thermodynamic forces X_j proportional to these gradients.

This principle appeared to be very fruitful in considering numerous irreversible processes near the thermodynamic equilibrium of the system. The corresponding general relationship

$$J_i = \sum_j L_{ij} X_j \tag{2.4}$$

is today called the *phenomenological linear Onsager reciprocity equation*. The interacting thermodynamic processes are referred here to as conjugate.

There is a natural reason for relations like (2.4) in cases where the interference of thermodynamic forces affects all of the fluxes of thermodynamic parameters of the system. In fact, let the values of fluxes J_i be functions of all of the thermodynamic forces X_j ($j = 1,2, \ldots, m$) operating in the system: $J_i = J_i(\{X_j\})$. In equilibrium, $X_1 = X_2 = \ldots = X_m = 0$ and $J_i(\{X_j\}) = 0$ for all i. Therefore, near equilibrium, function J_i can be expanded in terms of small parameters X_j:

$$J_i = J_i(0) + \sum_{j=1}^{m} \frac{\partial J_i}{\partial X_j} X_j + \frac{1}{2} \sum_{j=1}^{m} \sum_{k=1}^{m} \frac{\partial^2 J_i}{\partial X_j \partial X_k} X_j X_k + \ldots$$

When we allow for $J_i(0) = 0$ in the equilibrium state and confine ourselves to the first nonzero terms of the series, we have

$$J_i = \sum_{j=1}^{m} \left. \frac{\partial J_i}{\partial X_j} \right|_{\{X_j\}=0} X_j \equiv \sum_{j=1}^{m} L_{ij} X_j,$$

where L_{ij} is a matrix.

The coefficients L_{ij} are called the Onsager's phenomenological reciprocity coefficients. Type (2.4) relations are applicable, for example, to concurrent processes of matter diffusion and heat transfer, or electric current and ion diffusion, as well as to the case of several concurrent chemical reaction in the system (see Section 2.3.4).

In the simplest case, the reciprocation of two processes 1 and 2 is written in accordance with the Onsager's principle as

$$\begin{aligned} J_1 &= L_{11} X_1 + L_{12} X_2, \\ J_2 &= L_{21} X_1 + L_{22} X_2, \end{aligned}$$

where J_1, J_2 and X_1, X_2 describe the fluxes of two parameters and their corresponding thermodynamic forces, while the Onsager's reciprocity cross coefficients L_{12} and L_{21} correspond to the probable interrelation of two fluxes.

The invariance of regularities in the particle's motion to the reversal of time led to Onsager's discovery of an important reciprocal relation between the nondiagonal reciprocity coefficients L_{ij} and L_{ji}:

$$L_{ij} = L_{ji}.$$

This relationship shows that if the flux of an irreversible process i is affected by thermodynamic force X_j of another irreversible process j through the mediation of coefficient L_{ij}, then the flux of process j is also influenced by thermodynamic force X_i through the mediation of the same coefficient $L_{ji} = L_{ij}$.[*] In the case of interacting chemical processes, this statement reflects the principles of detailed (intimate) equilibrium and mass balance of the reactants that underlie the concepts of chemical kinetics.

It is important in an isotropic medium that the reciprocity coefficients L_{ij} are nonzero only when the interacting thermodynamic forces X_j have the same spatial dimensions (for example, they are both scalars, vectors, or tensors). This is the so called Curie principle. In nonisotropic systems—for example, at the interaction of processes on functional membranes—the Curie principle may be inoperable.

Expression (2.4) allows the total rate of entropy production or energy dissipation in complex systems to be described in the form of a simple functional. In general cases when several simultaneous processes i (i = 1, 2, . . . , m) occur in a system,

$$\boldsymbol{P} = \mathrm{T}\frac{d_i S}{dt} = \sum_{i=1}^{m} J_i X_i > 0. \tag{2.5}$$

At $J_i = \sum_{j\ 1}^{m} L_{ij} X_j$ and $L_{ij} = L_{ji}$, this implies a simple expression for the total rate of the energy dissipation

$$\boldsymbol{P} = \mathrm{T}\frac{d_i S}{dt} = \sum_{i=1}^{m}\sum_{j=1}^{m} L_{ij} X_i X_j > 0. \tag{2.6}$$

This positively determined quadratic expression is referred to as the Rayleigh Onsager dissipative function.

While $\boldsymbol{P} = \mathrm{T}\frac{d_i S}{dt}$ is always positive in the system with irreversible processes, and the thermodynamic forces are independent arbitrary quantities,

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[*] In 1945, H. Casimir established that in the case of interaction with a magnetic field and nonzero angle rotation velocities, the relationship $L_{ij} \quad L_{ij}$ is satisfied for some reciprocity coefficients. For peculiarities of the relationship between the nondiagonal reciprocity coefficients in the case of chemical reactions, see Section 2.3.5.

the following relations, apart from the reciprocity equations, are also valid for the Onsager coefficients:

$$L_{ii} \geq 0; \quad L_{ij} > -(L_{ii}X_i^2 + L_{jj}X_j^2)/\,2\,X_iX_j.$$

The sign of the nondiagonal reciprocity coefficients may be arbitrary.

The dimensions of thermodynamic forces and coefficients L_{ij} should be chosen so that the dimensions of the left and right parts are identical in the type (2.4) expressions (for example, $J\cdot s^{-1}$). Evidently, in the linear approximation under discussion, it is possible to express the rate of entropy production (or the rate of energy dissipation) as a quadratic function of fluxes J_i, too:

$$\boldsymbol{P} = T\frac{d_iS}{dt} = \sum_{i=1}^{m}\sum_{j=1}^{m}\tilde{L}_{ij}J_iJ_j.$$

Coefficients $\tilde{L}_{ij}$ are also called Onsager coefficients because they have the same properties as coefficients L_{ij}. The "flux" form of writing the function $\boldsymbol{P}$ or d_iS/dt is identical to the "force" form (2.6) and may appear sometimes to be preferable for mathematical analysis.

The phenomenological Onsager reciprocal relations are very important for thermodynamics of nonequilibrium processes and can be directly applied for analysis of some properties of membrane, chemical, catalytic, and biological systems near thermodynamic equilibrium. For example, combined with empiric (experimentally found) coefficients L_{ij}, these relations allow some quantitative relationships between concurrent processes to be established, even though the detailed information about the mechanisms of the processes under consideration is unavailable. In some cases (for example, conjugate chemical reactions with the known schemes of elementary transformations, or interacting physical processes with the known mathematical description of the involved phenomena), the reciprocity coefficients can be calculated theoretically on the basis of knowledge on the specific mechanism of the process under consideration (see Sections 2.3.3–2.3.5). However, the coefficients are mostly used for qualitative analysis as phenomenological parameters.

It is essential that the relations that are similar to the phenomenological Onsager reciprocal equations are also valid for many types of chemically reactive systems that are far from thermodynamic equilibrium (see Section 2.3.4).

2.3. THERMODYNAMIC CONJUGATION OF THE PROCESSES

In this section, we look at some typical examples of thermodynamic conjugation of processes. We will particularly emphasize the conjugation of stepwise chemical processes that proceed in the stationary mode in respect to the concentrations of reaction intermediates.

2.3.1. The Transport of Matter through a Membrane during Osmosis

Let us imagine that a permeable membrane separates phases I and II of a diluted (e.g., aqueous) solution of some compound. Obviously, the flux of water, J_1, and the flux of the solute, J_2, can pass simultaneously through such the membrane. The driving force for the solvent (water) flux J_1 is the difference between hydrostatic pressures, Δp, in the separated phases, whereas the solute flux relative to the solvent, J_2, is caused by the difference (gradient) between osmotic pressures, $\Delta\pi$, of this compound on both sides of the membrane ($\Delta\pi = \Delta cRT$).*

In accordance with the Onsager relationships, each of the fluxes under consideration is conjugate with both thermodynamic forces $X_1 = \Delta p$ and $X_2 = \Delta\pi$. Then

$$J_1 = L_{11}X_1 + L_{12}X_2 = L_{11}\Delta p + L_{12}\Delta\pi,$$
$$J_2 = L_{21}X_1 + L_{22}X_2 = L_{21}\Delta p + L_{22}\Delta\pi.$$

These equations mean that the water flux J_1 that passes through the membrane is, generally, determined not only by the difference between hydrostatic pressures on both sides of the membrane but also on the flux of the solute caused by the difference between osmotic pressures of this matter. Hence, the interrelationship between both processes can be described as best at the phenomenological level.

In particular, one can introduce a coefficient of the membrane selectivity

$$\gamma = -L_{21}/L_{11},$$

which characterizes the membrane permeability for the chosen solvent and solute and, at the same time, indicates some specific features of the mechanism of the solute transfer.

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*Osmosis in its "pure" form is the diffusion of solvent molecules through a semipermeable membrane, which is permeable for the solvent only.

For example, for a coarse (macroporous) membrane, $\gamma \rightarrow 0$, and necessarily $L_{21} \rightarrow 0$ at $L_{11} \neq 0$. Hence, the solute transfer through the coarse membrane is independent of the water motion. For a fine porous membrane, it is possible that $\gamma = 1$ and, as a consequence, $L_{11} = -L_{21}$ that indicates a strong interrelationship between the fluxes of the solute and solvent (water) and is characteristic of a semipermeable membrane. The coefficient γ can be found experimentally by determining the value of the water flux in the absence of hydrostatic pressure ($\Delta p = 0$); in this situation the driving force is only difference of osmotic pressures ($\Delta\pi \neq 0$). More complex processes of conjugate transporting the matter and electrically charged particles through membranes can be treated in the same way.

2.3.2. The Active Transport of Matter through a Membrane

In the course of conjugate chemical transformations that occur on both sides of a partly permeable membrane due to the existence of conjugating processes (for example, metabolism in living organisms), an "active" transport of the matter through the membrane may emerge. In principle, the transport may result in an increase in chemical potential of individual components of the system in respect to their values in equilibrium. In particular, this possibility underlies the so called Mitchell hypothesis on the mechanism of synthesis of energy saturated ATP molecules inside mitochondria owing to the conjugation of this process with the induced proton transport through the mitochondrion membrane, the proton transport being provided by the conjugating reactions of oxidation of an alimentary substrate outside the mitochondrion.

Notice that, formally, the possibility of this conjunction violates the Curie principle, which forbids the conjunction of a scalar process (synthesis of a substance) and a vectorial process (the proton transport through the membrane). Nevertheless, this contradiction is avoided due to the presence of a special conjugation tool like an anisotropic membrane.

Consider two conjugate processes that are characterized by fluxes J_1 and J_2:

$$J_1 = L_{11}X_1 + L_{12}X_2,$$
$$J_2 = L_{21}X_1 + L_{22}X_2,$$

where the former process—conjugate—runs counter to the driving force X_1 ($J_1X_1 < 0$) due to the energy dissipation by the latter conjugating process ($J_2X_2 > 0$). As a quantitative measure of the process conjugation, we can use parameter

$$q = L_{12}/\sqrt{L_{11}L_{22}},$$

which varies within the range

$$-1 \leq q \leq 1.$$

At $q = 0$, it is necessarily $L_{12} = L_{21} = 0$, and both processes are indepen dent of one another, while the fluxes of corresponding thermodynamic parameters are proportional to their "own" thermodynamic forces:

$$J_1 = L_{11}X_1 \quad \text{and} \quad J_2 = L_{22}X_2.$$

The quantity $q = \pm 1$ refers to the complete conjugation of both processes. At $q < 0$, the increase in the driving force of one process leads to a decrease in the flux of its conjugate process. The energy efficiency of the conjugation is determined by the ratio $\left|\frac{J_1X_1}{J_2X_2}\right|$ and may attain 80–90% in perfect biological systems (an example is the process of oxidative phosphorylation).

In the energy transformation processes that occur on functional mono or bilayer membranes in living organisms, the conjugation mechanism controls the fluxes of the conjugate J_1 (for example, synthesis of ATP from ADP in mitochondria) and conjugating J_2 (oxidation of an alimentary sub strate) processes. In the starting period of the system functioning, the rate J_2 is low but accompanied by establishing the maximal value of driving force X_1 for the conjugate process of the ATP synthesis. As soon as the sta tionary mode in respect to the ATP concentration is established, the con jugate flux $\bar{J}_1 = 0$, and X_1 minimizes to the value $X_1 = \frac{L_{12}}{L_{11}}X_2$. Then the stationary flux of the conjugating process

$$\bar{J}_2 = L_{21}X_1 + L_{22}X_2 = L_{12}\left(-\frac{L_{12}}{L_{11}}X_2\right) + L_{22}X_2 = L_{22}(1 - q^2)X_2.$$

At $q^2 \neq 1$, this flux is nonzero even at the stationary conditions. However, in the fully conjugate system ($q^2 = 1$), the rate of the food oxidation decreases and $\bar{J}_2 = 0$ at the stationary state. Thus, the respiration control system in the mitochondria of living organisms determines the rate J_2 of the oxidation of alimentary substrates, depending on the variations in the ADP and ATP concentration ratio—in other words, in the driving force X_1 of the conjugate process. Obviously, the maintenance of a constant sta tionary ATP concentration, even though low, at $q^2 \neq 1$ needs a nonzero rate of the oxidation of alimentary substrates.

The preceding use of the reciprocity relationships is evidently of a phenomenological nature; the validity of the relationship per se does not elucidate the specific mechanisms of functioning the oxidative phosphorylation systems.

2.3.3. Conjugate Processes in Spatially Inhomogeneous Systems

In the spatially inhomogeneous systems, gradients of T, p, and other thermodynamic parameters may occur. That means you must take into account these gradients when considering the thermodynamic conjugation of some irreversible processes. “Classical” conjugate processes in the systems, which are free from chemical transformations, are thermoelectric phenomena in nonuniform electric conductors. These systems are the subject of a wide range of speculations by physicists. Consequence of the conjugation of thermodynamic processes in the nonuniform conductors are the Seebeck, Peltier, and Thomson effects.

The Seebeck effect is involved in the generation of thermoEMF in a closed electric circuit that is composed of different metals whose junctions are maintained at different temperatures. This phenomenon is widely used, for example, for measuring the temperature with the help of thermocouples. In this case, the thermoEMF is caused by the redistribution of the current carriers through the conductors due to the existence of the temperature gradient.

Apparently, the interaction of the electricity flux (electric current) and the heat flux creates the thermoEMF value, which is the thermodynamic force that provides the electric current. This current runs linear to the thermodynamic force of the conjugating process of thermodiffusion of electric charges—that is, to the temperature difference (gradient) between the junctions $\Delta T = T_2 - T_1$ (Figure 2.1). When the current equals zero in the circuit, the measurable thermoEMF is exactly proportional to ΔT. This is the basis for measuring the temperature using thermocouples.

The Peltier effect is related to the release and/or absorption of heat at the junction of two conductors of different natures when an electric current passes through them. The effect is applied in special kinds of

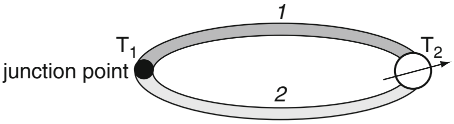

Figure 2.1 Generation of thermoelectromotive force in a closed electric circuit made of two different metals *1* and *2*. T_1 and T_2 are the junction temperatures.

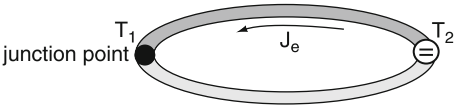

Figure 2.2 Generation of temperature difference between junctions of conductors of different natures on passing electric current J_e from an external source (conventionalized on the right) through a closed circuit.

refrigerators where one junction of two specially chosen semiconductors behaves as a cooling agent (Figure 2.2). In the case under consideration, the difference between the junction temperatures will be proportional to current J_e in the circuit.

The Thomson effect is related to the release of extra heat in a conductor (in addition to the well known "Joule" heat released due to the finite value of the electric conductivity) owing to the combined action of heat and electro conduction.[*] In physical chemistry, classical examples of conjugate processes in nonuniform systems are thermomechanical and mechanocaloric effects.

Like the thermoelectric Seebeck effect, the thermomechanical effect implies the appearance of a pressure difference $\Delta p = p_2 - p_1$ in the capillary connected vessels filled with a mobile substance—a liquid or gas—when the vessels are maintained at different temperatures with the temperature difference $\Delta T = T_2 - T_1$. The case of the vessels separated by a porous partition rather than one capillary is called thermoosmosis. The inverse phenomenon—the appearance of a temperature difference as a result of the pressure difference in the vessels—is called the mechanocaloric effect.

Consider the reason for the appearance of the thermomechanical effect and its expected value. Let us say that two vessels, *1* and *2,* are filled with some identical fluid (liquid or gas) and connected by a capillary, the fluids being held at preset constant temperatures T and T + dT. Let J_Q designate the heat flux that passes through the capillary between the vessels, while J_c designates a potential fluid flux that diffuses through the same capillary (Figure 2.3). In accordance to the preceding deduced relationships (also see Section 1.5), the thermodynamic forces that initiate the fluxes are determined by the formula

$$X_1 = -\frac{1}{T}\nabla T, \quad X_2 = -\nabla\frac{\mu}{T}.$$

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[*] For more details on thermoelectric phenomena, see the Bibliography.

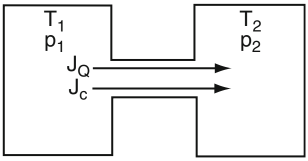


Figure 2.3 On initiation of thermomechanical effect. The connecting capillary between two vessels is drawn schematically.

The linear Onsager relations give

$$\begin{aligned} J_Q &= L_{11}X_1 + L_{12}X_2, \\ J_c &= L_{21}X_1 + L_{22}X_2. \end{aligned} \tag{2.7}$$

In the fluid stationary state, the flux J_c of the matter through the capillary equals zero in the system under consideration, but the heat flux J_Q is non zero and remains constant. Therefore, for the given stationary state, the preceding formulas give

$$-L_{22}X_2 = L_{21}X_1,$$

or

$$L_{22}\nabla\frac{\mu}{T} = -\frac{L_{21}}{T^2}\nabla T.$$

This gives

$$d\left(\frac{\mu}{T}\right) = -\frac{L_{21}}{L_{22}}\frac{dT}{T^2}.$$

For one mole of a one component fluid

$$d\left(\frac{\mu}{T}\right) = \frac{d\mu}{T} - \frac{\mu}{T^2}dT = \frac{-SdT + Vdp}{T} - \frac{\mu}{T^2}dT = \frac{V}{T}dp - \frac{H}{T^2}dT,$$

where V, S, and H are respectively the molar volume, entropy, and enthalpy of the fluid, since $\mu = H - ST$ in our case.

By comparing both expressions for $d\left(\frac{\mu}{T}\right)$, we find

$$\frac{dp}{dT} = \frac{H - L_{21}/L_{22}}{VT},$$

or, using the Onsager reciprocal relation $L_{12} = L_{21}$,

$$\frac{dp}{dT} = -\frac{L_{12}/L_{22} - H}{VT}.$$

Here, the thermomechanical effect is seen only when the molar enthalpy of the fluid is unequal to ratio L_{12}/L_{22}.

Let us elucidate the sense of this relation by considering two vessels at equal temperature (thermodynamic force X_1 equals zero). From equation (2.7) we have

$$J_Q = \frac{L_{12}}{L_{22}} J_c;$$

that is, the value $L_{12}/L_{22} \equiv E^*$ is some specific "transfer energy" (energy transferred by fluid unit mass from the first vessel to another in an isothermal process). In this energy transfer, temperature T and pressure p in vessel *1* are held constant due to absorption of heat Q^* from an external source and due to mechanical work done by the fluid. Therefore, according to the First Law of thermodynamics, the change in the fluid internal energy in vessel *1* upon escaping one mole of the fluid equals

$$U = Q^* - E^* - pV = H - pV.$$

Thus,

$$Q^* = E^* - H.$$

Heat $Q^* = E^* - H$, which is absorbed in vessel *1* by one mole of the fluid transferred from vessel *1* to vessel *2* at constant temperature and pressure differences, is referred to as molar transfer heat. Thus,

$$\frac{dp}{dT} = -\frac{Q^*}{VT}, \tag{2.8}$$

and thus at the positive Q^* value, the pressure is established higher in the vessel that has a lower temperature.

A particular example of the application in equation (2.8) is the Knudsen effect for the stationary state of the vessels with the same rarefied ideal gases at various temperatures and a small hole between the vessels. The small hole means in this case that the fluid molecules collide with the hole walls rather than with one another. In other words, the Knudsen diffusion mode occurs.

The kinetic theory of gases makes it easy to find that the transfer energy E^* per mole of a gas is

$$E^* = 2RT.$$

In fact, in the absence of molecule collisions, for the molecule motion through the hole arranged perpendicularly to axis *x,* we have

$$J_Q = \int_0^\infty \frac{mv^2}{2} v_x dn(v_x) = \frac{m(v_y^2 + v_z^2)}{2} \int_0^\infty v_x dn(v_x) + \frac{m}{2} \int_0^\infty v_x^3 dn(v_x);$$

$$J_c = \int_0^\infty v_x dn(v_x).$$

Here the fluxes are attributed to the molecules, m is the mass of one molecule, v is its velocity, v_i is the velocity along the corresponding coordinate i (i = x,y,z), and $n(v_i)$ is the number of particles with the prescribed v_i in unit volume. Hence,

$$\frac{J_Q}{J_c} = \frac{m(v_y^2 + v_z^2)}{2} + \frac{\frac{m}{2}\int_0^\infty v_x^3 dn(v_x)}{\int_0^\infty v_x dn(v_x)}.$$

When the Maxwell velocity distribution for the molecules takes place,

$$\frac{dn(v_x, v_y, v_z)}{n} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m}{2k_B T}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z,$$

and the integral relations

$$\int_0^\infty e^{\ ax^2} x^3 dx = \frac{1}{2a^2}, \quad \int_0^\infty e^{\ ax^2} x dx = \frac{1}{2a}$$

are true, then the equation

$$\frac{\mathrm{dn}(v_x)}{\mathrm{n}} = \left(\frac{\mathrm{m}}{2\pi \mathrm{k_B T}}\right)^{1/2} \mathrm{e}^{\frac{\mathrm{m}v_x^2}{2\mathrm{k_B T}}} \mathrm{d}v_x$$

is valid and, as a result,

$$\int_0^\infty v_x^3 \mathrm{dn}(v_x) = \left(\frac{\mathrm{m}}{2\pi \mathrm{k_B T}}\right)^{1/2} \int_0^\infty \mathrm{e}^{\frac{\mathrm{m}v_x^2}{2\mathrm{k_B T}}} v_x^3 \mathrm{d}v_x = \left(\frac{\mathrm{m}}{2\pi \mathrm{k_B T}}\right)^{1/2} \frac{1}{2(\mathrm{m}/2\mathrm{k_B T})^2},$$

$$\int_0^\infty v_x \mathrm{dn}(v_x) = \left(\frac{\mathrm{m}}{2\pi \mathrm{k_B T}}\right)^{1/2} \frac{1}{2(\mathrm{m}/2\mathrm{k_B T})}.$$

Therefore, for the one molecule transfer,

$$\frac{\mathrm{J_Q}}{\mathrm{J_C}} = \mathrm{k_B T} + \frac{\mathrm{m}}{2}\left(\frac{2\mathrm{k_B T}}{\mathrm{m}}\right) = 2\mathrm{k_B T}.$$

While for one mole of molecules of an ideal one atomic gas, the enthalpy equals

$$\mathrm{H} = \mathrm{U} + \mathrm{pV} = \frac{3}{2}\mathrm{RT} + \mathrm{RT} = \frac{5}{2}\mathrm{RT},$$

then the heat transfer for this gas

$$\mathrm{Q}^* = \mathrm{E}^* - \mathrm{H} = -\frac{1}{2}\mathrm{RT}$$

is a negative value.

In considering that the gas temperatures are not too different in the vessels and, consequently, $T_1 \approx T_2$, substitution of the expression for Q^* in equation (2.8) gives

$$\frac{\mathrm{p}_2 - \mathrm{p}_1}{\mathrm{T}_2 - \mathrm{T}_1} = \frac{\mathrm{R}}{2\mathrm{V}} = \frac{\mathrm{p}_1}{2\mathrm{T}_1},$$

or

$$\frac{p_2 - p_1}{p_1} = \frac{1}{2}\frac{(T_2 - T_1)}{T_1}.$$

Thus,

$$\frac{p_2}{p_1} = 1 + \frac{1}{2}\left(\frac{T_2 - T_1}{T_1}\right) \approx \sqrt{1 + \frac{T_2 - T_1}{T_1}} = \sqrt{\frac{T_2}{T_1}}.$$

The Knudsen relation follows from the preceding consideration as

$$\frac{p_1}{\sqrt{T_1}} = \frac{p_2}{\sqrt{T_2}}.$$

From this relation, when two vessels are connected by a narrow capillary (free path of molecules is larger than the capillary diameter), the pressure will be higher in the vessel that is hotter.

In the case of an ideal gas and a large hole between the vessels—in other words, when the gas passes through the hole as a macroscopic flux—the components of the transfer energy E^* are both the internal energy U and mechanical work pV. Therefore, for ideal gas

$$E^* = U + pV \equiv H, \quad Q^* = E^* - H = 0,$$

where

$$dp/dT = 0,$$

which means

$$p_1 = p_2.$$

Thus, no thermomechanical effect is observed in the case of the large holes.

2.3.4. Thermodynamic Conjugation of Cocurrent Chemical Reactions

The presence of conjugation in chemically reactive systems can be reflected using the Onsager reciprocal equations, too. However, when writing this kind of reciprocal equation, some specific features are required. In reactive chemical systems, thermodynamic forces are determined for only individual elementary reactions and stoichiometric stepwise transformations. At the same time, a consideration of the overall kinetics of complex chemical transformations usually does not treat the fluxes (rates) of particular elementary reactions but the rate of changes in the concentrations of individual chemical components. When these components can participate in several simultaneously occurring transformations, it is generally impossible to introduce one integrated chemical variable for the component. Therefore, a successive consideration of thermodynamic conjugation of chemical transformations in a complex system is possible only when identifying in the mix of the transformations the linearly independent cocurrent stoichiometric (i.e., stationary) stepwise reactions (the linearly independent transformation channels), each being characterized by a certain affinity.

In addition, as shown in Section 1.3, the fluxes of the concentration of chemical components are determined generally by the differences in the thermodynamic rushes of corresponding reaction groups rather than by true thermodynamic forces (chemical affinities of the reactions). Consider the simplest pathway of cocurrent transformations, which includes two parallel channels of independent reversible transformation of initial reactant R into products P_1 and P_2:

$$R \overset{\Sigma 1}{\rightleftarrows} P_1, \tag{2.9}$$

$$R \overset{\Sigma 2}{\rightleftarrows} P_2. \tag{2.10}$$

We will treat the spontaneous transformation of R to P_1 as the "main" process route (process Σ1). This transformation is possible when chemical potential μ_R (and, consequently, thermodynamic rush $\tilde{R} \equiv \exp(\mu_R/RT)$) of compound R is higher than potential μ_{P_1} (correspondingly, higher than the thermodynamic rush $\tilde{P}_1 \equiv \exp(\mu_{P_1}/RT)$) of compound P_1. An analogous relation between μ_R and μ_{P_2} is necessary for the transformation of compound R to the "by product" P_2 (Figure 2.4A).

When both channels of the transformations under consideration are in fact elementary reactions and, therefore, free of common intermediates, the transformation rates are described by a simple kinetic scheme:

$$J_{\Sigma 1} = v_{\Sigma 1} = \frac{d[P_1]}{dt} = \varepsilon_1(\tilde{R} - \tilde{P}_1),$$

$$J_{\Sigma 2} = v_{\Sigma 2} = \frac{d[P_2]}{dt} = \varepsilon_2(\tilde{R} - \tilde{P}_2).$$

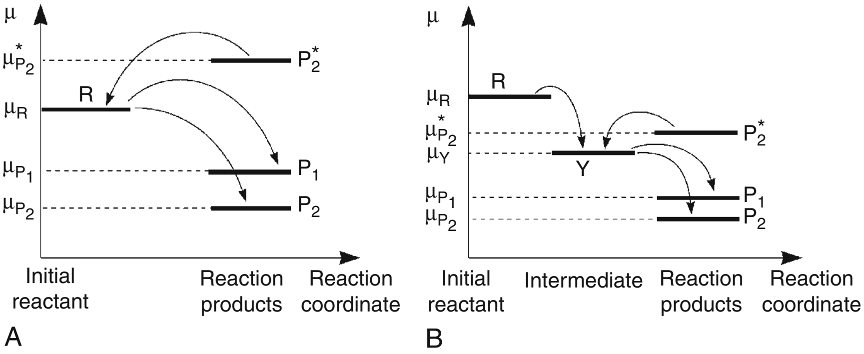


Figure 2.4 Graphical interpretation of processes in a system with two conjugate reactions in respect to current chemical potentials in the presence (A) and absence (B) of a common intermediate for synthesis of products P_1 and P_2. Asterisks indicate points of the process reversion to involve the by-product P_2 in synthesis of the "main" product P_1.

The discussed chemical transformations can be visualized in the coordinates of current chemical potential values (see Figure 2.4a), where chemical potentials of components R, P_1, and P_2 are the "external" parameters. While this is the case of the absence of common intermediates, an indirect influence of the second reaction on the first reaction is possible only when chemical potential μ_{P2} of compound P_2 (its thermodynamic rush $\tilde{P}_2$) is higher than the chemical potential of compound R (its thermodynamic rush $\tilde{R}$). When so, the consecutive reaction $P_2 \rightarrow R \rightarrow P_1$ becomes possible, and this compound P_2 can be involved as an additional substrate into the main reaction $R \rightarrow P_1$. In the considered example, the phenomenon of conjugation of chemical processes is not observed. The conjugation takes place only in the presence of common intermediates for both channels of the transformations.

Let us demonstrate this on the preceding example of two parallel reactions. Let transformations $\Sigma 1$ and $\Sigma 2$ be not elementary but stepwise processes described by the simplest scheme:

$$\begin{aligned} &R \overset{\varepsilon_Y}{\rightleftarrows} Y, \\ &Y \overset{\varepsilon_1}{\rightleftarrows} P_1, \\ &Y \overset{\varepsilon_2}{\rightleftarrows} P_2, \end{aligned} \tag{2.11}$$

with a common intermediate Y. The rate of the formation of intermediate Y is

$$\mathrm{v_Y} = \frac{\mathrm{d[Y]}}{\mathrm{dt}} = \varepsilon_{\mathrm{Y}}(\tilde{\mathrm{R}} - \tilde{\mathrm{Y}}) - \varepsilon_1(\tilde{\mathrm{Y}} - \tilde{\mathrm{P}}_1) - \varepsilon_2(\tilde{\mathrm{Y}} - \tilde{\mathrm{P}}_2).$$

In the stationary mode in respect to intermediate Y, $\mathrm{v_Y} = 0$ and the corresponding stationary value $\tilde{\mathrm{Y}}$ is

$$\tilde{\mathrm{Y}} = \frac{\varepsilon_{\mathrm{Y}}\tilde{\mathrm{R}} + \varepsilon_1\tilde{\mathrm{P}}_1 + \varepsilon_2\tilde{\mathrm{P}}_2}{\varepsilon_{\mathrm{Y}} + \varepsilon_1 + \varepsilon_2}.$$

It is obvious here that when $\tilde{\mathrm{R}} > \tilde{\mathrm{P}}_1, \tilde{\mathrm{P}}_2$, the $\tilde{\mathrm{Y}}$ value is between those of $\tilde{\mathrm{R}}$ and minimal of $\tilde{\mathrm{P}}_1$ and $\tilde{\mathrm{P}}_2$. The stationary rates of the accumulation of components P_1 and P_2 are, respectively,

$$\begin{aligned} \mathrm{J}_{\Sigma 1} = \mathrm{v}_{\Sigma 1} = \frac{\mathrm{d[P_1]}}{\mathrm{dt}} &= \varepsilon_1(\tilde{\mathrm{Y}} - \tilde{\mathrm{P}}_1) = \\ &= \frac{\varepsilon_1}{\varepsilon_{\mathrm{Y}} + \varepsilon_1 + \varepsilon_2}\{\varepsilon_{\mathrm{Y}}(\tilde{\mathrm{R}} - \tilde{\mathrm{P}}_1) + \varepsilon_2(\tilde{\mathrm{P}}_2 - \tilde{\mathrm{P}}_1)\}; \end{aligned} \tag{2.12}$$

$$\begin{aligned} \mathrm{J}_{\Sigma 2} = \mathrm{v}_{\Sigma 2} = \frac{\mathrm{d[P_2]}}{\mathrm{dt}} &= \varepsilon_2(\tilde{\mathrm{Y}} - \tilde{\mathrm{P}}_2) = \\ &= \frac{\varepsilon_2}{\varepsilon_{\mathrm{Y}} + \varepsilon_1 + \varepsilon_2}\{\varepsilon_{\mathrm{Y}}(\tilde{\mathrm{R}} - \tilde{\mathrm{P}}_2) + \varepsilon_1(\tilde{\mathrm{P}}_1 - \tilde{\mathrm{P}}_2)\}. \end{aligned} \tag{2.13}$$

Here, index Σ emphasizes that the fluxes that are characteristic of the stepwise processes are under consideration.

The preceding consideration leads us to state that the higher the $\tilde{\mathrm{P}}_2$ value, the faster the rate of the formation of component P_1. When $\tilde{\mathrm{P}}_2 > \tilde{\mathrm{Y}}$, which is the case at $\tilde{\mathrm{P}}_2 > \frac{\varepsilon_{\mathrm{Y}}\tilde{\mathrm{R}} + \varepsilon_1\tilde{\mathrm{P}}_1}{\varepsilon_{\mathrm{Y}} + \varepsilon_1}$ (the case marked with the asterisk in Figure 2.4b), the rate of the accumulation of compound P_2 takes the negative value. This means that both compound R and by product P_2 are involved in the reaction of the compound P_1 formation as a result of the conjugate transformations.

Formally, at the condition under discussion, compound P_2 is not formed from R, even though $\mu_{\mathrm{R}} > \mu_{\mathrm{P}_2}$; that is, the thermodynamic conjugation of two stepwise processes results now in the thermodynamically "wrong" route of process Σ2 with the participation of P_2 (see Section 1.2.4).

The physical reason for the conjugation of several concurrent chemical reactions is that the same intermediate (with its chemical potential that is an "internal" variable with respect to main reactants) may be involved in several transformation channels simultaneously. It is easy to discover that equations (2.12)–(2.13) can be transformed to equations

$$\begin{aligned} J_{\Sigma 1} &= \frac{d[P_1]}{dt} = \Lambda_{11}(\tilde{R} - \tilde{P}_1) + \Lambda_{12}(\tilde{R} - \tilde{P}_2), \\ J_{\Sigma 2} &= \frac{d[P_2]}{dt} = \Lambda_{21}(\tilde{R} - \tilde{P}_1) + \Lambda_{22}(\tilde{R} - \tilde{P}_2), \end{aligned} \tag{2.14}$$

where

$$\begin{aligned} &\Lambda_{11} = \frac{\varepsilon_1(\varepsilon_Y + \varepsilon_2)}{\varepsilon_Y + \varepsilon_1 + \varepsilon_2}, \quad \Lambda_{22} = \frac{\varepsilon_2(\varepsilon_Y + \varepsilon_1)}{\varepsilon_Y + \varepsilon_1 + \varepsilon_2}, \\ &\Lambda_{12} = \Lambda_{21} = -\frac{\varepsilon_1\varepsilon_2}{\varepsilon_Y + \varepsilon_1 + \varepsilon_2}. \end{aligned} \tag{2.15}$$

It is clear that the equation system (2.14) for the preceding set of reactions conjugated via a common intermediate is the full analogue of the Onsager equations

$$J_{\Sigma i} = \sum_j \Lambda_{ij} X'_{\Sigma j} \tag{2.16}$$

for conjugate fluxes $J_{\Sigma i}$ of thermodynamic parameters (these are the rates of stepwise reactions Σi) and related to them "dynamic" driving forces $X'_{\Sigma i} = \tilde{R} \quad \tilde{P}_i$, Λ_{ij} being the "reciprocity coefficient" to characterize the degree of the process conjugation. Evidently, the Λ_{ij} fits the rule $\Lambda_{ii} \geq 0$ necessary for the ordinary Onsager reciprocal coefficients. Moreover, relation $\Lambda_{ij} = \Lambda_{ji}$ is also met in the case under consideration. However, there is an essential difference of equations (2.14) and (2.16) from the traditional Onsager equations: The $X'_{\Sigma i}$ values in the equation set (2.16) are the differences of thermodynamic rushes (differences of absolute activities) of the initial reactant and the transformation products $X'_{\Sigma j} = \tilde{R} \quad \tilde{P}_j$ rather than the thermodynamic affinities (i.e., simple differences between chemical potentials of the initial reactant and the products of the stepwise transformation) for the chosen conjugate process channel that is characteristic of the "linear" nonequilibrium thermodynamics.

This specific feature of equations (2.16) is very important. It allows the Onsager equations to be expanded to the systems that are arbitrarily far from the thermodynamic equilibrium. In the case of an arbitrary number of cocurrent stoichiometric stepwise reactions $R_{\Sigma i} \rightleftarrows P_{\Sigma i}$ ($i = 1, \ldots, m$) that have common intermediates of the transformations, the rates of these stepwise reactions are interdependent. (Here, $R_{\Sigma i}$ and $P_{\Sigma i}$ are the initial and final reaction groups, respectively, of the stepwise transformations by the channel Σi.)

When intermediate transformations via all channels of the stepwise reactions occur under stationary conditions with respect to the intermediate concentrations, and their reaction pathways are linear (or reduced to linear) with respect to the intermediates, equation (2.16) can be easily generalized into "modified" Onsager reciprocal equations:

$$J_{\Sigma i} \equiv v_{\Sigma i} = \sum_{j=1}^{m} \Lambda_{ij} X'_{\Sigma j} \equiv \sum_{j=1}^{m} \Lambda_{ij} (\tilde{R}_{\Sigma j} - \tilde{P}_{\Sigma j}), \tag{2.17}$$

where $J_{\Sigma i} \equiv v_{\Sigma i} \equiv \frac{d\xi_{\Sigma i}}{dt}$ is the transformation rate via stepwise channel Σi.

"Dynamic" driving forces $X'_{\Sigma j} \equiv \tilde{R}_{\Sigma j} \quad \tilde{P}_{\Sigma j}$ are prescribed by external (in respect to the processes of the intermediate transformations inside the system in its stationary state) parameters, such as the difference between thermodynamic rushes of the initial and final reaction groups in corresponding channels of the resulting stepwise transformations. The validity of equation (2.17) is easy to check by considering specific pathways of conjugate transformations in a variety of examples presented in Section 2.3.5.

Equations of type (2.17) for the interrelation of the rates of conjugate stepwise reactions are valid for any intermediate linear transformation pathways (including catalytic reactions). The value of Λ_{ij} may be expressed by relations that are much more complicated than (2.15) and depends not only on parameters ε_{ij} but also on thermodynamic rushes of some "external" reactants of the stepwise reactions (see Section 2.3.5 for examples). At the same time, $\Lambda_{ii} \geq 0$ always. However, the relationship between the cross coefficients Λ_{ij} and Λ_{ji} may be more intricate than that in the traditional Onsager equations.

Equations like (2.17) can be treated as a generalization of the known Horiuti Boreskov relation over an arbitrary pathway of cocurrent reactions with the common intermediates and is thus called the Horiuti Boreskov Onsager equations. A typical example of such complex interrelated stepwise transformations is the catalytic reactions with the main ("target") catalyzed process and its side processes that cause nonselectivity of the main catalytic transformation.

2.3.5. The Onsager Reciprocal Relations for Cocurrent Stepwise Processes with Common Intermediates

In this section, we look at a few simple examples of finding the modified Onsager equations and the calculation of coefficients Λ_{ij} for particular schemes of the interrelated chemical transformations that are not very complicated.

Example 1

Consider two cocurrent stoichiometric stepwise processes:

$$R \overset{\Sigma 1}{\rightleftarrows} P_1; \tag{2.18}$$

$$R + A \overset{\Sigma 2}{\rightleftarrows} P_2 \tag{2.19}$$

that follow the pathway

$$\begin{aligned} R &\overset{\varepsilon_1}{\rightleftarrows} Y \\ Y &\overset{\varepsilon_2}{\rightleftarrows} P_1 \\ Y + A &\overset{\varepsilon_3}{\rightleftarrows} P_2. \end{aligned}$$

with a common intermediate Y and components R, A, P_1, and P_2 as the "external" reactants. The dynamic driving forces of the stepwise processes in the system are the following:

$$\begin{aligned} X'_{\Sigma 1} &= \tilde{R} \quad \tilde{P}_1, \\ X'_{\Sigma 2} &= \tilde{R}{\cdot}\tilde{A} \quad \tilde{P}_2. \end{aligned}$$

Let us express the stationary rates via all channels of the concurrent stepwise reactions in the form that conforms to the modified Onsager relations:

$$J_{\Sigma 1} \equiv v_{\Sigma 1} = \frac{d[P_1]}{dt} = \varepsilon_2(\tilde{Y} \quad \tilde{P}_1) = \Lambda_{11}(\tilde{R} \quad \tilde{P}_1) + \Lambda_{12}(\tilde{R}{\cdot}\tilde{A} \quad \tilde{P}_2),$$

$$J_{\Sigma 2} \equiv v_{\Sigma 2} = \frac{d[P_2]}{dt} = \varepsilon_3(\tilde{Y}{\cdot}\tilde{A} \quad \tilde{P}_2) = \Lambda_{21}(\tilde{R} \quad \tilde{P}_1) + \Lambda_{22}(\tilde{R}{\cdot}\tilde{A} \quad \tilde{P}_2).$$

Under the intermediate Y stationary conditions,

$$\frac{d[Y]}{dt} = \varepsilon_1(\tilde{R} - \tilde{Y}) - \varepsilon_2(\tilde{Y} - \tilde{P}_1) - \varepsilon_3(\tilde{Y}\cdot\tilde{A} - \tilde{P}_2) = 0$$

and thus,

$$\tilde{Y} = \frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}_1 + \varepsilon_3\tilde{P}_2}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3\tilde{A}}.$$

Therefore,

$$\begin{aligned} v_{\Sigma 1} = \frac{d[P_1]}{dt} &= \frac{\varepsilon_2}{\alpha}(\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}_1 + \varepsilon_3\tilde{P}_2 - \varepsilon_1\tilde{P}_1 - \varepsilon_2\tilde{P}_1 - \varepsilon_3\tilde{A}\cdot\tilde{P}_1) \\ &= \frac{\varepsilon_2}{\alpha}(\varepsilon_1\tilde{R} + \varepsilon_3\tilde{P}_2 - \varepsilon_1\tilde{P}_1 - \varepsilon_3\tilde{A}\cdot\tilde{P}_1 \pm \varepsilon_3\tilde{R}\cdot\tilde{A}) \\ &= \frac{\varepsilon_2}{\alpha}\{\varepsilon_1(\tilde{R} - \tilde{P}_1) - \varepsilon_3(\tilde{R}\cdot\tilde{A} - \tilde{P}_2) + \varepsilon_3\tilde{A}(\tilde{R} - \tilde{P}_1)\} \\ &= \frac{\varepsilon_2(\varepsilon_1 + \varepsilon_3\tilde{A})}{\alpha}(\tilde{R} - \tilde{P}_1) - \frac{\varepsilon_2\varepsilon_3}{\alpha}(\tilde{R}\cdot\tilde{A} - \tilde{P}_2), \end{aligned}$$

where

$$\alpha = \varepsilon_1 + \varepsilon_2 + \varepsilon_3\tilde{A}.$$

By analogy,

$$\begin{aligned} v_{\Sigma 2} = \frac{d[P_2]}{dt} &= \frac{\varepsilon_3}{\alpha}(\varepsilon_1\tilde{R}\cdot\tilde{A} + \varepsilon_2\tilde{P}_1\cdot\tilde{A} + \varepsilon_3\tilde{P}_2\cdot\tilde{A} - \varepsilon_1\tilde{P}_2 - \varepsilon_2\tilde{P}_2 - \varepsilon_3\tilde{A}\cdot\tilde{P}_2) \\ &= -\frac{\varepsilon_2\varepsilon_2\tilde{A}}{\alpha}(\tilde{R} - \tilde{P}_1) + \frac{\varepsilon_3(\varepsilon_1 + \varepsilon_2)}{\alpha}(\tilde{R}\cdot\tilde{A} - \tilde{P}_2). \end{aligned}$$

Hence,

$$\begin{aligned} \Lambda_{11} &= \frac{\varepsilon_2}{\alpha}(\varepsilon_1 + \varepsilon_3\tilde{A}), \\ \Lambda_{12} &= -\frac{\varepsilon_2\varepsilon_3}{\alpha}, \\ \Lambda_{21} &= -\frac{\varepsilon_2\varepsilon_3\tilde{A}}{\alpha}, \end{aligned}$$

$$\boldsymbol{\Lambda}_{22} = \frac{\varepsilon_2(\varepsilon_1 + \varepsilon_3)}{\alpha}.$$

Note that in the preceding example, $\boldsymbol{\Lambda}_{12} \neq \boldsymbol{\Lambda}_{21}$. However, if the system under consideration is close to the equilibrium, the nondiagonal Onsager reciprocity coefficients $\boldsymbol{\Lambda}_{ij}$ transform to the conventional Onsager coefficients L_{ij}, which appear to be index symmetrical, too.

In fact, the real driving forces of the stepwise processes under consideration here are affinities of the respective stepwise transformations:

$$X_{\boldsymbol{\Sigma}1} = A_{r\boldsymbol{\Sigma}1} = \mu_R \quad \mu_{P1},$$
$$X_{\boldsymbol{\Sigma}2} = A_{r\boldsymbol{\Sigma}2} = \mu_R \quad \mu_A \quad \mu_{P2},$$

Near equilibrium, $X_{\boldsymbol{\Sigma}1} < RT$, and $X_{\boldsymbol{\Sigma}2} < RT$, the following speculations are reasonable:

$$\boldsymbol{\Lambda}_{12}(\tilde{R}\cdot\tilde{A} \quad \tilde{P}_2) = \frac{\varepsilon_2\varepsilon_3}{\alpha}(\tilde{R}\cdot\tilde{A} \quad \tilde{P}_2)$$
$$\approx \frac{\varepsilon_2\varepsilon_3}{\alpha}\cdot\tilde{R}\cdot\tilde{A}\cdot\frac{A_{r\boldsymbol{\Sigma}2}}{RT} \equiv \frac{\varepsilon_2\varepsilon_3\tilde{R}\cdot\tilde{A}}{\alpha\cdot RT}X_{\boldsymbol{\Sigma}2}.$$

On the other hand,

$$\boldsymbol{\Lambda}_{21}(\tilde{R} \quad \tilde{P}_1) = \frac{\varepsilon_2\varepsilon_3\tilde{A}}{\alpha}(\tilde{R} \quad \tilde{P}_1) \approx \frac{\varepsilon_2\varepsilon_3\tilde{A}}{\alpha}\cdot\tilde{R}\frac{A_{r\boldsymbol{\Sigma}1}}{RT} \equiv \frac{\varepsilon_2\varepsilon_3\tilde{A}\cdot\tilde{R}}{\alpha\cdot RT}X_{\boldsymbol{\Sigma}1}.$$

In other words, the traditional Onsager equations:

$$J_{\boldsymbol{\Sigma}1} = v_{\boldsymbol{\Sigma}1} = L_{11}A_{r\boldsymbol{\Sigma}1} + L_{12}A_{r\boldsymbol{\Sigma}2},$$
$$J_{\boldsymbol{\Sigma}2} = v_{\boldsymbol{\Sigma}2} = L_{21}A_{r\boldsymbol{\Sigma}1} + L_{22}A_{r\boldsymbol{\Sigma}2}$$

are seen to be valid when both stepwise processes are close to thermodynamic equilibrium. These equations are written using the real driving forces of the stepwise processes $X_{\boldsymbol{\Sigma}1} = A_{r\boldsymbol{\Sigma}1}$ and $X_{\boldsymbol{\Sigma}1} = A_{r\boldsymbol{\Sigma}2}$, the nondiagonal elements of the matrix being symmetrical:

$$L_{12} = L_{21} = \frac{\varepsilon_2\varepsilon_3\tilde{R}\cdot\tilde{A}}{\alpha\cdot RT}.$$

Example 2

Consider two cocurrent stoichiometric stepwise processes with the transformation channels **Σ**1 and **Σ**2:

$$R + A \overset{\Sigma 1}{\rightleftarrows} P_1; \tag{2.20}$$

$$R \overset{\Sigma 2}{\rightleftarrows} B + P_2 \tag{2.21}$$

that follow the pathway

$$\begin{aligned} &R \overset{\varepsilon_1}{\rightleftarrows} Y, \\ &A + Y \overset{\varepsilon_2}{\rightleftarrows} P_1, \\ &Y \overset{\varepsilon_3}{\rightleftarrows} P_2 + B \end{aligned}$$

with a common intermediate Y and external reactants R, A, B, P_1, and P_2.
This is the case of the transformations with the action of two dynamic driving forces

$$X'_{\Sigma 1} = \tilde{R}\cdot\tilde{A} \quad \tilde{P}_1$$

and

$$X'_{\Sigma 2} = \tilde{R} \quad \tilde{B}\cdot\tilde{P}_2.$$

Therefore, we can write the rates of the cocurrent stepwise reactions in the form

$$\begin{aligned} J_{\Sigma 1} &= v_{\Sigma 1} = \frac{d[P_1]}{dt} = \varepsilon_2(\tilde{A}\cdot\tilde{Y} \quad \tilde{P}_1) = \boldsymbol{\Lambda}_{11}(\tilde{R}\cdot\tilde{A} \quad \tilde{P}_1) + \boldsymbol{\Lambda}_{12}(\tilde{R} \quad \tilde{B}\cdot\tilde{P}_2), \\ J_{\Sigma 2} &= v_{\Sigma 2} = \frac{d[P_2]}{dt} = \varepsilon_3(\tilde{Y} \quad \tilde{P}_2\cdot\tilde{B}) = \boldsymbol{\Lambda}_{21}(\tilde{R}\cdot\tilde{A} \quad \tilde{P}_1) + \boldsymbol{\Lambda}_{22}(\tilde{R} \quad \tilde{B}\cdot\tilde{P}_2). \end{aligned}$$

At the intermediate-stationary conditions

$$\frac{d[Y]}{dt} = \varepsilon_1(\tilde{R} \quad \tilde{Y}) \quad \varepsilon_2(\tilde{A}\cdot\tilde{Y} \quad \tilde{P}_1) \quad \varepsilon_3(\tilde{Y} \quad \tilde{P}_2\cdot\tilde{B}) = 0$$

and

$$\tilde{Y} = \frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}_1 + \varepsilon_3\tilde{P}_2\cdot\tilde{B}}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3}.$$

This gives

$$\begin{aligned}
v_{\boldsymbol{\Sigma}1} &= \frac{d[P_1]}{dt} = \frac{\varepsilon_2\left(\varepsilon_1\tilde{A}\cdot\tilde{R} + \varepsilon_2\tilde{P}_1\cdot\tilde{A} + \varepsilon_3\tilde{B}\cdot\tilde{A} \quad \varepsilon_1\tilde{P}_1 \quad \varepsilon_2\tilde{A}\cdot\tilde{P}_1 \quad \varepsilon_3\tilde{P}_1\right)}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3}\\
&= \frac{\varepsilon_2}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3}\left\{\varepsilon_1(\tilde{A}\cdot\tilde{R} \quad \tilde{P}_1) + \varepsilon_3(\tilde{P}_2\cdot\tilde{A}\cdot\tilde{B} \quad \tilde{P}_1 \pm \tilde{A}\cdot\tilde{R})\right\}\\
&= \frac{\varepsilon_2}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3}\left\{(\varepsilon_1 + \varepsilon_3)(\tilde{A}\cdot\tilde{R} \quad \tilde{P}_1) \quad \varepsilon_3\tilde{A}(\tilde{R} \quad \tilde{P}_2\cdot\tilde{B})\right\},\\
v_{\boldsymbol{\Sigma}2} &= \frac{d[P_2]}{dt} = \frac{\varepsilon_3}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3}\left\{ \quad \varepsilon_2(\tilde{A}\cdot\tilde{R} \quad \tilde{P}_1) + (\varepsilon_1 + \varepsilon_2\tilde{A})(\tilde{R} \quad \tilde{B}\cdot\tilde{P}_2)\right\}.
\end{aligned}$$

Hence,

$$\begin{aligned}
\boldsymbol{\Lambda}_{11} &= \frac{\varepsilon_2(\varepsilon_1 + \varepsilon_3)}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3},\\
\boldsymbol{\Lambda}_{12} &= \quad \frac{\varepsilon_2\varepsilon_3\tilde{A}}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3},\\
\boldsymbol{\Lambda}_{21} &= \quad \frac{\varepsilon_2\varepsilon_3}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3},\\
\boldsymbol{\Lambda}_{22} &= \frac{\varepsilon_3(\varepsilon_1 + \varepsilon_2\tilde{A})}{\varepsilon_1 + \varepsilon_2\tilde{A} + \varepsilon_3}.
\end{aligned}$$

We must emphasize that in this example, again, $\boldsymbol{\Lambda}_{12} \neq \boldsymbol{\Lambda}_{21}$. However, it is also easy to demonstrate that $L_{12} = L_{21}$ on approaching the equilibrium of the stepwise transformations when the true Onsager coefficients L_{ij} relate to true thermodynamic forces (the affinities of the stepwise processes).

Example 3

Determine the reciprocal coefficients $\boldsymbol{\Lambda}_{ij}$ for two cocurrent stepwise processes:

$$R \overset{\Sigma 1}{\rightleftarrows} P_1 + P_3; \tag{2.22}$$

$$R \overset{\Sigma 2}{\rightleftarrows} P_2 \tag{2.23}$$

(the transformation channels are $\boldsymbol{\Sigma}1$ and $\boldsymbol{\Sigma}2$, respectively) that follow the pathway with two intermediates Y and W:

$$\begin{aligned}
&\mathrm{R} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{W},\\
&\mathrm{W} \overset{\varepsilon_2}{\rightleftarrows} \mathrm{P}_1 + \mathrm{Y},\\
&\mathrm{W} \overset{\varepsilon_3}{\rightleftarrows} \mathrm{P}_2,\\
&\mathrm{Y} \overset{\varepsilon_4}{\rightleftarrows} \mathrm{P}_3.
\end{aligned}$$

The dynamic driving forces of the stepwise processes are

$$X'_{\boldsymbol{\Sigma}1} = \tilde{R} - \tilde{P}_1{\cdot}\tilde{P}_3$$

and

$$X'_{\boldsymbol{\Sigma}2} = \tilde{R} - \tilde{P}_2.$$

Therefore,

$$\begin{aligned}
J_{\boldsymbol{\Sigma}1} = v_{\boldsymbol{\Sigma}1} = \frac{d[P_1]}{dt} = \frac{d[P_3]}{dt} = \varepsilon_2(\tilde{W} - \tilde{P}_1\tilde{Y}) = \boldsymbol{\Lambda}_{11}(\tilde{R} - \tilde{P}_1{\cdot}\tilde{P}_3) + \boldsymbol{\Lambda}_{12}(\tilde{R} - \tilde{P}_2),\\
J_{\boldsymbol{\Sigma}2} = v_{\boldsymbol{\Sigma}2} = \frac{d[P_2]}{dt} = \varepsilon_3(\tilde{W} - \tilde{P}_2) = \boldsymbol{\Lambda}_{21}(\tilde{R} - \tilde{P}_1{\cdot}\tilde{P}_3) + \boldsymbol{\Lambda}_{22}(\tilde{R} - \tilde{P}_2).
\end{aligned}$$

At the intermediate-stationary conditions,

$$\begin{aligned}
\frac{d[W]}{dt} &= \varepsilon_1(\tilde{R} - \tilde{W}) - \varepsilon_2(\tilde{W} - \tilde{P}_1{\cdot}\tilde{Y}) - \varepsilon_3(\tilde{W} - \tilde{P}_2) = 0,\\
\frac{d[Y]}{dt} &= \varepsilon_2(\tilde{W} - \tilde{P}_1{\cdot}\tilde{Y}) - \varepsilon_4(\tilde{Y} - \tilde{P}_3) = 0.
\end{aligned}$$

This gives

$$\begin{gathered}
\varepsilon_1(\tilde{R} - \tilde{W}) - \varepsilon_3(\tilde{W} - \tilde{P}_2) - \varepsilon_4(\tilde{Y} - \tilde{P}_3) = 0,\\
\tilde{W} = \frac{\varepsilon_1\tilde{R} + \varepsilon_3\tilde{P}_2 + \varepsilon_4\tilde{P}_3 - \varepsilon_4\tilde{Y}}{\varepsilon_1 + \varepsilon_3},\\
\tilde{Y} = \frac{\varepsilon_1\tilde{R} + \varepsilon_3\tilde{P}_2 + \varepsilon_4\tilde{P}_3 - \varepsilon_1\tilde{W} - \varepsilon_3\tilde{W}}{\varepsilon_4},
\end{gathered}$$

$$\begin{aligned}&\varepsilon_2[\varepsilon_4\tilde{W}\quad\tilde{P}_1(\varepsilon_1\tilde{R}+\varepsilon_3\tilde{P}_2\quad\varepsilon_4\tilde{P}_3\quad\varepsilon_1\tilde{W}\quad\varepsilon_3\tilde{W})]\\ &\quad\varepsilon_4(\varepsilon_1\tilde{R}+\varepsilon_3\tilde{P}_2+\varepsilon_4\tilde{P}_3\quad\varepsilon_1\tilde{W}\quad\varepsilon_3\tilde{W}\quad\varepsilon_4\tilde{P}_3)=0.\end{aligned}$$

Denote

$$\alpha\equiv\varepsilon_2\varepsilon_4+\varepsilon_1\varepsilon_4+\varepsilon_3\varepsilon_4+(\varepsilon_1\varepsilon_2+\varepsilon_2\varepsilon_3)\tilde{P}_1.$$

Then

$$\begin{aligned}\tilde{W}&=[\varepsilon_2\tilde{P}_1(\varepsilon_1\tilde{R}+\varepsilon_3\tilde{P}_2+\varepsilon_4\tilde{P}_3)+\varepsilon_4(\varepsilon_1\tilde{R}+\varepsilon_3\tilde{P}_2)]/\alpha,\\ \tilde{Y}&=(\varepsilon_1\varepsilon_2\tilde{R}+\varepsilon_1\varepsilon_4\tilde{P}_3+\varepsilon_2\varepsilon_3\tilde{P}_3+\varepsilon_3\varepsilon_4\tilde{P}_3+\varepsilon_2\varepsilon_3\tilde{P}_2)/\alpha.\end{aligned}$$

This gives

$$\begin{aligned}J_{\Sigma1}=v_{\Sigma1}&=\frac{d[P_1]}{dt}=\frac{d[P_3]}{dt}\\ &=\varepsilon_2\varepsilon_4\{\varepsilon_1(\tilde{R}\quad\tilde{P}_1\tilde{P}_3)+\varepsilon_3\tilde{P}_2\quad\varepsilon_3\tilde{P}_1\tilde{P}_3\pm\varepsilon_3\tilde{R}\}/\alpha\\ &=\varepsilon_2\varepsilon_4\{(\varepsilon_1+\varepsilon_3)(\tilde{R}\quad\tilde{P}_1\tilde{P}_3)\quad\varepsilon_3(\tilde{R}\quad\tilde{P}_2)\}/\alpha,\\ J_{\Sigma2}=v_{\Sigma2}&=\frac{d[P_2]}{dt}=\frac{\varepsilon_3}{\alpha}\{\varepsilon_1\varepsilon_2\tilde{P}_1\tilde{R}+\varepsilon_2\varepsilon_3\tilde{P}_1\tilde{P}_2+\varepsilon_2\varepsilon_4\tilde{P}_1\tilde{P}_3+\varepsilon_1\varepsilon_4\tilde{R}+\varepsilon_3\varepsilon_4\tilde{P}_2\\ &\qquad\qquad\varepsilon_2\varepsilon_4\tilde{P}_2\quad\varepsilon_1\varepsilon_4\tilde{P}_2\quad\varepsilon_3\varepsilon_4\tilde{P}_2\quad\varepsilon_1\varepsilon_2\tilde{P}_1\tilde{P}_2\quad\varepsilon_2\varepsilon_3\tilde{P}_1\tilde{P}_2\}\\ &=\frac{\varepsilon_3}{\alpha}\{\varepsilon_1\varepsilon_2\tilde{P}_1(\tilde{R}\quad\tilde{P}_2)+\varepsilon_1\varepsilon_4(\tilde{R}\quad\tilde{P}_2)+\varepsilon_2\varepsilon_4\tilde{P}_1\tilde{P}_3\quad\varepsilon_2\varepsilon_4\tilde{P}_2\pm\varepsilon_2\varepsilon_4\tilde{R}\}\\ &=\frac{\varepsilon_3}{\alpha}\{(\varepsilon_1\varepsilon_2\tilde{P}_1+\varepsilon_1\varepsilon_4+\varepsilon_2\varepsilon_4)(\tilde{R}\quad\tilde{P}_2)\quad\varepsilon_2\varepsilon_4(\tilde{R}\quad\tilde{P}_1\tilde{P}_3)\}.\end{aligned}$$

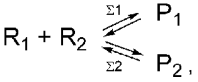
Hence,

$$\begin{aligned}\boldsymbol{\Lambda}_{11}&=\varepsilon_2\varepsilon_4(\varepsilon_1+\varepsilon_3)/\alpha,\\ \boldsymbol{\Lambda}_{12}=\boldsymbol{\Lambda}_{21}&=\quad\varepsilon_2\varepsilon_3\varepsilon_4/\alpha,\\ \boldsymbol{\Lambda}_{22}&=\varepsilon_3(\varepsilon_1\varepsilon_2\tilde{P}_1+\varepsilon_1\varepsilon_4+\varepsilon_2\varepsilon_4)/\alpha.\end{aligned}$$

In this example, the nondiagonal reciprocal coefficients are the index-symmetrical ones, $\boldsymbol{\Lambda}_{12}=\boldsymbol{\Lambda}_{21}$.

Example 4

Find the reciprocal coefficients Λ_{ij} for the cocurrent stoichiometric stepwise processes



(2.24)

(2.25)

that follow the pathway

$$\begin{gathered} R_1 \overset{\varepsilon_1}{\rightleftarrows} Y_1, \\ Y_1 + R_2 \overset{\varepsilon_2}{\rightleftarrows} Y_2, \\ Y_2 \overset{\varepsilon_3}{\rightleftarrows} P_1, \\ Y_2 \overset{\varepsilon_4}{\rightleftarrows} Y_3 \overset{\varepsilon_5}{\rightleftarrows} Y_4 \overset{\varepsilon_6}{\rightleftarrows} Y_5 \overset{\varepsilon_7}{\rightleftarrows} P_2 \end{gathered} \qquad (2.26)$$

where Y_i are intermediates.

The dynamic driving forces of the stepwise reactions are

$$X'_{\Sigma 1} = \tilde{R}_1 \cdot \tilde{R}_2 \quad \tilde{P}_1$$

and

$$X'_{\Sigma 2} = \tilde{R}_1 \cdot \tilde{R}_2 \quad \tilde{P}_2.$$

The rates of the stepwise reactions via parallel channels are

$$\begin{aligned} J_{\Sigma 1} &= v_{\Sigma 1} = \frac{d[P_1]}{dt} = \varepsilon_3(\tilde{Y}_2 \quad \tilde{P}_1) = \\ &= \Lambda_{11}(\tilde{R}_1 \cdot \tilde{R}_2 \quad \tilde{P}_1) + \Lambda_{12}(\tilde{R}_1 \cdot \tilde{R}_2 \quad \tilde{P}_2), \\ J_{\Sigma 2} &= v_{\Sigma 2} = \frac{d[P_2]}{dt} = \varepsilon_4(\tilde{Y}_2 \quad \tilde{P}_2) = \\ &= \Lambda_{21}(\tilde{R}_1 \cdot \tilde{R}_2 \quad \tilde{P}_1) + \Lambda_{22}(\tilde{R}_1 \cdot \tilde{R}_2 \quad \tilde{P}_2). \end{aligned}$$

Notice that at the intermediate stationary conditions, the consecutive process that is written in the first and second lines of the transformation pathway (2.26) can be substituted with one effective transformation

$$R_1 + R_2 \overset{\varepsilon_{\text{eff }1}}{\rightleftarrows} Y_2,$$

where $\varepsilon_{\text{eff }1} = \dfrac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2 \tilde{R}_2}$.

The same can be done for the last line of the transformation pathway:

$$Y_2 \overset{\varepsilon_{\text{eff }2}}{\rightleftarrows} P_2$$

where

$$\varepsilon_{\text{eff }2} = \left(\frac{1}{\varepsilon_4} + \frac{1}{\varepsilon_5} + \frac{1}{\varepsilon_6} + \frac{1}{\varepsilon_7}\right)^{-1}.$$

Therefore, the transformation pathway (2.26) can be largely simplified:

$$\begin{aligned} R_1 + R_2 &\overset{\varepsilon_{\text{eff }1}}{\rightleftarrows} Y_2, \\ Y_2 &\overset{\varepsilon_3}{\rightleftarrows} P_1, \\ Y_2 &\overset{\varepsilon_{\text{eff }2}}{\rightleftarrows} P_2. \end{aligned} \tag{2.27}$$

The resulting scheme is seen to resemble the scheme (2.11).

Analogously to the solution (2.15), we can introduce $\alpha \equiv \varepsilon_{\text{eff1}} + \varepsilon_3 + \varepsilon_{\text{eff2}}$ and find:

$$\begin{aligned} \Lambda_{11} &= \varepsilon_3(\varepsilon_{\text{eff1}} + \varepsilon_{\text{eff2}})/\alpha, \\ \Lambda_{22} &= \varepsilon_{\text{eff2}}(\varepsilon_{\text{eff1}} + \varepsilon_3)/\alpha, \\ \Lambda_{12} = \Lambda_{21} &= \quad \varepsilon_3\varepsilon_{\text{eff2}}/\alpha. \end{aligned}$$

In a similar way, substituting the series of certain transformations at their stationary modes by effective transformations will allow the exact expressions of the reciprocity coefficients Λ_{ij} to be found for even very complex schemes of cocurrent stepwise transformations, provided that these are linear with respect to the intermediates. Unfortunately, for an arbitrary case of cocurrent stepwise transformations that are nonlinear in respect to their intermediates and proceed far from equilibrium, it is not possible to write general equations that are analogous to the modified Onsager relations.

2.4. THERMODYNAMIC CRITERIA OF ACHIEVEMENT AND STABILITY OF STATIONARY STATES

Under constant external conditions, a nonequilibrium system may reach its stationary state. Specific features of such a state are the time constant values of internal thermodynamic parameters characterizing the system and, as a consequence, the absence (the zero value) of fluxes related to these parameters. The values of the internal parameters are determined by irreversible processes initiated by the internal thermodynamic forces.

An example is the stationary state of an open chemically reactive system, where the intermediate concentrations, which are settled in the course of the internal processes, are time constant. The rate of changing these intermediate concentrations (fluxes of these parameters) equals zero. Evidently, the stationary state is settled at a certain ratio of the rates of elementary reactions responsible for the formation and vanishing of the reactive intermediates.

A total of the entropy of any open system in its stationary state is constant as well: $dS/dt = d_eS/dt + d_iS/dt = 0$. However, terms d_eS/dt and d_iS/dt, which relate to the processes of exchange with the system environment and to internal irreversible processes, may be nonzero.

Another important consideration is that for any open system near its thermodynamic equilibrium, there is a relationship between establishing the stationary nonequilibrium state of the system and the rate of entropy production via spontaneous irreversible processes inside the system. Moreover, the dependence of parameter d_iS/dt and its conjugate parameter, which is the rate of energy dissipation, on time makes it possible to detect the evolution of the open system to its stationary state.

The deduction of a criterion for the evolution of an open system to its stationary state resembles the classical thermodynamic problem of predicting the direction of spontaneous irreversible evolution in an isolated system: According to the Second Law of thermodynamics, in the latter case the changes go only toward the increase in entropy, the entropy being maximal at the final equilibrium state.

The general theory of thermodynamics of nonequilibrium processes also tells us the stability of nonequilibrium stationary states with respect to spontaneous fluctuations of the internal thermodynamic parameters in the system. It turns out that this stability can also be investigated by analyzing the variations in the entropy production or energy dissipation rates on drawing the system away from its stationary state.

2.4.1. The Prigogine Criterion (Theorem) of the Evolution for Systems that Are Close to their Thermodynamic Equilibrium

Consider an open isothermal system where m internal irreversible processes related to a spontaneous evolution of several thermodynamic parameters a_i occur simultaneously. The rate of energy dissipation in the system is given by the positively determined expression (2.5):

$$\boldsymbol{P} = \mathrm{T}\frac{\mathrm{d_iS}}{\mathrm{dt}} = \sum_{\mathrm{i=1}}^{\mathrm{m}} \mathrm{J_i X_i} > 0.$$

Let the system be close to its thermodynamic equilibrium. Then the linear Onsager reciprocal relations between the values of fluxes and the conjugate thermodynamic forces are valid: $\mathrm{J_i} = \sum_{\mathrm{j\ \ 1}}^{\mathrm{m}} \mathrm{L_{ij} X_j}$. Therefore, the energy dissipation rate can be expressed here in the form of the Rayleigh Onsager function

$$\boldsymbol{P} = \boldsymbol{P}(\mathrm{X_1, X_2, \ldots, X_m}) = \mathrm{Td_iS/dt} = \sum_{\mathrm{i=1}}^{\mathrm{m}} \sum_{\mathrm{j=1}}^{\mathrm{m}} \mathrm{L_{ij} X_i X_j}. \tag{2.28}$$

This function is quadratic with respect to independent thermodynamic forces $\mathrm{X_i}$.

It is natural to suppose that approaching the stationary state with $\bar{\mathrm{J}}_\mathrm{i} = 0$ for the flux of internal parameters $\mathrm{a_i}$ is a consequence of spontaneous evolution of internal thermodynamic forces $\mathrm{X_i}$. Let us study the behavior of $\boldsymbol{P}$ as a function of $\mathrm{X_i}$ by taking partial derivative $\partial \boldsymbol{P}/\partial \mathrm{X_i}$ at constant $\mathrm{X_j}$ with $\mathrm{j} \neq \mathrm{i}$.

The specific construction of the Rayleigh Onsager function (2.6) as well as the $\mathrm{L_{ik}}$ independence of internal forces $\mathrm{X_i}$ gives

$$(\partial \boldsymbol{P}/\partial \mathrm{X_i})_{\mathrm{X_{j,j/i}}} = 2\left(\sum_{\mathrm{j=1}}^{\mathrm{m}} \mathrm{L_{ij} X_j}\right) = 2\mathrm{J_i}.$$

The condition of attaining the stationary state with respect to a particular internal parameter $\mathrm{a_i}$ (for example, the concentration of a chosen reaction intermediate) is the zero value of the flux corresponding to this parameter:

$$\bar{\mathrm{J}}_\mathrm{i} \equiv \frac{\mathrm{da_i}}{\mathrm{dt}} = 0.$$

Evidently, this condition and the condition of extremum of function $\boldsymbol{P}$ is respect to independent variable $\mathrm{X_i}$, which is

$$(\partial \boldsymbol{P}/\partial \mathrm{X_i})_{\mathrm{X_{j,j/i}}} = 0, \tag{2.29}$$

are identical at the validity region of linear thermodynamics of irreversible processes.

It is important that $\boldsymbol{P}$ is a positively determined quadratic expression over the entire range of spontaneous fluctuations of independent variable X_i. For this reason, the zero value of the derivative $(\partial \boldsymbol{P}/\partial X_i) = 0$ is the condition of minimum of function $\boldsymbol{P}(X_1, X_2, \ldots, X_m)$ with respect to independent variable X_i.

The stationarity conditions for the other internal variable fluxes are deduced in the same way. For example, the condition $\bar{J}_k = 0$ is identical to the condition

$$(\partial \boldsymbol{P}/\partial X_k)_{X_{j,j/k}} = 0, \tag{2.30}$$

and so on. Thus, the conclusion on the equivalence of the conditions of minimum of function $\boldsymbol{P} \equiv T\frac{d_iS}{dt}$ and the achievement of the stationary state is valid for an arbitrary system with any number of internal thermodynamic processes related to one another through the linear Onsager reciprocal equations. Evidently, the local processes in a given point of an isothermal system can be treated similarly. Therefore, the relations of type (2.29) and (2.30) express the following important feature of irreversible processes in open systems near their thermodynamically equilibrium state: At the invariable external conditions, the stationary state of the system is characterized by the constant, positive and minimal rate of entropy production.

This conclusion is a principal statement of the I. Prigogine theorem (1947, the Nobel Prize winner in 1977). It also is essential in view of the positively determined Rayleigh Onsager function that the spontaneous evolution of the system to its stationary state can be accompanied by only a monotonous decrease in $\boldsymbol{P}$ and, as a result, in $\frac{d_iS}{dt}$; that is,

$$d\boldsymbol{P}/dt < 0 \text{ and } \frac{d}{dt}(d_iS/dt) < 0. \tag{2.31}$$

Therefore, the principle of the minimal rate of entropy production appears to be the quantitative criterion (i.e., the necessary and sufficient condition) to determine the direction of spontaneous evolutions in any open systems near their thermodynamic equilibrium. In other words, this is the quantitative criterion of the evolution of a system toward its stationary state. In an isothermal system, the principle of the minimum of the entropy production rate is fully identical to the principle of the minimum of the energy dissipation rate. The last principle was formulated by L. Onsager (the Nobel Prize winner in 1968) in the 1930s when he was studying some particular problems of electrodynamics.

Thus, monitoring the behavior of the entropy production rate (or the energy dissipation rate) in near equilibrium systems allows the identification of the system transition to its stationary state. In fact, as the system evolves from some initial state to the stationary state, the possible value of $\boldsymbol{P} = \mathrm{Td_iS/dt}$ decreases monotonically but remains positive and gradually approaches the minimal and constant positive value related to the final stationary state.

The validity of the Prigogine criterion of evolution is easy to support by analyzing directly the evolution of chemically reactive systems with a large number of reversible chemical transformations near their thermodynamic equilibrium. Positive results in an experimental verification of this criterion in biology, for example, have been achieved by monitoring the rate of specific heat production in a living organism during the evolution of the embryo of the organism: The rate of the specific (per unit mass of the organism) heat production decreases sharply as the evolving organism approaches the maturity state and reaches the minimal value in the stationary mature state (see the Bibliography to the Chapter).

2.4.2. Stability of the Stationary State near Equilibrium

It follows from the Prigogine theorem that in cases where the system exists near its thermodynamic equilibrium, any deviation from the system stationary state due to a disturbance of some internal parameters causes an increase in the rate of entropy production. Simultaneously, the spontaneous evolution of the system will make the entropy production rate decreasing again to its minimal value. Hence, the stationary state of an open system nearly its equilibrium is stable. It is obvious here that the stability condition of the stationary state is inequality $\delta\boldsymbol{P} > 0$ at the appearance of any disturbance (fluctuation) of those internal parameters whose values are determined by the condition of the system stationarity.

This criterion of the stationary state stability is necessarily satisfied in any open systems where fluxes $\mathrm{J_k}$ and thermodynamic forces $\mathrm{X_k}$ of the occurring internal thermodynamic processes are interconnected by the Onsager reciprocal relations. Let us show that. Let some disturbance results in a change in the internal driving forces $\mathrm{X_k}$ ($\mathrm{k} = 1, 2, \ldots, \mathrm{m}$) by quantities $\delta\mathrm{X_k}$ relative to the stationary values $\overline{\mathrm{X}}_\mathrm{k}$ of the forces (for example, due to a fluctuation of the concentration of some reaction intermediates).

Then the stationary fluxes $\bar{J}_k$ will change by quantities δJ_k and the new values of the fluxes become equal to

$$J_k^* = \sum_{j=1}^{m} L_{kj}(\overline{X}_j + \delta X_j) = \sum_{j=1}^{m} L_{kj}\overline{X}_j + \sum_{j=1}^{m} L_{kj}\delta X_j \equiv \bar{J}_k + \sum_{j=1}^{m} L_{kj}\delta X_j.$$

While $\bar{J}_k = \sum_{j\ \ 1}^{m} L_{kj}\delta\overline{X}_j = 0$ in the stationary state, then

$$J_k^* = \sum_{j=1}^{m} L_{kj}\delta X_j;$$

that is, fluxes $J^*{}_k$ arising on the system disturbance appear proportional to the disturbances δX_j of the driving forces. Hence, the increment $\delta \boldsymbol{P}$ of the energy dissipation rate initiated by internal processes that result from the spoken disturbance in the system takes the positive value due to the properties of the Rayleigh Onsager function:

$$\delta \boldsymbol{P} = \sum_{k=1}^{m} J_k^*\delta X_k = \sum_{k=1}^{m}\sum_{j=1}^{m} L_{kj}\delta X_k\delta X_j > 0.$$

The inequality

$$\delta \boldsymbol{P} = \sum_{k=1}^{m} J_k^*\delta X_k > 0 \qquad (2.32)$$

implies as well that in any stable system, the direction of the disturbance induced flux J_k^* must coincide with the direction of disturbing thermodynamic force δX_k and tends to diminish the disturbance δX_k, thus turning the system back to its initial state.

The preceding conclusions about the stability of stationary states near stable thermodynamic equilibrium are graphically interpreted in Figure 2.5. Indeed, if an incidental fluctuation of thermodynamic force X_i around its stationary magnitude $\overline{X}_i$ results in a minor deviation of the system from the stationary state near thermodynamic equilibrium, the internal transformations must happen according to inequality (2.31), which will affect the value of X_i and return the system again to its initial stationary state (see Figure 2.5A). Thus, if the system is near thermodynamic equilibrium in the stationary state, it cannot escape this state spontaneously due to

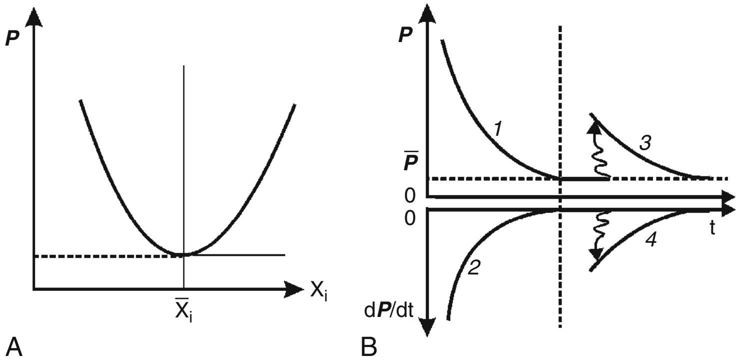


Figure 2.5 The rate of energy dissipation (entropy production) near the stationary point in a system close to thermodynamic equilibrium: dependence of $\boldsymbol{P} = Td_iS/dt$ on thermodynamic driving forces nearby stationary point $\bar{X}_i$ (A); time dependence of **P**(*1, 3*) and d**P**/dt(*2, 4*) on approaching the stationary state (B). The vertical dashed line stands for the moment of approaching the stationary state by the system, and wavy line for escaping the stationary state caused by an internal perturbation (fluctuation).

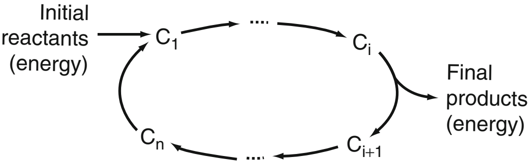
internal irreversible transformations. In other words, the given stationary state is stable. The spontaneous return to this state upon minor disturbances resembles the well known Le Chatelier principle, which also is a consequence of the stability of thermodynamically equilibrium states.

An important conclusion follows from the time monotonic manner (2.31) of changes in values $\boldsymbol{P}$ and d_iS/dt. In case the system exists near thermodynamic equilibrium, the system's spontaneous evolution cannot generate any periodical auto oscillating processes. In fact, periodical processes are described along the closed evolution trajectories, which would make some thermodynamic parameters (concentration, temperature, etc.) and, as a result, values J_i and X_i return periodically to the same values. This is inconsistent with the one directional time monotonic changes in the $\boldsymbol{P}$ value and with the constancy of the latter in the stationary point. In terms of Lyapunov's theory of stability, the stationary state under discussion corresponds to a particular point of "stable node" type (see Section 3.5.2).

2.5. THE THERMODYNAMICS OF METABOLIC CYCLES AND THE DIRECTION OF THE EVOLUTION OF LIVING SYSTEMS

The metabolic cycle of living organisms is an open sequence of reactions where an alimentary substrate (which is the initial reactant for the conjugating process) is transformed (assimilated) in such a way that the initial state of the "internal" components (intermediates) of the system is fully regenerated upon accomplishing the metabolic cycle. The chemical transformations at any intermediate step of the metabolic cycle may be accompanied by either releasing the metabolism products to the environment or supplying the alimentary substrate into the cycle from outside, as well as by dissipation of the energy released during the assimilation of the substrate molecules. The living cell utilizes the intermediate (or, when grows, final) products of metabolic transformations that, together with the energy release in the cycle, determines the key role of cyclic transformations in the cell metabolism.

The cycle under discussion can be treated as a fully deterministic "chemical machine" that is doing the work on the conversion of one type of substances and energy into the other types. The functioning of the simplest cycle of assimilation of initial reactants (alimentary substrates) and energy supplied from outside is similar to the cycle of catalytic transformations in the intermediate stationary regime (see Chapter 4):



Here, C_1, C_2, ... , C_m are the reaction intermediates of the cycle.

The internal irreversible processes in this machine are accompanied by the entropy rise. The value of this rise is determined by variations in the total Gibbs potential of the system components and the components from the environment:

$$Td_iS = -d(G + G^*).$$

Here, G and G^* are the Gibbs's potentials of the system components and components from environment (i.e., alimentary substrates for the chemical cycle to "work"), respectively.

After one turn of the cycle in time τ, the system is returned to its initial state. Hence, the changes in the thermodynamic Gibbs potential of the system will be zero in time τ: $\Delta G_\tau = 0$, while $\Delta G^*_\tau < 0$ due to the consumption of alimentary substrates from the surrounding medium. The average rate of energy dissipation in the metabolic cycle is

$$\boldsymbol{P} = T\frac{d_iS}{dt} = -\frac{\Delta G^*}{\tau}. \tag{2.33}$$

The given expression allows different cycles to be compared in their energetic efficiency. In fact, let two systems function due to the consumption of the same substrate. In these systems, $\Delta G^{*}{}_{1} = \Delta G^{*}{}_{2}$, and if $\tau_1 < \tau_2$, then equation (2.33) gives $\boldsymbol{P}_1 > \boldsymbol{P}_2$. Thus, the rate of energy dissipation is higher in the first cycle than in the second cycle. Hence, the second system must be considered as being at a higher level of biological evolution because of its proximity to "an ideal of the biological evolution." This seems to show the expected direction of the evolution of the metabolic systems of living organisms during their adaptive selection in nature.

Undoubtedly, the validity of this conclusion needs an assumption that the living system operates near thermodynamic equilibrium and thus falls into the range of linear thermodynamics. This is a rather serious restriction for analyzing real metabolic processes.[*] Nevertheless, some attempts are known to explain the direction of the natural evolution of living systems on the basis of the preceding simplified thermodynamic concepts. It is postulated there that the evolution of living systems goes toward a decrease in the rate of the specific energy dissipation (specific heat induction), and lower specific $\boldsymbol{P}$ values are characteristic of more perfect living systems.

In the course of biological evolution of living systems, there could be indeed a simultaneous complication of the network of biochemical transformations of the substances constituents of metabolic cycles as well as an increase of these transformations in number. The characteristic times of the elementary chemical transformations of evolutionary precursors remained typically unvaried. However, while the system complication causes an increase in the total number of the individual stages, the total time for accomplishing the entire metabolic cycle is increasing. That led to the conclusion that more complex systems must have lower rates of energy dissipation $\boldsymbol{P}$ at the same point in the cycle, and, therefore, they must be treated as more perfect from the point of the biological evolution.

The preceding conclusion does not interpret explicitly the driving forces that should initiate this evolution of biological systems in the required direction, since the real driving forces of physicochemical transformations must be certain chemical processes with the positive affinity values A_r. At the same time, it has been experimentally proved that all

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[*] Section 3.4 shows that the speculations can be expanded to chemically reactive systems far from thermodynamic equilibrium at least for a rather simple (linear in respect to the intermediates) set of chemical transformations.

of the principal evolutionary jumps in the biosphere when new classes of living arose were linked with the dramatic changes in the nature of the energy carrying molecules inside the organisms and, thus, with restructuring the metabolic cycles. The comparison of the transformation cycles illustrated on pages 18 and 106 indicates a close similarity to the catalytic transformation cycles in nonliving systems and the cycles of food assimilation in living organisms. The processes in catalytic systems will be discussed in more detail in Chapter 4.

2.6. CHAPTER EXERCISES

1. Explain the emergence of the Seebeck, Peltier and Thomson effects in nonuniform conductors using the tools of phenomenological linear thermodynamics. What is the physical sense of parameters that determine the magnitude of these effects?
2. Explain the movement of ions through a membrane under electric potential applied to it using the tools of linear thermodynamics.
3. Derive an equation for the phenomenological description of active transport of a substance through a membrane (Section 2.3.2) for the case of conjugate substance transfer through the membrane and chemical processes far from equilibrium (i.e., at $|A_{rij}| > RT$).
4. What properties are inherent in the Onsager reciprocal coefficients? What can be said about the values of the Onsager reciprocal coefficients allowing for an interrelation of diffusion and stepwise chemical transformations?
5. What can be said about the values of the Onsager reciprocal coefficients allowing for an interrelation of heat conductance and stepwise chemical transformations? What is the difference between the coefficients of "classic" and "modified" Onsager coefficients?
6. Write the phenomenological Horiuti Boreskov Onsager equations for three cocurrent interacting stepwise reactions

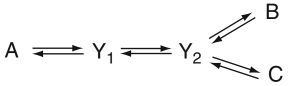
   $A \rightleftarrows B$

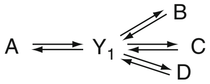
   $A \rightleftarrows C$

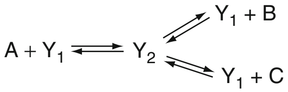
   $A \rightleftarrows D,$

   which proceed through monomolecular transformations of intermediates. Explain the meaning of all of the values in the expression and write the relations between them. What will the equations be, provided that the concentration of component D is stationary?

7. Find reciprocity coefficients Λ_{ij} for the case of stationary rate of cocurrent stepwise reactions described by schemes:







The stationary state is established with respect to intermediates symbolized as Y_i.

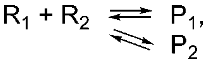
Find the expression for the Horiuti Boreskov Onsager equations to describe the reciprocal influence of the given stepwise reactions in the presence of the chemical components diffusion. The diffusion coefficient is the same for all of the components.

8. Stepwise reaction $R + A_1 \rightleftarrows P_1$ is accompanied by a parallel stepwise reaction $R + A_2 \rightleftarrows P_2$. Find the reciprocity coefficients Λ_{ij} for the case of reciprocal influence of these stepwise reactions occurring in the stationary mode in respect to their intermediates. The reactions follow the mechanism

$R \rightleftarrows X,$
$A_1 + X \rightleftarrows P_1,$
$R \rightleftarrows Y_1 \rightleftarrows Y_2 \rightleftarrows Y_3 \rightleftarrows Y_4 \rightleftarrows Y_5,$
$Y_4 + A_2 \rightleftarrows P_2,$

where X and Y_i are intermediates. What are the expected conditions for the consumption of the by product P_2 instead of its formation?

9. Find coefficients Λ_{ij} for the stationary mode of cocurrent stepwise reactions



achieved by the mechanism with intermediates X_i and Y_j:
$R_1 \rightleftarrows X_1 \rightleftarrows\rightarrow X_2 \rightleftarrows X_3 \rightleftarrows \rightarrow X_4,$
$X_2 + R_2 \rightleftarrows Y_1 \rightleftarrows Y_2 \rightleftarrows Y_3 \rightleftarrows Y_4 \rightleftarrows Y_5,$
$Y_2 \rightleftarrows P_1,$
$Y_2 \rightleftarrows P_2.$

10. Biotechnological synthesis of enzyme AHD_{80} is achieved by a well cloned strain of microorganisms in the course of processes conjugate with the reaction of glucose assimilation, the chemical affinity of the reaction being 42 kJ/mol. Estimate the required rate of glucose assimilation in a closed fermenter at 37 °C if the rate of the entropy decline due to the reaction of the enzyme synthesis is 8 kJ/h·K in the fermenter.

11. In a homogeneous reactive system, cocurrent stepwise reactions

$$A_1 + A_2 \rightleftarrows B_1$$
$$A_1 + A_2 \rightleftarrows B_2$$

proceed in the stationary mode via the mechanism

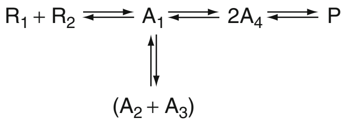
$$A_1 \rightleftarrows Y_1 \rightleftarrows Y_2 \rightleftarrows Y_3 \rightleftarrows Y_4,$$
$$Y_3 + A_2 \rightleftarrows Y_5 \rightleftarrows B_1,$$
$$Y_4 + A_2 \rightleftarrows B_2,$$

where Y_i are intermediates.

Find the expression for the modified Onsager equations to describe reciprocal influence of the given stepwise reactions in the presence of the chemical components diffusion generated by the system nonuniformity. The diffusion coefficient is the same for all of the components.

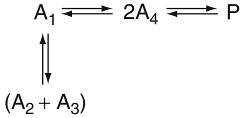
12. Why is the Prigogine theorem on the rate of entropy production significant to the field of chemistry, and what are the conditions of its applicability?

13. Transformation of starting components R_i to product P follows the scheme



Express the relationship between the chemical potentials and concentrations of the reaction intermediates A_i in the stationary mode of the process. Write the expression for the rate of entropy production. Formulate the Prigogine theorem on the rate of entropy production in the stationary state for the case of the given system. To what extent is this theorem applicable for the given system at the temperature 1200 K if the affinity of stepwise reaction $R_1 + R_2 \leftarrow P$ equals 2 kJ/mol? 50 kJ/mol?

14. Transformation of starting component R to product P follows the scheme R + $A_1 \rightleftarrows 2\ A_1$



Here, A_i are intermediates. Show the relationship between the chemical potentials and the concentrations of the reaction intermediates in the stationary mode of the process. Write the expression for the rate of entropy production. Formulate the Prigogine theorem on the rate of entropy production in the stationary state for the case of the given system. To what extent is this theorem applicable for the given system at the temperature 500 K if the affinity of stepwise reaction R → P equals 2 kJ/mol? 50 kJ/mol?

15. Transformation of starting component R to product P follows the scheme

$$R \rightleftarrows A_1 \rightleftarrows A_2 \rightleftarrows A_3 \rightleftarrows P,$$
$$A_1 + 2\,S \rightleftarrows 2A_4 \rightleftarrows A_2 + 2\,S \rightleftarrows A_5.$$

Here, A_i are intermediate compounds, and S is a solvent molecule. Show the relationship between chemical potentials and concentrations of the reaction intermediates S_i in the stationary mode of the process. Write the expression for the rate of entropy production. Formulate the Prigogine theorem on the rate of entropy production in the stationary state for the case of the given system. To what extent is this theorem applicable for the given system at the temperature 300 K if the affinity of stepwise reaction R ← P equals 2 kJ/mol? 30 kJ/mol?

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CHAPTER 3

Thermodynamics of Systems that Are Far from Equilibrium

Contents

3.1. THERMODYNAMIC AND KINETIC APPROACHES

Far from thermodynamic equilibrium we find nonlinear interdependence of thermodynamic fluxes and forces. In this case, the Onsager reciprocal relations are generally not satisfied, and the formalism developed in Chapter 2 is not fully applicable for analysis of the state of open systems. Analysis of systems that are far from thermodynamic equilibrium is the subject of nonlinear nonequilibrium thermodynamics.

The development of a theoretical basis for the analysis of strongly non equilibrium systems was initiated mainly by I. Prigogine and P. Glansdorf (1954). Particular interest in this area of thermodynamics developed after the discovery of the phenomenon of spatial or temporal self organization—that is, the spontaneous arrangement of ordered structures, in strongly nonequilibrium open systems at a strong nonlinearity in relations between thermodynamic parameters.

Some examples of self organization were well known before Prigogine reported his works, including the processes of the formation of cellular structures in a nonuniformly heated horizontal fluid layer and the emergence of turbulence and vortices in quickly flowing fluids. Since the late 1950s, "nonlinear self organizing" processes have also become widely known to chemists. The most spectacular examples of this self organization are "self oscillating" catalytic reactions.

A common feature of all phenomena of the formation of ordered structures in the course of irreversible processes in strongly nonequilibrium open systems is a joined (cooperative) motion or chemical transformation of large groups of molecules. Sometimes, the specificity of these processes is emphasized by using the term *synergism* (from the Greek *synergeia,* meaning "a cooperative action"). The physical nature of synergism is that when it is far from equilibrium, the system loses its stability in the nonlinear region, and minor fluctuations lead to a new mode of the system's existence, implying the matched motion or transformation of many particles at once.

The possibility of self organization in strongly nonequilibrium systems is important to catalysis and biology. Any functioning catalysts, as well as living organisms, are strongly nonequilibrium chemically reactive systems, where steep gradients of concentrations and chemical potentials of reactants (and sometimes steep gradients of temperature, pressure, electric potential, etc.) may occur.

The conclusion about the potential possibility of spontaneous self organization of matter under strongly nonequilibrium conditions was of great ideological importance; it highlighted the way natural laws established a certain order in nonequilibrium systems and then more complex and evolved ordered structures. In the 1960s–1970s, M. Eigen (Nobel Prize in chemistry, 1967) showed that in strongly nonequilibrium complex systems with specific catalytic properties, the process of recording the information in the form of some molecular code may arise. This process enables self reproduction of these catalytic systems. As a result, the nonlinear nonequilibrium thermodynamics became an indispensable element of any physicochemical justifications of all modern hypotheses on the origin of life and evolution.

It is essential to note that nonlinear thermodynamics of nonequilibrium processes critically change the status of the Second Law of thermodynamics. It appeared that in open systems that are far from equilibrium, this law determines not only the inevitability of the destruction of equilibrium ordered structures but also the possibility of the creation of new nonequilibrium but ordered structures. While representing the irreversibility of all real processes, the Second Law of thermodynamics stands for the law of material evolution. Such an understanding of the Second Law of thermodynamics cancels the apparent inconsistency between the asserted necessity of an increase in entropy and, consequently, in disorder in an isolated system and, for example, the theory of biological evolution, which implies the appearance of more and more complex self reproducing systems in nature. At present, the common opinion is that the reasons for the possibility of the progressive or adoptive evolution of living systems are not only that these living systems are open (note that in the case of considering them together with the surrounding medium, they form a closed system with the entropy rising as the living system becomes more complex) but also that under conditions of large energy and material fluxes, matter has a self organizing ability.

As to chemical transformations, the strict satisfaction of the linear Onsager reciprocal relations is ensured only at a small magnitude (in comparison with RT) of the affinity of these transformations (see Section 2.1). For example, this is a very small value RT $\approx$ 2.5 kJ/mol at room temperature. At the same time, the deep (*quantitative*) performance of typical laboratory or industrial reactions (for example, quantitative synthesis of various compounds via direct or catalyzed transformations) is obviously provided under conditions when the thermodynamic equilibriums of the target transformations are shifted toward the desired product formation. Therefore, the initial affinities of the respective stepwise processes appear high enough and often equal to 40–100 kJ/mol, which certainly exceeds RT. Affinities of many biochemical transformations in living organisms equal 4–8 kJ/mol (in other words, they also exceed RT).

Hence, any chemical and biochemical transformations of practical importance occur usually far from thermodynamic equilibrium—that is, far from the region of applicability of the relations of linear nonequilibrium thermodynamics. As a result, thermodynamic analysis of these processes is considerably complicated and usually requires the application of direct kinetic methods for describing the system evolution in terms of differential equations.

Note, however, that the concept of the entropy production rate is of critical importance for analyzing the evolution of systems that are close to equilibrium rather than of dynamic systems, which are described by rigid kinetic schemes with time deterministic behavior (“dynamic machines”).

In fact, evolution courses in the latter systems are strongly deterministic, and thus, the final result of the evolution is unambiguously conditioned by the starting state of the system and preset rules of the development. Therefore, it is impossible in this case to predict the final states of the system by means of comparative statistic ordering of the beginning and ending states. The probability of and routes to accomplishing one or more final states depend on the starting conditions and the specific set of differential equations describing the kinetics of the transformations. This, of course, is provided that these equations represent correctly the kinetic regularities of the involved processes. The evolution trajectories in these nonequilibrium systems as well as the properties of specific (e.g., stationary) points and/or states can only be found by analyzing the initial set of differential equations.

An obvious advantage of direct kinetic approaches to describing the nonequilibrium processes is the existence of thoroughly explored algorithms of deriving and solving the kinetic equations, as well as convenient procedures of analyzing these equations. It is important, however, that the "purely" kinetic approach is identical to describing the dynamic properties of a "chemical machine" with the rigidly preset rules of the system evolution. The necessary conditions to obtain adequate analytic results using the direct kinetic methods are obviously the validity of the a priori concepts on pathways of the chemical transformations under study, as well as sufficiently precise knowledge of the rate constants of individual elementary steps of the transformations.

For example, a specific feature of chemical transformations in a reactive system that is far from thermodynamic equilibrium is the *kinetic* irreversibility of both the whole stepwise process and its individual steps (see Section 1.4.2). At the same time, we saw in Section 1.4.4 that a priori assumptions on kinetic irreversibility of particular steps of the process often appear inconsistent and, as a result, lead to inaccurate results of the kinetic analysis.

It seems reasonable to expand ideas of thermodynamics over strongly nonequilibrium dynamic systems because the thermodynamic approach allows a number of questions on the state or course of the system evolution to be answered, even when knowledge of the real kinetic scheme of the dynamic process under consideration is limited or incomplete. Here, typical problems are those that involve finding probable stationary states. Such problems relate usually to the solution of another principal problem—that is, whether the knowledge of only some or a few of the kinetic peculiarities of the reaction system is sufficient for predicting, based on thermodynamic consideration, such properties of the stationary state as its stability or, vice versa, the potentiality of the spontaneous transition of the system from one stationary state to another in the presence of infinitesimal disturbances or identifying conditions of the existing small stable oscillating regime.

3.2. EVOLUTION IN NONLINEAR THERMODYNAMICS

We saw in Chapter 2 that in the range of validity of linear nonequilibrium thermodynamics (i.e., in the scope of linear Onsager relations), a system approaching its stationary state is characterized by a monotonous decrease in the rate of entropy production (energy dissipation rate) resulting from the existence of internal irreversible processes: $\mathrm{d}\boldsymbol{P} \leq 0$ and $\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{dt}} \leq 0$.

The Onsager reciprocal relations are not satisfied in open strongly non equilibrium systems. As a result, the assumption on minimization of the entropy production rate is not substantiated. Therefore, the universal criterion of the system that is evolution far from equilibrium should be a generalization of the principle of the minimized entropy production rate in specific terms of nonlinear thermodynamics.

Far from the point of thermodynamic equilibrium, the evolution of a system toward its stationary state is governed by the particular behavior of function $\boldsymbol{P}$ in the phase space of thermodynamic forces X_i and fluxes J_j ($i,j = 1, \ldots, m$). In the point describing the system stationary state in this phase space, the final value of function $\boldsymbol{P}$ is independent of the starting conditions and of the way of arriving at this point. This implies equivalence of the transition to the final stationary state of the system and of the movement normally to equipotential surfaces of function $\boldsymbol{P}$:

$$\boldsymbol{P}(X_1, X_2, \ldots, X_m) = \text{const.}$$

In a spatially homogeneous system,

$$\boldsymbol{P} = \sum_{i=1}^{m} J_i X_i.$$

Therefore, the total differential of function $\boldsymbol{P}$ is written as

$$\mathrm{d}\boldsymbol{P} = \sum_{i=1}^{m} J_i \mathrm{d}X_i + \sum_{i=1}^{m} X_i \mathrm{d}J_i \equiv \mathrm{d}_X\boldsymbol{P} + \mathrm{d}_J\boldsymbol{P},$$

where summands $\mathrm{d}_X\boldsymbol{P}$ and $\mathrm{d}_J\boldsymbol{P}$ are accounted for by infinitesimal variations in thermodynamic forces and fluxes, respectively.

Close to the system's equilibrium, the Onsager reciprocal relations are valid:

$$\mathrm{J_i} = \sum_{\mathrm{j}=1}^{\mathrm{m}} \mathrm{L_{ij}X_j} \text{ and } \mathrm{L_{ij}} = \mathrm{L_{ij}}.$$

Therefore,

$$\mathrm{d_X}\boldsymbol{P} = \mathrm{d_J}\boldsymbol{P} = \frac{1}{2}\mathrm{d}\boldsymbol{P};$$

that is, each of summands $\mathrm{d_J}\boldsymbol{P}$ and $\mathrm{d_X}\boldsymbol{P}$ is also the total differential. Correspondingly,

$$\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{dt}} = \sum_{\mathrm{i}=1}^{\mathrm{m}} \mathrm{J_i}\frac{\mathrm{dX_i}}{\mathrm{dt}} + \sum_{\mathrm{i}=1}^{\mathrm{m}} \mathrm{X_i}\frac{\mathrm{dJ_i}}{\mathrm{dt}} \equiv \frac{\mathrm{d_X}\boldsymbol{P}}{\mathrm{dt}} + \frac{\mathrm{d_J}\boldsymbol{P}}{\mathrm{dt}},$$

where

$$\frac{\mathrm{d_X}\boldsymbol{P}}{\mathrm{dt}} = \frac{\mathrm{d_J}\boldsymbol{P}}{\mathrm{dt}} = \frac{1}{2}\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{dt}}.$$

In the general case of a spatially inhomogeneous system, the total rate of energy dissipation is described by the space integral:

$$\boldsymbol{P} = \int_{\mathrm{V}} \mathrm{T}\sigma\mathrm{dv} = \int_{\mathrm{V}} \sum_{\mathrm{i}=1}^{\mathrm{m}} \mathrm{J_iX_i}\mathrm{dv}.$$

Correspondingly,

$$\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{dt}} = \int_{\mathrm{V}} \sum_{\mathrm{i}=1}^{\mathrm{m}} \mathrm{J_i}\frac{\mathrm{dX_i}}{\mathrm{dt}}\mathrm{dv} + \int_{\mathrm{V}} \sum_{\mathrm{i}=1}^{\mathrm{m}} \frac{\mathrm{dJ_i}}{\mathrm{dt}}\mathrm{X_i}\mathrm{dv} \equiv \frac{\mathrm{d_X}\boldsymbol{P}}{\mathrm{dt}} + \frac{\mathrm{d_J}\boldsymbol{P}}{\mathrm{dt}}, \tag{3.1}$$

where the first summand determines the rate of variations in entropy production, which is dependent in turn on the variations in the ther modynamic forces, while the second summand depends on the flux variations.

In the region of the linear Onsager relations validity, both summands in expression (3.1) also are identical, and derivative $\mathrm{d}\boldsymbol{P}/\mathrm{dt}$ represents the principle of the minimized rate of entropy production:

$$\frac{\mathrm{d_X}\boldsymbol{P}}{\mathrm{dt}} = \int_V \sum_{i=1}^{m} J_i \frac{\mathrm{d}X_i}{\mathrm{dt}}\,\mathrm{dv} = \int_V \sum_{i=1}^{m}\sum_{j=1}^{m} L_{ij}X_i \frac{\mathrm{d}X_j}{\mathrm{dt}}\,\mathrm{dv}$$

$$= \int_V \sum_{i=1}^{m}\sum_{j=1}^{m} X_i \frac{\mathrm{d}}{\mathrm{dt}}(L_{ij}X_j)\,\mathrm{dv} = \int_V \sum_{i=1}^{m} \frac{\mathrm{d}J_i}{\mathrm{dt}} X_i\,\mathrm{dv} = \frac{\mathrm{d_J}\boldsymbol{P}}{\mathrm{dt}} = \frac{1}{2}\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{dt}}.$$

Far from equilibrium, the linear Onsager relations are not satisfied, so "partial" differentials $\mathrm{d_X}\boldsymbol{P}$ and $\mathrm{d_J}\boldsymbol{P}$ are no longer total differentials. Hence, variations of parameter $\boldsymbol{P}$ in time depend on the transition route and are not applicable as an unambiguous criterion of the system evolution. However, Glansdorf and Prigogine demonstrated that far from equilibrium, any spontaneous evolution is characterized by a monotone decrease in the partial "force" differential $\mathrm{d_X}\boldsymbol{P}$ expressed as the inequality

$$\mathrm{d_X}\boldsymbol{P} \le 0 \tag{3.2}$$

or

$$\frac{\mathrm{d_X}\boldsymbol{P}}{\mathrm{dt}} \le 0. \tag{3.3}$$

The zero equal expressions mean the accomplishment of the stationary state; after that, there are no changes to $\mathrm{d_X}\boldsymbol{P}$ ($\mathrm{d_X}\boldsymbol{P}_{\mathrm{stationary}} = 0$). This state, as before, corresponds to those zero fluxes that are induced by the internal thermodynamic forces and relate to time variable values of internal thermodynamic parameters.

Let us prove the Glansdorf–Prigogine theorem with an example of an arbitrary spatially homogeneous chemical reactive system. The "internal" parameters for such a system are the concentrations of intermediates of the stepwise chemical transformations. Any spontaneous changes of the system (and, as a result, changes in internal driving forces) relate namely to changes in the intermediate concentrations. Therefore, the "partial force" differential $\mathrm{d_X}\boldsymbol{P}$ may be substituted for by its full analogue related thermodynamic rushes (concentrations) of intermediates A_α (α 1, . . ., k) of the stepwise transformations:

$$
\begin{aligned}
\mathrm{d}_X\boldsymbol{P} = \mathrm{d}_\alpha\boldsymbol{P} &= \sum_{\alpha=1}^{k}\sum_{i=1}^{m}\sum_{j=1}^{m} J_{ij}\frac{\partial X_{ij}}{\partial \tilde{A}_\alpha}\mathrm{d}\tilde{A}_\alpha \\
&= RT\sum_{\alpha=1}^{k}\left\{\sum_{i=1}^{n}\sum_{j=1}^{n}\varepsilon_{ij}\left(\tilde{n}_i-\tilde{n}_j\right)\frac{\partial\left[\ln(\tilde{n}_i)-\ln(\tilde{n}_j)\right]}{\partial\ln(\tilde{A}_\alpha)}\right\}\frac{\mathrm{d}\tilde{A}_\alpha}{\tilde{A}_\alpha} \qquad (3.4)\\
&\equiv RT\sum_{\alpha=1}^{k}\left\{\sum_{i=1}^{n}\sum_{j=1}^{n}\varepsilon_{ij}(\nu_{i\alpha}-\nu_{j\alpha})(\tilde{n}_i-\tilde{n}_j)\right\}\mathrm{d}\ln\tilde{A}_\alpha,
\end{aligned}
$$

where $\tilde{A}_\alpha$ are thermodynamic rushes of these intermediates. When the "partial force" differential achieves its absolute minimum, then

$$\mathrm{d}_\alpha\boldsymbol{P} = 0.$$

If so, expression (3.4) becomes identical to the kinetic condition of stationarity with respect to all intermediates A_α in any reactive systems, including the systems that are far from thermodynamic equilibrium. In fact,

$$
\begin{aligned}
J_\alpha = v_\alpha = \frac{\mathrm{d}[A_\alpha]}{\mathrm{d}t} \equiv \frac{\mathrm{d}c_\alpha}{\mathrm{d}t} &= \sum_{i=1}^{m}\sum_{j=1}^{m}\varepsilon_{ij}(\tilde{n}_i-\tilde{n}_j)\frac{\partial(\ln\tilde{n}_j-\ln\tilde{n}_i)}{\partial\ln\tilde{A}_\alpha}\\
&= \sum_{i}^{m}\sum_{j}^{m}\varepsilon_{ij}(\tilde{n}_i-\tilde{n}_j)(\nu_{ji\alpha}-\nu_{ij\alpha})
\end{aligned}
$$

(see expression for J(α), page 26).

Inequalities (3.2) and (3.3) are generalizations of the principle of the minimal entropy production rate in the course of spontaneous evolution of its system to the stationary state. They are independent of any assumptions on the nature of interrelations of fluxes and forces under the conditions of the local equilibrium. Expression (3.2), due to its very general nature, is referred to as the *Glansdorf-Prigogine universal criterion of evolution.* The criterion implies that in any nonequilibrium system with the fixed boundary conditions, the spontaneous processes lead to a decrease in the rate of changes of the entropy production rate induced by spontaneous variations in thermodynamic forces due to processes inside the system (i.e., due to the changes in "internal" variables). The equals sign in expression (3.2) refers to the stationary state.

Obviously, the Glansdorf Prigogine universal criterion of evolution (3.2) is an indirect consequence of the Second Law of thermodynamics for nonequilibrium processes. The evolution criterion (3.2) determines only that part of the rate increase that relates to the variations in the internal thermodynamic forces due to processes inside the system. Therefore, in the general case, it does not allow the introduction of the function of the state, which, like entropy, Gibbs, or other thermodynamic potentials, would have an extremum at the infinitesimal spontaneous deviations (fluctuations) of internal variables from their stationary values. Nevertheless, in some cases $d_X\boldsymbol{P}$ or other functions that are similar to this "partial" differential acquire the properties of the total differential, and the respective functions of the local potential type with extremums at particular system states may be applied in the strongly nonequilibrium regions as well. A pertinent example for chemically reactive systems is the Lyapunov functions that are considered in Section 3.4.1.

A fundamental corollary of the Glansdorf Prigogine criterion (3.2) is a potentiality of the formation of ordered structures at the occurrence of irreversible processes in the region of nonlinear thermodynamics in open systems that are far from their equilibrium. Prigogine created the term *dissipative structures* to describe the structures that arise when some "controlling" parameters exceed certain critical values and are classified as spatial, temporal, or spatial temporal. Some typical dissipative structures are discussed in Sections 3.5 and 4.6.

3.3. THERMODYNAMIC CRITERIA OF THE STABILITY OF STATIONARY STATES THAT ARE FAR FROM EQUILIBRIUM

A typical problem in thermodynamics of systems that are far from their equilibrium is the analysis of the stability of stationary states of the system. Thermodynamic criteria of the stability of stationary states are found the same way as for systems that are far from and close to thermodynamic equilibrium (see Section 2.4): by analyzing signs of thermodynamic fluxes and forces arising upon infinitesimal deviation of the system from the inspected stationary state. If the system is in the stable stationary state, then any infinitesimal deviation from this state must induce the forces that push it to return to the initial position.

Consider the algorithm of the speculations with the simplest chemical reactions as an example. In the stationary state of some chemical process, let the rate v and the affinity A_r be equal to v and A_r, which are the functions of an internal variable. On an infinitesimal disturbance (fluctuation) of this internal parameter from its value, given by the stationary condition (for example, a fluctuation of the concentration of one of the intermediate reactant), the disturbed values v^* and A_r^* become equal to

$$v^* = v + \delta v, \quad A_r^* = A_r + \delta A_r,$$

where δv and δA are deviations of variables v and A_r from their stationary values caused by the function.

We saw in Section 2.4 that in cases where the stationary state occurs near thermodynamic equilibrium and, therefore, is stable, an increase in the energy dissipation rate caused by the fluctuation of internal parameters is positive and equal at the first approximation to the product $\delta v(= \delta J)$ и $\delta A_r(= \delta X)$:

$$\delta \boldsymbol{P} = \delta J \cdot \delta X = \delta v \delta A_r > 0. \tag{3.5}$$

The positive sign of $\delta \boldsymbol{P}$ means that the system in its disturbed state dissipates energy at a higher rate, and, for this reason, it spontaneously returns from the disturbed to the initial stationary state.

The violation of this criterion means that the initial state is unstable, and, therefore, the system will not come back after escaping it. In other words, if the change in the rate of energy dissipation (entropy production) is a negative value

$$\delta \boldsymbol{P} = \delta v \delta A_r < 0,$$

then the fluctuation in the reaction driving force and the fluctuation induced increment in the reaction rate are opposite in sign. Hence, the fluctuation in the stationary state will "drive" the system farther and farther from this state. This is implied namely as the state instability.

Consider a reversible bimolecular reaction

$$A_1 + A_2 \rightleftarrows A_3 + A_4$$

as an example, where A_α are different independent intermediate reactants of a more complex stepwise process. We shall assume that the system where the reaction proceeds is in some stationary state with respect to the concentrations of these intermediates determined, for example, by the rate of feeding the initial reactants to the system. The rate and affinity of the reaction under consideration are expressed by the equations

$$v = \frac{d\xi}{dt} = \varepsilon(\tilde{A}_1 \cdot \tilde{A}_2 - \tilde{A}_3 \cdot \tilde{A}_4),$$

$$A_r = \mu_1 + \mu_2 - \mu_3 - \mu_4 = RT(\ln\tilde{A}_1 + \ln\tilde{A}_2 - \ln\tilde{A}_3 - \ln\tilde{A}_4).$$

Let us look at how the rate of energy dissipation (entropy production) changes at an infinitesimal variation in the concentration of, for example, substance A_1 around its stationary state when the concentrations of the rest of the reactants are constant. The fluctuation in the concentration of A_1 results in the fluctuation of parameter $\tilde{A}_1$ by quantity $\delta\tilde{A}_1$ to give

$$\delta v = \varepsilon\tilde{A}_2\delta\tilde{A}_1, \quad \delta A_r = RT\frac{\delta\tilde{A}_1}{\tilde{A}_1.}$$

Therefore, for the reaction under consideration, at any $\delta\tilde{A}_1$

$$\delta \boldsymbol{P} = \varepsilon RT\tilde{A}_2\frac{(\delta\tilde{A}_1)^2}{\tilde{A}_1} > 0.$$

The positive sign of $\delta\boldsymbol{P}$ implies the stability of the stationary state of this bimolecular reaction with the mutually independent reaction groups.

Violation of the stability condition (3.5) is allowed in bimolecular auto catalytic reactions, where the reaction groups of the initial reactants and of transformation products are interrelated. Consider the simplest bimolecular reaction of the autocatalytic formation of an intermediate A_1 by the process similar to the considered one:

$$A_1 + A_2 \rightleftarrows 2A_1.$$

Say the reaction is accomplished in a certain state that is stationary with respect to the concentration of this substance A_1. Apparently,

$$v = \frac{d\xi}{dt} = \varepsilon(\tilde{A}_1 \cdot \tilde{A}_2 - \tilde{A}_1^2),$$

$$A_r = \mu_1 + \mu_2 - 2\mu_1 = RT(\ln\tilde{A}_2 - \ln\tilde{A}_1).$$

In this case, upon a fluctuation in the concentration of A_2 at the constant concentration of A_1

$$\delta v = \varepsilon \tilde{A}_1 \delta \tilde{A}_2$$

$$\delta A_r = RT \frac{\delta \tilde{A}_1}{\tilde{A}_2}$$

and

$$\delta \boldsymbol{P} = \varepsilon RT \frac{\tilde{A}_1}{\tilde{A}_2} (\delta \tilde{A}_2)^2 > 0.$$

Thus, the system is stable with respect to the fluctuation of the A_2 concentration.

On the other hand, with a fluctuation in the concentration of A_1 at the constant concentration of A_2

$$\delta v = \varepsilon(\tilde{A}_2 - 2\tilde{A}_1)\delta \tilde{A}_1,$$

$$\delta A_r = -RT \frac{\delta \tilde{A}_1}{\tilde{A}_1}.$$

Hence,

$$\delta \boldsymbol{P} = -\varepsilon RT(\tilde{A}_2 - 2\tilde{A}_1)\frac{(\delta \tilde{A}_1)^2}{\tilde{A}_1}.$$

At $\tilde{A}_2 > 2\tilde{A}_1$, the increment $\delta \boldsymbol{P}$ becomes negative. This means a violation of the condition of stability of the stationary state in the given autocatalytic chemical system when the fluctuation of the concentration of A_1 appears with respect to its stationary value provided that $\tilde{A}_2 > 2\tilde{A}_1$. The violation of the stability happens because the fluctuation in the driving force under the discussed conditions and the increment of the reaction rate caused by the fluctuation appear to be opposite in sign.

It is important to emphasize that the condition $\tilde{A}_2 > 2\tilde{A}_1$ is identical to the condition $\tilde{A}_2 \gg \tilde{A}_1$—that is, to the kinetic irreversibility of the autocatalytic reaction or (what is the same) the remoteness of the process under consideration from the point of its equilibrium.

In the case of an arbitrary elementary chemical reaction ij or a stationary stepwise process "reducible" to an elementary reaction (see Section 1.3), any fluctuation of the concentration of intermediate A_α will lead to the following changes:

$$\delta\tilde{n}_i = \delta\left(\prod_\beta \tilde{A}_\beta^{\nu_{i\beta}}\right) = \nu_{\alpha i}\left(\prod_\beta \tilde{A}_\beta^{\nu_{i\beta}}\right)\delta\tilde{A}_\alpha/\tilde{A}_\alpha = \nu_{\alpha i}\frac{\tilde{n}_i}{\tilde{A}_\alpha}\delta\tilde{A}_\alpha,$$

$$\delta\ln\tilde{n}_i = \delta\nu_{i\alpha}\ln\tilde{A}_\alpha = \nu_{i\alpha}\frac{\delta\tilde{A}_\alpha}{\tilde{A}_\alpha},$$

$$\delta A_{rij} = RT(\delta\ln\tilde{n}_i - \delta\ln\tilde{n}_j) = RT(\nu_{i\alpha} - \nu_{j\alpha})\frac{\delta\tilde{A}_\alpha}{\tilde{A}_\alpha}.$$

Here, as before, for descriptive reasons symbols $\tilde{A}_\alpha$, $\tilde{A}_\beta$ and $\tilde{n}_i$, $\tilde{n}_j$ relate to thermodynamic rushes of particular substances and reaction groups, respectively.

The fluctuation induced changes in the reaction rate are equal to

$$\delta v_{ij} = \varepsilon_{ij}(\delta\tilde{n}_i - \delta\tilde{n}_j) = \varepsilon_{ij}(\nu_{i\alpha}\tilde{n}_i - \nu_{j\alpha}\tilde{n}_j)\frac{\delta\tilde{A}_\alpha}{\tilde{A}_\alpha},$$

and the corresponding changes in the energy dissipation during the reaction are given by the expression

$$\delta\boldsymbol{P} = \varepsilon_{ij}RT(\nu_{i\alpha} - \nu_{j\alpha})(\nu_{i\alpha}\tilde{n}_i - \nu_{j\alpha}\tilde{n}_j)\left(\frac{\delta\tilde{A}_\alpha}{\tilde{A}_\alpha}\right)^2.$$

In the general case, the stationary state of the elementary chemical reaction is seen to always be stable if the "fluctuating" intermediate component enters only one of the reaction groups (i.e., either $\nu_{i\alpha}$ or $\nu_{j\alpha}$ equals zero). The following sections discuss the application of thermodynamic criteria of stability for analyzing the particular simple cases of typical model chemical stepwise processes.

Obviously, the inspection of stability of a system comprising several elementary chemical reactions needs analysis of the sign of the parameter

$$\delta\boldsymbol{P} = \frac{1}{2}\sum_i\sum_j \delta v_{ij}\delta\tilde{A}_{rij},$$

while the possibility of simultaneous and independent fluctuations of the concentrations of all intermediate reactants at once should be taken into consideration. Usually, such an analysis is intricate enough. For this reason, the Lyapunov kinetic criteria of stability (see Section 3.5.2) are used commonly instead of the thermodynamic criteria. Indeed, it is often simpler to use kinetic rather than thermodynamic criteria for inspecting the stability of complex transformation pathways through a large set of independent intermediates.

3.4. REACTIVE SYSTEMS THAT ARE FAR FROM THERMODYNAMIC EQUILIBRIUM

When a reactive system is far from its thermodynamic equilibrium, corollaries of the Prigogine theorem, which were derived for the case of the "linear" nonequilibrium thermodynamics, cannot be applied to analysis directly. Nevertheless, tools of thermodynamics of nonequilibrium processes allow the deduction of some important conclusions on properties of the system, even though strongly nonequilibrium, including in some cases on the stability of stationary states of complex stepwise processes. For several particular cases, theorems similar to the Prigogine theorem can be proved, too.

3.4.1. Stationary State Functionals of Reactive Systems that Are Far from Equilibrium

The Rayleigh Onsager functional (2.6) relates to the energy dissipation rate. It is minimized upon accomplishing the stationary state of the system only in the case when the conditions of linear nonequilibrium thermodynamics are satisfied. For this reason, this functional cannot be applied for analysis of the course of evolution and stability of any reactive system that is far from equilibrium. In some cases, however, the other types of positively defined functionals can be constructed with their monotonically decreasing values during spontaneous evolution of the system to reach, like the Rayleigh Onsager functional, their minimums in the stationary state. These are the so called Lyapunov* functions. The possibility of constructing such a functional corresponds to the stability of the stationary state even though it is far from the equilibrium.

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*A. M. Lyapunov (1857 1918) was an outstanding Russian mathematician who created the theory of stability of dynamic systems.

The simplest case is to find the Lyapunov function for systems with an arbitrary set of the intermediate linear chemical transformations. In proximity to thermodynamic equilibrium, this function becomes identical to the Rayleigh Onsager functional and thus relates to the principle of the minimal rate of entropy production.

To find a typical form of the functional of our interest, consider an arbitrary chemically reactive system close to its thermodynamic equilibrium. The energy dissipation rate in such a system is described by the equation

$$\boldsymbol{P} = \frac{\mathrm{RT}}{2}\sum_{\mathrm{i}}\sum_{\mathrm{j}} \varepsilon_{\mathrm{ij}}(\tilde{\mathrm{n}}_{\mathrm{i}} - \tilde{\mathrm{n}}_{\mathrm{j}})\left[\ln(\tilde{\mathrm{n}}_{\mathrm{i}}) - \ln(\tilde{\mathrm{n}}_{\mathrm{j}})\right].$$

The proximity of the system to thermodynamic equilibrium implies that chemical potentials of all of the reaction groups are close to one another—that is, $\tilde{\mathrm{n}}_{\mathrm{i}} \approx \tilde{\mathrm{n}}_{\mathrm{j}} \approx \tilde{\mathrm{n}}^{*}$. Hence,

$$\ln(\tilde{\mathrm{n}}_{\mathrm{i}}) - \ln(\tilde{\mathrm{n}}_{\mathrm{j}}) \approx \frac{\tilde{\mathrm{n}}_{\mathrm{i}} - \tilde{\mathrm{n}}_{\mathrm{j}}}{\tilde{\mathrm{n}}^{*}}.$$

Therefore, under conditions close to equilibrium

$$\boldsymbol{P} \approx \frac{\mathrm{RT}}{2\tilde{\mathrm{n}}^{*}}\sum_{\mathrm{i}}\sum_{\mathrm{j}} \varepsilon_{\mathrm{ij}}(\tilde{\mathrm{n}}_{\mathrm{i}} - \tilde{\mathrm{n}}_{\mathrm{j}})^{2}.$$

Here, indices i, j run through all of the reaction groups in the system.

So, in accordance with the principle of the minimal rate of entropy production in chemically reactive systems close to thermodynamic equilibrium, the stationary state must be coupled with the minimum of the positively defined functional

$$\Phi\left(\left\{\tilde{\mathrm{A}}_{\alpha}\right\}\right) = \sum_{\mathrm{i}}\sum_{\mathrm{j}} \varepsilon_{\mathrm{ij}}(\tilde{\mathrm{n}}_{\mathrm{i}} - \tilde{\mathrm{n}}_{\mathrm{j}})^{2}. \tag{3.6}$$

Here, $\Phi\left(\left\{\tilde{\mathrm{A}}_{\alpha}\right\}\right)$ symbolizes a function of independent variables that are thermodynamic rushes of all linearly independent components A_{α} in the system. In an open system, obviously, the component rushes may either be controlled by external conditions due to the fixed concentrations of initial reactants and, often, final reaction products (if so, all $\tilde{\mathrm{A}}_{\alpha}$ serve as the "external" variables) or be determined by spontaneous internal processes that occur in the system (such as internal variables $\tilde{A}_\alpha$ of the intermediate components).

It is easy to demonstrate that in the reactive system with an arbitrary set of monomolecular (or reduced to monomolecular) reactions, the stationary state with respect to the intermediate concentration corresponds to the minimum in the value of functional (3.6) even under conditions that are far from equilibrium of the system. In other words, the functional $\Phi\left(\left\{\tilde{A}_\alpha\right\}\right)$ is, by definition, the Lyapunov function of this system. In fact, for a system that consists of monomolecular reactions in its stationary state, in respect to linearly independent (i.e., not related via mass balance with other intermediates) intermediate A_α, the following expression is valid:

$$J_\alpha = \frac{d[A_\alpha]}{dt} \equiv \frac{dc_\alpha}{dt} = -\sum_{j=1}^{n} \varepsilon_{\alpha j}\left(\tilde{A}_\alpha - \tilde{n}_j\right) \equiv -\frac{1}{4}\frac{\partial \Phi}{\partial \tilde{A}_\alpha} = 0. \qquad (3.7)$$

Here, index i and parameter $\tilde{n}_i$ are substituted for by index α and parameter $\tilde{A}_\alpha$, which is always allowed for monomolecular processes. Thus, the functional Φ derivative with respect to thermodynamic rush of an intermediate is proportional to the rate of this intermediate concentration changes everywhere, even far from thermodynamic equilibrium. For this reason, in the state stationary with respect to the intermediate concentration, this derivative turns zero (cf. the case of the Rayleigh Onsager functional).

It is important that expression (3.6) describes dissipation of energy (Joule heat) in an electric analogue of the system under consideration (see, for example, an identical schematic (1.35)). The heat power dissipated by the system is

$$W = \frac{1}{2}\sum_i \sum_j W_{ij} = \frac{1}{2}\sum_i \sum_j \frac{(U_i - U_j)^2}{R_{ij}} = \frac{1}{2}\sum_i \sum_j I_{ij}(U_i - U_j).$$

It is easy to check here that for the stepwise process just considered (see Section 1.3.2)

$$R \rightleftarrows \left\{Y_i \rightleftarrows Y_j\right\} \rightleftarrows P,$$

in its stationary state

$$\Phi\left(\left\{\tilde{A}_\alpha\right\}\right) = \varepsilon_\Sigma(\tilde{R} - \tilde{P})^2,$$

that is fully consistent with the electric analogue because

$$W = \frac{(U_R - U_P)^2}{R_\Sigma}.$$

Here, ε_Σ is the effective value of the truncated rate constant of the stepwise transformation (1.34), while R_Σ is the total effective electric resistance of the electric circuit that is its analogue.

It is important that in the course of spontaneous system evolution toward the stationary state with respect to the concentrations of independent intermediates A_α, the positively defined functional (3.6) decreases monotonically in time. Let us demonstrate this for a thermodynamically ideal system where

$$[A_\alpha] \equiv c_\alpha \equiv \tilde{A}_\alpha \cdot \exp(-\mu_\alpha^o/RT).$$

If so, then

$$\frac{d\Phi}{dt} = \sum_\alpha \frac{\partial\Phi}{\partial\tilde{A}_\alpha} \cdot \frac{d\tilde{A}_\alpha}{dt} = \sum_\alpha \left(\sum_i \frac{\partial\Phi}{\partial\tilde{n}_i} \cdot \frac{\partial\tilde{n}_i}{\partial\tilde{A}_\alpha} \right) \cdot e^{\frac{\mu_\alpha^o}{RT}} \frac{dc_\alpha}{dt}$$

$$= \quad \frac{1}{4}\sum_\alpha \left(\sum_i \frac{\partial\Phi}{\partial\tilde{n}_i} \nu_{i\alpha} \frac{\tilde{n}_i}{\tilde{A}_\alpha} e^{\frac{\mu_\alpha^o}{RT}} \nu_{i\alpha} \frac{\partial\Phi}{\partial\tilde{n}_i} \right) = \quad \frac{1}{4}\sum_\alpha \frac{e^{\frac{\mu_\alpha^o}{RT}}}{\tilde{A}_\alpha} \left\{ \sum_i \tilde{n}_i \left(\nu_{i\alpha} \frac{\partial\Phi}{\partial\tilde{n}_i} \right)^2 \right\} < 0,$$

while

$$\frac{d[A_\alpha]}{dt} \equiv \frac{dc_\alpha}{dt} = -\sum_i \sum_j \nu_{i\alpha}\varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j) = -\frac{1}{4}\sum_i \nu_{i\alpha} \frac{\partial\Phi}{\partial\tilde{n}_i}$$

and

$$\frac{\partial\tilde{n}_i}{\partial\tilde{A}_\alpha} = \nu_{i\alpha} \frac{\tilde{n}_i}{\tilde{A}_\alpha}.$$

This seems to be a reason for satisfying inequality

$$\frac{d\Phi}{dt} < 0$$

in the case of unchanging external conditions and of reciprocal independency of the reaction groups that involve the intermediates. Note that this conclusion remains valid for any reactive system rather than for an arbitrary system with monomolecular reactions only. The spontaneous evolution of the system under consideration is coupled with the monotonous decrease in the value of the positively determined functional Φ. It is also important that in the stationary state of the system, the value of functional Φ must reach its extremum (minimum) not only close to but also arbitrarily far from equilibrium.

Practically, the stationary state of the systems where the mentioned conditions are met can be found using numerical methods by minimizing functionals of type (3.6). In some cases, this way of derivation of the stationary concentrations of intermediates may be preferable compared to the direct solution of differential equations (3.7).

In conditions of a stable thermodynamic equilibrium, thermodynamic rushes of all of the involved interacting reaction groups are equal to one another and, therefore, Φ equals zero for any chemically reactive system.

The rates of chemical reactions are in linear dependence on thermodynamic rushes of the reaction groups of several reactants. When the pertinent kinetic schemes are reducible to a set of the intermediate monomolecular reactions (see Section 1.3.2), the minimization of functional $\Phi\left(\left\{\tilde{A}_\alpha\right\}\right)$ can be used to find the stationary state of these systems that are far from equilibrium. Let us demonstrate this.

Suppose that all thermodynamic rushes $\tilde{n}_i$ and $\tilde{n}_j$ are "independent" of one another in that the thermodynamic rushes $\tilde{A}_\alpha$ of one or several intermediates (i.e., reactants whose concentrations are not fixed by external conditions but determined by the stationary mode) if they are included in rush $\tilde{n}_i$, are absent in all of the rest of rushes $\tilde{n}_j$ $(j \neq i)$. Formally, this is proved by expression

$$\frac{\partial \tilde{n}_j}{\partial \tilde{n}_i} = \delta_{ij}, \tag{3.8}$$

where $\delta_{ij} = 0$ at $i \neq j$ and $\delta_{ij} = 1$ at $i = j$, index i being only used for labeling the intermediate containing reaction groups and index j for any reaction groups in the system. In this case one can easily verify that

$$\frac{\partial \Phi}{\partial \tilde{n}_i} = 4 \sum_j \varepsilon_{ij} (\tilde{n}_i - \tilde{n}_j), \tag{3.9}$$

and, therefore, the following equality is true to the stationary state

$$\frac{\partial \Phi}{\partial \tilde{n}_i} = 0.$$

The right hand side of expression (3.9) is evidently proportional to the rate of changing the concentration of intermediate A_α:

$$\frac{d[A_\alpha]}{dt} \equiv \frac{dc_\alpha}{dt} = -\frac{\nu_{i\alpha}}{4}\frac{\partial \Phi}{\partial \tilde{n}_i} = -\nu_{i\alpha} \cdot \sum_j \varepsilon_{ij}(\tilde{n}_i - \tilde{n}_j). \tag{3.10}$$

The situation when both $\tilde{n}_i$ and $\tilde{n}_j$ can depend on rush $\tilde{A}_\alpha$ of the same intermediate A_α is much more intricate, since expression (3.8) is not valid in this case, and partial derivatives of Φ for rushes $\tilde{n}_i$ of the corresponding reaction groups are nonzero in the stationary state. Nevertheless, an arbitrary reaction system also allows the changes in the intermediate concentrations to be written using functional Φ with the relationship

$$\frac{d[A_\alpha]}{dt} \equiv \frac{dc_\alpha}{dt} = -\frac{1}{4}\sum_i \nu_{i\alpha}\frac{\partial \Phi}{\partial \tilde{n}_i} = -\sum_{i,j} \nu_{i\alpha}\varepsilon_{ij}(\tilde{n}_j - \tilde{n}_i), \tag{3.11}$$

where functional Φ under differentiation is considered as a function of internal variables $\tilde{n}_i$ instead of equation (3.6).

With due regards of the properties of expression (3.6), one can find the Lyapunov functionals for various types of kinetic schemes. This can be done, for example, by consecutive integrating kinetic equations of type (3.10) over rushes of each of the intermediates and combining the results into one expression. Such a procedure is always available for the intermediate linear schemes of the transformations.

We can demonstrate this with an example of stepwise process

$$R_1 + R_2 \rightleftarrows P_1 + P_2,$$

that follows the scheme

$$R_1 \overset{\varepsilon_1}{\rightleftarrows} Y,$$

$$Y + R_2 \overset{\varepsilon_2}{\rightleftarrows} Z,$$

$$Z \overset{\varepsilon_3}{\rightleftarrows} P_1 + W,$$

$$W \overset{\varepsilon_4}{\rightleftarrows} P_2,$$

where Y, Z, and W are the intermediates.

Apparently, for the given scheme

$$v_Y = \frac{d[Y]}{dt} = \varepsilon_1(\tilde{R}_1 - \tilde{Y}) - \varepsilon_2(\tilde{R}_2 \cdot \tilde{Y} - \tilde{Z}),$$

$$v_Z = \frac{d[Z]}{dt} = \varepsilon_2(\tilde{Y} \cdot \tilde{R}_2 - \tilde{Z}) - \varepsilon_3(\tilde{Z} - \tilde{P}_1 \cdot \tilde{W}),$$

$$v_W = \frac{d[W]}{dt} = \varepsilon_3(\tilde{Z} - \tilde{P}_1 \cdot \tilde{W}) - \varepsilon_4(\tilde{W} - \tilde{P}_2).$$

These kinetic equations make it easy to find the functions where derivatives are proportional to the corresponding rates. This is done by integrating rates v_Y, v_Z, and v_W over $\tilde{Y}$, $\tilde{Z}$, and $\tilde{W}$, respectively.

For example, let us find function Φ_Y, for which

$$\frac{\partial \Phi_Y}{\partial \tilde{Y}} \sim v_Y.$$

Its easy to find

$$\Phi_Y = \int \frac{d[Y]}{dt} \cdot d\tilde{Y} = -\frac{1}{2}\left\{\varepsilon_1(\tilde{R}_1 - \tilde{Y})^2 + \frac{\varepsilon_2(\tilde{R}_2 \cdot \tilde{Y} - \tilde{Z})^2}{\tilde{R}_2}\right\} + f(\tilde{Z}, \tilde{W}),$$

where $f(\tilde{Z}, \tilde{W})$ means a function of only variables $\tilde{Z}$ and $\tilde{W}$.

Let us find functions Φ_Z and Φ_W in a similar way. For them,

$$\frac{\partial \Phi_Z}{\partial \tilde{Z}} \sim v_Z \quad \text{and} \quad \frac{\partial \Phi_W}{\partial \tilde{W}} \sim v_W.$$

Thus,

$$\Phi_Z = \int \frac{d[Z]}{dt} \cdot d\tilde{Z} = -\frac{\varepsilon_2}{2}(\tilde{Y} \cdot \tilde{R}_2 - \tilde{Z})^2 - \frac{\varepsilon_3}{2}(\tilde{Z} - \tilde{P}_1 \cdot \tilde{W})^2 + f(\tilde{Y}, \tilde{W}),$$

$$\Phi_W = \int \frac{d[W]}{dt} \cdot d\tilde{W} = -\frac{\varepsilon_3}{2\tilde{P}_1}(\tilde{Z} - \tilde{P}_1 \cdot \tilde{W})^2 - \frac{\varepsilon_4}{2}(\tilde{W} - \tilde{P}_2)^2 + f(\tilde{Y}, \tilde{Z}).$$

Here, symbol f(. . .) stands for some functions of only the parenthesized internal parameters.

Expressions of Φ_Y, Φ_Z, and Φ_W can be combined into one common positively defined expression

$$\begin{aligned}\Phi = {} & \frac{\varepsilon_1}{\tilde{P}_1}(\tilde{R}_1 - \tilde{Y})^2 + \frac{1}{\tilde{R}_2 \cdot \tilde{P}_1}\left\{\varepsilon_2(\tilde{R}_2 \cdot \tilde{Y} - \tilde{Z})^2 + \varepsilon_3(\tilde{Z} - \tilde{P} \cdot \tilde{W})^2\right\} \\ & + \frac{\varepsilon_4}{\tilde{R}_2}(\tilde{W} - \tilde{R}_2)^2,\end{aligned} \tag{3.12}$$

which is namely the Lyapunov function for the transformation scheme under consideration. The Lyapunov functions for more intricate interme diate linear schemes are exemplified in Section 3.4.2 (examples 1 3). Section 4.3.1 presents examples of the Lyapunov functions for the schemes of catalytic transformations.

If the positively defined Lyapunov function exists for a particular kinetic scheme, this scheme has the stationary state that is stable in respect to the concentrations of the intermediates, whether they are close to or far from thermodynamic equilibrium.

Functions with the zero value of the first order derivatives with respect to the intermediate rush at the stationary state can be found for some nonlinear schemes, too. For example, let a stepwise process

$$R \rightleftarrows P$$

follow the scheme with an autocatalytic step with respect to interme diate Y:

$$R + Y \overset{\varepsilon_1}{\rightleftarrows} 2Y,$$

$$Y \overset{\varepsilon_2}{\rightleftarrows} P.$$

Upon the rate v_Y integration with respect to parameter $\tilde{Y}$, we obtain

$$\Phi = 2\varepsilon_1\left(\frac{\tilde{Y}^3}{3} - \frac{\tilde{R} \cdot \tilde{Y}^2}{2}\right) + \varepsilon_2\left(\tilde{Y} - \tilde{P}\right)^2.$$

This function also obeys the relationship

$$v_Y = \frac{d[Y]}{dt} = -\frac{1}{2}\frac{\partial \Phi}{\partial \tilde{Y}},$$

and as a result, $\frac{\partial \Phi}{\partial \tilde{Y}} = 0$ in the Y stationary state in respect to intermediate. However, the derived function Φ is not the Lyapunov function in this case, since the first parenthesized expression can indeed change the sign and be negative at $\tilde{Y} < \frac{2}{3}\tilde{R}$. As a result, function Φ also can change the sign, and, therefore, it is not positively defined over the whole range of changes in the internal parameter $\tilde{Y}$; that is, it does not meet all of the features required of the Lyapunov function. Thus, the possibility of finding function Φ does not ensure the stability of the stationary state with respect to intermediate Y in this case. It is shown in Section 3.3 that the system that involves an autocatalytic step may be unstable when this step is kinetically irreversible. A more intricate scheme with an autocatalytic step is discussed in Section 3.5.1 (Example 6).

To summarize, for many reactive systems that operate far from their equilibrium, there exist some analogues of the Rayleigh Onsager functionals from the linear nonequilibrium thermodynamics. The physical meaning of the positively defined Lyapunov functions like functionals (3.6) and (3.12) can be in many cases interpreted as the energy dissipations in the electric analogues of the reactive system under consideration. The stationary states of the reactive systems, which allow the Lyapunov function to be found, are necessarily stable like the stationary states of dynamic systems functioning in the region of "linear nonequilibrium thermodynamics." When these Lyapunov functions exist, the conclusion on the stability is valid for systems functioning even arbitrarily far from their thermodynamic equilibrium. One should keep in mind, however, that the absence of the Lyapunov function is not a sufficient condition to conclude the necessary instability stationary state of the system (see Example 6 in Section 3.5.1).

The preceding speculations demonstrate that the necessary conditions of instability of the stationary state of a chemically reactive system are (1) the occurrence of at least one elementary chemical reaction that proceeds far from its partial thermodynamics equilibrium (i.e., the kinetically irreversible step), and (2) the occurrence of at least one step with intermediate nonlinear transformations.

3.4.2. The Lyapunov's Functions for Simple Kinetic Schemes

Example 1

Consider a stepwise process

$$A_1 + A_2 \rightarrow P,$$

that goes via consecutive transformation of reactant A_1 into an arbitrary set of intermediates X_i followed by the interaction of initial reactant A_2 (which is the “external” one with respect to the intermediates) with these intermediates X_i to produce an arbitrary set of intermediates Y_j. Suppose also that intermediates X_i and Y_j undergo arbitrary monomolecular disjoint transformations in each set of the intermediates:

$$A_1 \overset{\varepsilon_{A_i,X_i}}{\rightleftarrows} \{X_i\},$$

$$A_2 + X_i \overset{\varepsilon_{A_2,X_i,Y_j}}{\rightleftarrows} \{Y_j\} \overset{\varepsilon_{Y_j,P}}{\rightleftarrows} P.$$

As before, $\{X_i\}$ and $\{Y_j\}$ symbolize arbitrary arrays of monomolecular intermediate transformations X_i ($i = 1, \ldots, k$) and Y_j ($j = 1, \ldots, m$).

It is easy to verify for these systems that

$$\begin{aligned}\Phi = {} & 2\sum_{i\ \ 1}^{k} \varepsilon_{A_1,X_i}(\tilde{A}_1 \quad \tilde{X}_i)^2 + \sum_{i\ \ 1}^{k}\sum_{j\ \ 1}^{k} \varepsilon_{X_i,X_j}(\tilde{X}_i \quad \tilde{X}_j)^2 \\ & + \frac{1}{\tilde{A}_2}\left\{ 2\sum_{i\ \ 1}^{k}\sum_{j\ \ 1}^{m} \varepsilon_{A_2X_i,Y_j}(\tilde{A}_2 \cdot \tilde{X}_i \quad \tilde{X}_j)^2 \right. \\ & \left. + \sum_{i\ \ 1}^{m}\sum_{j\ \ 1}^{m} \varepsilon_{Y_i,Y_j}(\tilde{Y}_i \quad \tilde{Y}_j)^2 + 2\sum_{j\ \ 1}^{m} \varepsilon_{Y_j,P}(\tilde{Y}_j \quad \tilde{P})^2 \right\}.\end{aligned} \tag{3.13}$$

Parameters $\tilde{A}_1$, $\tilde{A}_2$, and $\tilde{P}$ behave here as fixed external parameters.

It is easy to show that equations of type (3.13) can be expanded over systems with similar interactions between “external” reactants and intermediates in the case of an arbitrary number of both initial reactants A_i ($i = 1, \ldots, L$) and of final products. We shall demonstrate that this statement is true.

Example 2

Consider a stepwise reaction

$$A_1 + A_2 + A_3 \rightleftarrows P,$$

that goes via a series of consecutive transformations

$$A_1 \overset{\varepsilon_{A_i,X_i}}{\rightleftarrows} \{X_i\}$$

$$A_2 + X_i \overset{\varepsilon_{A_2X_i,Y_j}}{\rightleftarrows} \{Y_j\}$$

$$A_3 + Y_j \overset{\varepsilon_{A_3Y_j,Z_m}}{\rightleftarrows} \{Z_m\}$$

$$\{Z_m\} \overset{\varepsilon_{Z_m,P}}{\rightleftarrows} P.$$

As before, $\{X_i\}$, $\{Y_j\}$, and $\{Z_m\}$ symbolize arbitrary arrays of monomolecular intermediate transformations X_i ($i = 1, \ldots, k$), Y_j ($j = 1, \ldots, m$), and Z_m ($m = 1, \ldots, n$).

The relevant Lyapunov function for the state stationary in respect to independent "internal" variables $\tilde{X}_i, \tilde{Y}_j$, and $\tilde{Z}_m$ will be written in the form

$$\begin{aligned}\Phi = {} & 2\sum_{i\ 1}^{k}\varepsilon_{A_1,X_i}\left(\tilde{A}_1 \quad \tilde{X}_i\right)^2 + \sum_{i\ 1}^{k}\sum_{j\ 1}^{k}\varepsilon_{X_i,X_j}\left(\tilde{X}_i \quad \tilde{X}_j\right)^2 \\ & + \frac{1}{\tilde{A}_2}\left\{2\sum_{i\ 1}^{k}\sum_{j\ 1}^{l}\varepsilon_{A_2X_i,Y_j}\left(\tilde{A}_2 \cdot \tilde{X}_i \quad \tilde{Y}_j\right)^2 + \sum_{i\ 1}^{l}\sum_{j\ 1}^{l}\varepsilon_{Y_i,Y_j}\left(\tilde{X}_i \quad \tilde{Y}_j\right)^2\right\} \\ & + \frac{1}{\tilde{A}_2 \cdot \tilde{A}_3}\left\{2\sum_{i\ 1}^{l}\sum_{j\ 1}^{n}\varepsilon_{A_3Y_i,\ Z_j}\left(\tilde{A}_3 \cdot \tilde{Y}_i \quad \tilde{Z}_j\right)^2\right. \\ & \left. + \sum_{i\ 1}^{n}\sum_{j\ 1}^{n}\varepsilon_{Z_iZ_j}\left(\tilde{Z}_i \quad \tilde{Z}_j\right)^2 + 2\sum_{i\ 1}^{n}\varepsilon_{Z_i,P}\left(\tilde{Z}_i \quad \tilde{P}\right)^2\right\}.\end{aligned} \tag{3.14}$$

Parameters $\tilde{A}_i$ and $\tilde{P}$ are treated here as fixed "external" variables.

Example 3

Consider a stepwise reaction

$$A_1 + A_2 \rightleftarrows P_1 + P_2$$

that goes via a series of consecutive transformations

$$A_1 \overset{\varepsilon_{A_1,X_i}}{\rightleftarrows} \{X_i\}$$

$$A_2 + X_i \overset{\varepsilon_{A_2,X_i}}{\rightleftarrows} \{Y_i\}$$

$$Y_j \xrightleftharpoons{\varepsilon_{Y_j,P_1 Z_m}} P_1 + \{Z_m\}$$

$$\{Z_m\} \xrightleftharpoons{\varepsilon_{Z_m,P_2}} P_2.$$

Here, $\{X_i\}$, $\{Y_j\}$, and $\{Z_m\}$ means the same as before: $i = 1, \ldots, k$; $j = 1, \ldots, l$; and $m = 1, \ldots, n$.

The relevant Lyapunov function is written in the form

$$\begin{aligned}\Phi = \frac{1}{\tilde{P}_1}\left\{2\sum_{i=1}^{k}\varepsilon_{A_1X_i}\left(\tilde{A}_1 - \tilde{X}_i\right)^2 + \sum_{i=1}^{k}\sum_{j=1}^{k}\varepsilon_{X_i,X_j}\left(\tilde{X}_i - \tilde{X}_j\right)^2\right\}\\ + \frac{1}{\tilde{A}_2\cdot\tilde{P}_1}\left\{2\sum_{i=1}^{k}\sum_{j=1}^{l}\varepsilon_{A_2X_i,Y_j}\left(\tilde{A}_2\cdot\tilde{X}_i - \tilde{Y}_j\right)^2 + 2\sum_{i=1}^{l}\sum_{j=1}^{n}\varepsilon_{Y_i,P_1Z_j}\left(\tilde{Y}_i - \tilde{P}_1\cdot\tilde{Z}_j\right)^2\right\}\\ + \frac{1}{\tilde{A}_2}\left\{\sum_{i=1}^{n}\sum_{j=1}^{n}\varepsilon_{Z_i,Z_j}\left(\tilde{Z}_i - \tilde{Z}_j\right)^2 + 2\sum_{i=1}^{n}\varepsilon_{Z_i,P_2}\left(\tilde{Z}_i - \tilde{P}_2\right)^2\right\}.\end{aligned} \tag{3.15}$$

The Lyapunov functions can be found in the same way for different stepwise reactions with the intermediate linear transformations and an arbitrary number of initial reactants A_i and final products P_j.

It is essential that the functionals are positively defined in all of the considered examples to imply stability of the stationary state in the relevant stepwise processes. Strongly nonlinear kinetic schemes need special procedures for analyzing the stability. While doing so, it is easy to demonstrate that the positive definition of functional is indeed the sufficient condition of stability of the chemical process (in the case, naturally, when these functionals exist).

Example 4

Consider a stepwise reaction

$$2R \rightleftarrows P$$

that goes via a series of consecutive transformations nonlinear with respect to intermediate Y:

$$\begin{aligned} R &\overset{\varepsilon_1}{\rightleftarrows} Y\\ 2Y &\overset{\varepsilon_2}{\rightleftarrows} P.\end{aligned}$$

While

$$v_Y = \frac{d[Y]}{dt} = \varepsilon_1(\tilde{R} - \tilde{Y}) - 2\varepsilon_1(\tilde{Y}^2 - \tilde{P}),$$

then function

$$\Phi = \int \frac{d[Y]}{dt} d\tilde{Y} = \frac{1}{2}\varepsilon_1(\tilde{R} - \tilde{Y})^2 + 2\varepsilon_2\left(\frac{1}{3}\tilde{Y}^3 - \tilde{P}\tilde{Y}\right) + \text{const}$$

also features

$$\frac{\partial \Phi}{\partial \tilde{Y}} \sim v_Y;$$

that is, it has an extremum in the stationary point $v_Y = 0$. However, it is evident that function $\Phi(\tilde{Y})$ is not positively defined and, therefore, cannot be considered as the Lyapunov function. Nevertheless, as shown in Section 3.5.1, the Y-stationary state is stable in the kinetic scheme under consideration at any values of external parameters $\tilde{R}$ and $\tilde{P}$. With this example, we have shown that the absence of the Lyapunov function is not the necessary condition of the stable stationary state of a nonlinear system.

Example 5

Consider a stepwise reaction

$$R \rightleftarrows P$$

that goes via a series of consecutive transformations including nonlinear autocatalytic steps:

$$R \overset{\varepsilon_{R,Y_i}}{\rightleftarrows} \{Y_i\}$$

$$R + Y_i \overset{\varepsilon_{RY_i,2Y_i}}{\rightleftarrows} 2Y_i$$

$$\{Y_i\} \overset{\varepsilon_{Y_i,P}}{\rightleftarrows} P.$$

As before, $\{Y_i\}$ symbolizes an arbitrary array of monomolecular transformations of intermediate Y_i ($i = 1, \ldots, k$).

In the given kinetic scheme, the function with the derivative turning zero in the stationary state in respect to "internal" variables $\tilde{Y}_i$ is given by

$$\begin{aligned}\Phi = {} & 2\sum_{i=1}^{k}\varepsilon_{R,Y_i}\left(\tilde{R} - \tilde{Y}_i\right)^2 + \sum_{i=1}^{k}\sum_{j=1}^{k}\varepsilon_{Y_i,Y_j}\left(\tilde{Y}_i - \tilde{Y}_j\right)^2 \\ & + 2\sum_{i=1}^{k}\varepsilon_{Y_i,P}\left(\tilde{Y}_i - \tilde{P}\right)^2 + 4\sum_{i=1}^{k}\varepsilon_{RY_i,2Y_i}\left(\frac{\tilde{Y}_i^3}{3} - \frac{\tilde{R}\cdot\tilde{Y}_i^2}{2}\right).\end{aligned} \tag{3.16}$$

In the stationary state in respect to intermediates Y_i, we have

$$\begin{aligned}J_{Y_i} = \frac{d[Y_i]}{dt} = -\frac{1}{4}\frac{\partial\Phi}{\partial\tilde{Y}_i} = -\varepsilon_{R,Y_i}\left(\tilde{Y}_i - \tilde{R}\right) - \sum_{j=1}^{k}\varepsilon_{Y_i,Y_j}\left(\tilde{Y}_i - \tilde{Y}_j\right) \\ - \varepsilon_{Y_i,P}\left(\tilde{Y}_i - \tilde{P}\right) + \varepsilon_{RY_i,2Y_i}\left(\tilde{R}\cdot\tilde{Y}_i - \tilde{Y}_i^2\right) = 0.\end{aligned}$$

However, equation (3.16) is not always positive. This implies a not necessarily stable stationary state of the stepwise reaction under consideration. Indeed, it was shown previously that autocatalytic reactions at certain ratios of internal parameters the reactant concentrations (thermodynamic rushes) are a spectacular example of processes with the unstable stationary state.

3.5. THERMODYNAMICS AND STABILITY OF NONLINEAR KINETIC SYSTEMS

As we saw in Section 3.4.1, the stable stationary state always exists in any chemical reactive system where the intermediate components enter only the independent reaction groups. This state relates to the minimum of the Lyapunov function Φ described by equations of type (3.6). If the condition of the reaction group independence is not satisfied, there is a "necessary condition" of the emergence of instability of the stationary state: The same intermediate (whose concentration is not fixed by external conditions) enters several reaction groups at once and, thus, bears two or more different functions in the stepwise scheme. The thermodynamic tools are hardly applicable for analyzing such complex kinetic schemes. In this case the stability of the stationary state, if any, at given external conditions can be analyzed using the kinetic criterion of stability that is based on the inspection of the evolution of infinitesimal deviations of internal variables from their stationary values (see following).

In accordance with the said criterion, the stationary state will only be stable at the negative definiteness of all intrinsic values of matrix $M_{\alpha\beta}$ of eigenvalue equation:

$$M_{\alpha\beta} = \frac{\partial(d[A_\alpha]/dt)}{\partial[A_\beta]},$$

where A_α and A_β relate to intermediates only ($\alpha,\beta = 1,\ldots, m$).

The matrix eigenvalues are analyzed for the stationary state in respect to the concentrations of all independent intermediates. In the thermodynamic representation of kinetic equations, independent variables that describe the system evolution in time are not the concentrations but thermodynamic rushes $\tilde{A}_\alpha$ of the intermediates. Hence, the analysis of the stability criterion in terms of thermodynamic variables needs an inspection of eigenvalues of matrix $\tilde{M}'_{\alpha\beta} = \frac{\partial(d\tilde{A}_\alpha/dt)}{\partial\tilde{A}_\beta}$. However, the specific form of the representation of kinetic equations for the rate of changes in the intermediate concentrations makes it more practicable to inspect the identical condition for matrix $\tilde{M}_{\alpha\beta} = \frac{\partial(d[A_\alpha]/dt)}{\partial\tilde{A}_\beta}$. The matrix entries $\tilde{M}'_{\alpha\beta}$ and $\tilde{M}_{\alpha\beta}$ are in a simple relationship

$$\tilde{M}'_{\alpha\beta} = \tilde{M}_{\alpha\beta} \cdot \gamma_\alpha \cdot \exp\left(\frac{\mu^o_\alpha}{RT}\right)$$

(see Section 1.3.1 on the interrelation of parameters $[A_\alpha]$, $\tilde{A}_\alpha$, and μ_α). The negative definiteness of eigenvalues of one matrix corresponds to the negative definiteness of eigenvalues of another matrix. In an explicit form, the eigenvalues of matrices $\tilde{m}_{\alpha\beta}$ are written as

$$\tilde{M}_{\alpha\beta} = \frac{\partial(d[A_\alpha]/dt)}{\partial\tilde{A}_\beta} = \frac{1}{\tilde{A}_\beta}\sum_i\sum_j \varepsilon_{ij}\nu_{i\beta}(\nu_{j\alpha} - \nu_{i\alpha})\tilde{n}_i.$$

From analyzing this expression, the symmetry of coefficients $\tilde{M}_{\alpha\beta}$ in respect to the permutation of indices α and β occurs necessarily only in the case of independent rushes $\tilde{n}_i$ of "internal" parameters (concentrations of intermediates involved in the reaction groups). It was shown previously that these are namely the systems allowing the construction of the Lyapunov function to describe their evolution through the entire region of applicability of the thermodynamic approach. It is usually impossible to find the Lyapunov functional for the intermediate nonlinear schemes.

The stability and other thermodynamic properties of nonlinear kinetic systems far from thermodynamic equilibrium are commonly accepted to analyze by inspecting the system behavior as functions of some external "controlling" parameters. Chemical affinity of stepwise processes or those related to it values that characterize the remoteness from the equilibrium point of the system are often chosen as such a "controlling" parameter of general nature.

We just saw that in the systems that fall into the range of linear thermodynamics, the stable stationary state is characterized by a special point where the evolution of the system, if slightly deviated from this point, will necessarily turn it back again to the same point. This conclusion becomes invalid as the system escapes the neighboring of the equilibrium state.

Numerous examples exist of chemical processes that have the unstable stationary state. Some of these systems can form temporal and spacial temporal dissipative structures that are far from equilibrium. Almost all of the known examples are catalytic systems, the instability of the stationary state being caused by unstable stationary concentrations of catalytic intermediates.

3.5.1. One-Parameter Systems

When internal transformations in a system result from the evolution of an internal only parameter (for example, the concentration of a sole existing intermediate), both stable and unstable stationary states are allowed. However, time periodical processes (oscillations) are unavailable in the system. Let us demonstrate this.

Let the system under consideration be in the stationary state with respect to an internal parameter Y with its stationary value Y. If a minor fluctuation of Y happens to make $Y = Y + y$, then the evolution of the infinitesimal y in time will be described by some kinetic equation

$$\frac{dy}{dt} = Q(Y, \alpha) = Q(Y + y, \alpha),$$

where α is the controlling parameter. Due to the small, by definition, quantity of the fluctuation near stationary value Y, this expression may usually be reduced to the form of a y linear differential equation:

$$\frac{dy}{dt} = q(Y, \alpha) \cdot y. \qquad (3.17)$$

Here, $q(Y, \alpha) \equiv q$ is an effective coefficient independent of time but dependent on Y, which is determined by controlling parameter α.

The solution of the reduced equation is

$$y = y_0 \cdot \exp(qt),$$

where y_o is the starting point of the fluctuation. If $q < 0$ at $t \to \infty$, then $y \to 0$ always—that is, the fluctuation vanishes in time and the system comes back to the initial stationary state. Equation (3.17) does not allow solutions for the time oscillating y quantity. Nevertheless, of the stationary states, one intermediate systems may have very specific peculiarities that allow not only stability or instability but also, for example, a multiplicity of these states.

It is easy to demonstrate that the condition $q < 0$ is always met for the kinetic schemes that are linear with respect to the sole intermediate. The case of $q > 0$ is only possible in the intermediate nonlinear schemes, but the nonlinearity is an insufficient condition. We shall demonstrate this by analyzing simple nonlinear schemes.

Example 6 Systems that are nonlinear with respect to intermediates but stable over the entire range of the external parameter variations

Consider the stability of a stepwise reaction

$$2\,R \to P \tag{3.18}$$

that follows a simple scheme

$$\begin{gathered} R \overset{\varepsilon_1}{\rightleftarrows} Y \\ Y + Y \overset{\varepsilon_2}{\rightleftarrows} P, \end{gathered} \tag{3.19}$$

which is the intermediate Y nonlinear one (see also (1.41) (1.42)). Both thermodynamic and kinetic considerations will be used for the analysis.

Thermodynamic Analysis of the System Stability: The rate of energy dissipation in this system is written as

$$\begin{aligned} \boldsymbol{P} &= v_1 \cdot A_{r1} + v_2 \cdot A_{r2} \\ &= RT\left\{\varepsilon_1 (\tilde{R} \quad \tilde{Y})(\ln \tilde{R} \quad \ln \tilde{Y}) + \varepsilon_2 \left(\tilde{Y}^2 \quad \tilde{P}\right)(2 \ln \tilde{Y} \quad \ln \tilde{P})\right\}. \end{aligned}$$

Find a change in the energy dissipation rate on a fluctuation of the stationary value $\tilde{Y} = \tilde{Y}$ by quantity y at the preserved first order of infinitesimals of y changes:

$$\begin{aligned}\delta \boldsymbol{P} &= \delta v_1 \cdot \delta A_{r1} + \delta v_2 \cdot \delta A_{r2} \\ &= RT\left\{ \varepsilon_1 \cdot y \cdot \frac{y}{\tilde{Y}} + \varepsilon_2 \cdot 2\tilde{Y} \cdot y \cdot 2\frac{y}{\tilde{Y}} \right\} = RT\left\{ \frac{\varepsilon_1}{\tilde{Y}} + 4\varepsilon_2 \right\}(y)^2. \end{aligned} \tag{3.20}$$

Obviously, the sign of $\delta \boldsymbol{P}$ is independent of the sign of y and always positive. Hence, the stationary state of the nonlinear system under consideration is always stable.
Kinetic Analysis of the System Stability: The stationary value $\tilde{Y} \equiv \tilde{Y}$ is found from equation

$$\frac{d[Y]}{dt} = \varepsilon_1\left(\tilde{R} \quad \tilde{Y}\right) \quad 2\varepsilon_2\left(\tilde{Y}^2 \quad \tilde{P}\right).$$

Consider the evolution of a minor fluctuation y of the stationary value $\tilde{Y}$, when

$$\tilde{Y} \equiv \tilde{Y} + y$$

and

$$[Y] = [\tilde{Y}] + \lambda_Y \cdot y,$$

where [Y] is the stationary concentration of intermediate Y and $\lambda_Y = \exp(\quad \mu_Y^o/RT)$ is a positive coefficient independent of y.

While retaining the terms dependent linearly on infinitesimal y, we have

$$\frac{d[Y]}{dt} = \lambda_y \frac{dy}{dt} = \quad \varepsilon_1\left(\tilde{R} \quad \tilde{Y} \quad y\right) \quad 2\varepsilon_2\left[\left(\tilde{Y} \quad y\right)^2 \quad \tilde{P}\right] \approx \quad \left(\varepsilon_1 + 4\varepsilon_2\tilde{Y}\right)y.$$

Thus, the evolution of y in time is described by time-exponential function

$$y = y_0 \cdot \exp\left\{ \quad \left(\varepsilon_1 + 4\varepsilon_2\tilde{Y}\right) \cdot \lambda_Y t\right\},$$

where y_o is the starting quantity of fluctuation y. One can see that there is always negative exponential power that is, the exponential decay of y in time. Hence, any stationary state of this scheme always is stable.

Example 7 The simplest system with two stationary states: bifurcation and instability of one of its stationary states

Consider a kinetically irreversible stepwise process

$$\mathrm{R} \longrightarrow \mathrm{P}$$

that follows a nonlinear scheme with autocatalytic transformation of a sole intermediate-autocatalyst Y:

$$\begin{gathered} \mathrm{R} + \mathrm{Y} \overset{\varepsilon_1}{\rightleftarrows} 2\,\mathrm{Y} \\ \mathrm{Y} \overset{\varepsilon_2}{\longrightarrow} \mathrm{P}. \end{gathered} \tag{3.21}$$

As earlier, R and P are the starting reactant and final product, respectively, of the stepwise transformation (see also Section 3.4.1). External parameter $\tilde{R}$ can be taken here as the controlling parameter. The kinetic irreversibility of the second step means that this step is a priori far from thermodynamic equilibrium. This is the necessary condition of the instability of stationary states. Let us check this.

The evolution of the intermediate concentration is correctly given by

$$\frac{d[Y]}{dt} = \varepsilon_1 (\tilde{R} \cdot \tilde{Y} \quad \tilde{Y}^2) \quad \varepsilon_2 \tilde{Y}.$$

Hence, its stationary state implies two solutions:

$$\tilde{Y}_1 = 0$$

and

$$\tilde{Y}_2 = \tilde{R} \quad \frac{\varepsilon_2}{\varepsilon_1}.$$

Only the solutions with $\tilde{Y} \geq 0$ have physical meaning.

Hence, at $\tilde{R} < \tilde{R}_{cr} \equiv \varepsilon_2/\varepsilon_1$, only one real solution $\tilde{Y} = 0$ exists. However, at $\tilde{R} > \tilde{R}_{cr} \equiv \varepsilon_2/\varepsilon_1$, there are two real solutions: $\tilde{Y}_1 = 0$ and $\tilde{Y}_2 = \tilde{R} \quad \frac{\varepsilon_2}{\varepsilon_1} > 0$ (Figure 3.1). The point $\tilde{R} = \frac{\varepsilon_2}{\varepsilon_1} \equiv \tilde{R}_{cr}$ can be treated as a certain critical value of the controlling parameter. Here, it is the so-called bifurcation point of the stationary solutions.

We shall demonstrate that solution $\tilde{Y}_1 = 0$ is unstable when two solutions exist (i.e., at $\tilde{R} > \tilde{R}_{kp}$). This is done, as in the preceding example, by considering both thermodynamic and kinetic criteria of stability.

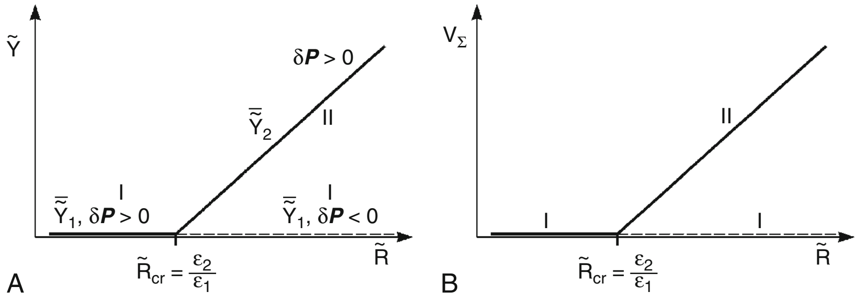

Figure 3.1 Dependencies of the stationary thermodynamic rushes of intermediate Y (A) and the relevant rate of the stepwise process (B) on the value of the controlling parameter for autocatalytic scheme (3.21)—thermodynamic rush of initial reactant $\tilde{R}$. Point $\tilde{R}_{cr} = \epsilon_2/\epsilon_1$ is the point of bifurcation of stationary states. Symbols I and II indicate different branches of the stationary states.

Thermodynamic Analysis of the System Stability: The rate of energy dissipation in the system under consideration is given by the equation

$$\boldsymbol{P} = \sum_i v_i A_i = RT\left\{\varepsilon_1(\tilde{R}\cdot\tilde{Y} \quad \tilde{Y}^2)(\ln\tilde{R} \quad \ln\tilde{Y}) + \varepsilon_2\tilde{Y}(\ln\tilde{Y} \quad \ln\tilde{P})\right\}.$$

Find a change in the energy dissipation rate upon fluctuation of $\tilde{Y}$ from its stationary value $\tilde{Y}_i$ by infinitesimal quantity y:

$$\delta\boldsymbol{P} = \sum_i \delta v_i \cdot \delta A_{ri} = \delta v_1 \cdot \delta A_{r1} + \delta v_2 \cdot \delta A_{r2},$$

$$\tilde{Y} = \tilde{Y}_i + y,$$

$$v_1 = \varepsilon_1\left(\tilde{R}\cdot\tilde{Y} \quad \tilde{Y}^2\right),$$

$$\delta v_1 = \varepsilon_1\left(\tilde{R}\cdot y \quad 2\tilde{Y}\cdot y\right),$$

$$A_{r1} = RT(\ln\tilde{R} \quad \ln\tilde{Y}_i),$$

$$\delta A_{r1} = \quad RT\left[\ln\left(\tilde{Y}_i + y\right) \quad \ln\tilde{Y}_i\right] = \quad RT\ln\left(1 + \frac{y}{\tilde{Y}_i}\right) \approx \quad RT\frac{y}{\tilde{Y}_i}.$$

Similarly,

$$v_2 = \varepsilon_2(\tilde{Y} \quad \tilde{P}),$$

$$\delta v_2 = \varepsilon_2 y,$$

$$A_{r1} = RT\left(\ln\tilde{Y} \quad \ln\tilde{P}\right),$$

$$\delta A_{r2} = RT\frac{y}{\tilde{Y}_i}.$$

Therefore,

$$\begin{aligned}\delta\boldsymbol{P} &= \varepsilon_1(\tilde{R}y \quad 2\tilde{Y}_i y)\cdot\left(\quad\frac{y}{\tilde{Y}_i}\right) + \varepsilon_2 y\cdot\left(\frac{y}{\tilde{Y}_i}\right)\\ &= \left\{\quad\varepsilon_1\left(\tilde{R} \quad 2\tilde{Y}_i\right) + \varepsilon_2\right\}\frac{y^2}{\tilde{Y}_i}.\end{aligned} \tag{3.22}$$

1. For stationary solution $\tilde{Y}_1 = 0$ (strictly speaking, at $\tilde{Y}_1 \rightarrow 0$)

$$\delta\boldsymbol{P} = (\quad\varepsilon_1\tilde{R} + \varepsilon_2)\frac{y^2}{\tilde{Y}_i^2}.$$

Thus, $\delta\boldsymbol{P} > 0$ at $\tilde{R} < \varepsilon_2/\varepsilon_1 \equiv \tilde{R}_{cr}$ and the stationary solution $\tilde{Y}_1 = 0$ is stable, while $\delta\boldsymbol{P} < 0$ at $\tilde{R} > \tilde{R}_{cr}$ that is, the stationary solution $\tilde{Y}_1$ is unstable.

2. For stationary solution $\tilde{Y}_2 = \tilde{R} \quad \dfrac{\varepsilon_2}{\varepsilon_1}$

$$\delta\boldsymbol{P} = \left\{\quad\varepsilon_1(\quad\tilde{R} + \frac{\varepsilon_2}{\varepsilon_1}) + \varepsilon_2\right\}\frac{y^2}{\tilde{Y}^2} = \left(\varepsilon_1\tilde{R} \quad \varepsilon_2\right)\frac{y^2}{\tilde{Y}^2}.$$

Thus, within the range of existence of $\tilde{Y}_2$ that is, at $\tilde{R} > \varepsilon_2/\varepsilon_1 \equiv \tilde{R}_{cr}$ the state is stable. It is important that the probable instability of the stationary state $\tilde{Y}_1 = 0$ is a consequence of the assumption on kinetic irreversibility of reaction $Y \rightleftarrows P$ and relates with the position of controlling parameter $\tilde{R}$ around bifurcation point $\tilde{R}_{cr}$ (see Example 8).

Kinetic Analysis of the System Stability: Pure kinetic inspection of the occurrence of stability implies kinetic consideration of the relaxation of fluctuation y as related to stationary state $\tilde{Y}_i$:

$$\frac{d[Y]}{dt} = \lambda_Y\cdot\frac{dy}{dt} = \varepsilon_1\left(\tilde{R}y \quad 2\tilde{Y}_i y\right) \quad \varepsilon_2 y = \left\{\varepsilon_1\left(\tilde{R} \quad 2\tilde{Y}_i\right) \quad \varepsilon_2\right\}y,$$

where $\lambda_Y = \exp\left(\quad\mu_Y^o/RT\right)$.

The solution of this equation is exponent

$$y = y_o\exp\left\{\left[\varepsilon_1\left(\tilde{R} \quad 2\tilde{Y}_i\right) \quad \varepsilon_2\right]\frac{t}{\lambda_Y}\right\}.$$

Apparently, instability arises at

$$\varepsilon_1\left(\tilde{R}\quad 2\tilde{Y}_i\right)\quad \varepsilon_2 > 0,$$

which is fully consistent with the result of the preceding thermodynamic analysis.

The speculations about bifurcation in autocatalytic systems lead us to conclude that the adaptive natural selection of biological systems analogue may have a primitive in analogue, and even in abiogenic autocatalytic, systems where chemical “mutations” of the autocatalyst may occur [2].

Let several “populations” of autocatalysts Y_α ($\alpha = 1, 2, \ldots$) that are generated by the same “food” R function simultaneously in the system. A decrease in $\tilde{R}$ to the value $\tilde{R}^*$ results in the complete “extinction” of those autocatalysts for which $\tilde{R}_{cr\alpha} = \varepsilon_{2\alpha}/\varepsilon_{1\alpha} < \tilde{R}^*$. If the amount (concentration) of “food” then increases (i.e., if $\tilde{R}$ rises), the populations of the extinct autocatalysts do not restore because of the disappearance of the respective autocatalyst inoculants. However, if the autocatalysts are capable of mutating toward a decrease in critical parameter $\tilde{R}_{cr\ \alpha}$, the inoculants of the autocatalysts with minimal $\tilde{R}_{cr\ \alpha}$ can persist even at the reduced concentration of food. For this reason, the population of these selected autocatalysts will start growing with the increase in $\tilde{R}$, if any. In other words, an analogue of natural selection adapts the autocatalyst system to the conditions of “starvation” in “food” R.

In the considered example, the last step in the kinetic scheme (3.21) was a priori assumed to be kinetically irreversible. Interestingly, the multiplicity of stationary states in this scheme can arise namely at the kinetic irreversibility of the steps. Let us demonstrate this.

Example 8 The simplest autocatalytic reaction with the reversibility of all steps

Consider a stepwise reaction

$$R \rightleftarrows P$$

that follows an autocatalytic scheme with a sole intermediate-autocatalyst Y:

$$\begin{gathered} R + Y \overset{\varepsilon_1}{\rightleftarrows} 2\,Y \\ Y \overset{\varepsilon_1}{\rightleftarrows} P. \end{gathered} \tag{3.23}$$

Unlike Example 7, the kinetic irreversibility of the second step is not a priori assumed.

Let us apply the thermodynamic method for finding the conditions of arising instability of the stationary state. The kinetics of changes in the concentration of intermediate X are described by the equation

$$\frac{d[Y]}{dt} = \varepsilon_1(\tilde{R}\cdot\tilde{Y} \quad \tilde{Y}^2) \quad \varepsilon_2(\tilde{Y} \quad \tilde{P}).$$

The stationary value $\tilde{Y}$ is determined by solving the quadratic equation

$$\tilde{Y}^2 \quad 2\alpha\tilde{Y} \quad \beta = 0,$$

where $\alpha = \frac{1}{2}\left(\tilde{R} \quad \frac{\varepsilon_2}{\varepsilon_1}\right)$, and $\beta = \frac{\varepsilon_2}{\varepsilon_1}\tilde{P}$.
This equation has two stationary solutions:

$$\tilde{Y}_{1,2} = \alpha \pm \sqrt{\alpha^2 + \beta}.$$

But only one positive solution is physically meaningful:

$$\tilde{Y}_1 = \alpha + \sqrt{\alpha^2 + \beta};$$

in other words, in the case under consideration, no multiplicity of stationary states exist.

The increment of the dissipation energy upon emergence of a small fluctuation in the stationary concentration thermodynamic (rush) of this intermediate is described by equation

$$\delta\boldsymbol{P} = \delta v_1 \cdot \delta A_{r1} + \delta v_2 \cdot \delta A_{r2}.$$

An instability arises at $\delta\boldsymbol{P} < 0$ that is, at $\varepsilon_1\left(\tilde{R} \quad 2\tilde{Y}_i\right) + \varepsilon_2 > 0$.

With the determined stationary value $\tilde{Y}$, we have

$$\begin{aligned}\varepsilon_1\left(\tilde{R} \quad 2\tilde{Y}\right) + \varepsilon_2 &= \varepsilon_1\left(\tilde{R} \quad 2\alpha \quad 2\sqrt{\alpha^2 + \beta}\right) + \varepsilon_2 \\ &= \varepsilon_1(\tilde{R} \quad \tilde{R} + \frac{\varepsilon_2}{\varepsilon_1} \quad 2\sqrt{\alpha^2 + \beta}) + \varepsilon_2 = 2\varepsilon_1\left(\frac{\varepsilon_2}{\varepsilon_1} \quad \sqrt{\alpha^2 + \beta}\right).\end{aligned}$$

Hence, the instability of the stationary state occurs at

$$\frac{\varepsilon_2}{\varepsilon_1} \quad \sqrt{\alpha^2 + \beta} > 0,$$

or, that is the same,

$$\left(\frac{\varepsilon_2}{\varepsilon_1}\right)^2 > \frac{1}{4}\left(\tilde{R} \quad \frac{\varepsilon_2}{\varepsilon_1}\right)^2 + \frac{\varepsilon_2}{\varepsilon_1}\tilde{P}.$$

When $\tilde{P} \rightarrow 0$, this is identical to the solution given in Example 7 for the process where step 2 of the transformation scheme is a priori considered as kinetically irreversible ($\tilde{P} \rightarrow 0$). Examples 6 and 7 demonstrate that an open system that is nonlinear in respect to intermediates may have multiplicity. The next example considers a system with more than two stationary states.

Example 9 The simplest “trigger” system with three stationary states

Consider a kinetically irreversible stepwise process

$$R \rightarrow P$$

that follows an autocatalytic “Schloegl's scheme”:

$$\begin{gathered} R + 2Y \overset{\varepsilon_1}{\rightleftarrows} 3\,Y, \\ Y \xrightarrow{\varepsilon_2} P, \end{gathered} \tag{3.24}$$

where Y is the reaction intermediate.

Changes in the concentration of intermediate Y follow the equation

$$\frac{d[Y]}{dt} = \varepsilon_1(\tilde{R} \cdot \tilde{Y}^2 - \tilde{Y}^3) - \varepsilon_2\tilde{Y} \equiv (\varepsilon_1\tilde{R} \cdot \tilde{Y} - \varepsilon_1\tilde{Y}^2 - \varepsilon_2)\tilde{Y}. \tag{3.25}$$

The equation has three stationary solutions:

$$\begin{gathered} \tilde{Y}_1 = 0, \\ \tilde{Y}_{3,2} = \frac{1}{2}\tilde{R} \pm \sqrt{\frac{1}{4}\tilde{R}^2 - \frac{\varepsilon_2}{\varepsilon_1}}. \end{gathered}$$

While the physical meaning is only inherent in the real solutions with $\tilde{Y} \geq 0$, without virtual parts at $\tilde{R} < \tilde{R}_{cr} \equiv 2\sqrt{\frac{\varepsilon_2}{\varepsilon_1}}$, the system has only one stationary state with $\tilde{Y}_1 = 0$. However, at $\tilde{R} > \tilde{R}_{cr} \equiv 2\sqrt{\frac{\varepsilon_2}{\varepsilon_1}}$, there are three real solutions:

$$\tilde{Y}_1 = 0,$$

$$\tilde{Y}_2 = \frac{1}{2}\tilde{R} - \sqrt{\frac{1}{4}\tilde{R}^2 - \frac{\varepsilon_2}{\varepsilon_1}},$$

$$\tilde{Y}_3 = \frac{1}{2}\tilde{R} + \sqrt{\frac{1}{4}\tilde{R}^2 - \frac{\varepsilon_2}{\varepsilon_1}},$$

(Figure 3.2) and for this reason the system under consideration has three stationary states. Like Example 7, point $\tilde{R}_{cr} = 2\sqrt{\frac{\varepsilon_2}{\varepsilon_1}}$ is also the bifurcation point of the stationary states.

Let us analyze the stability of these stationary states using the kinetic method by considering the relaxation of a minor fluctuation of thermodynamic rush $\tilde{Y}$ about stationary solution $\tilde{Y}_i$. Let $\tilde{Y} = \tilde{Y}_i + y$, with y as the minor fluctuation. When retaining only linear terms in respect to y, from equation (3.25) we receive the kinetic equation for the y evolution:

$$\lambda_Y \frac{dy}{dt} = \varepsilon_1(\tilde{R}\cdot\tilde{Y}_i^2 + 2\tilde{R}\cdot\tilde{Y}_i\cdot y - \tilde{Y}_i^3 - 3\tilde{Y}_i^2\cdot y) - \varepsilon_2(\tilde{Y}_i + y)$$
$$= \left\{\varepsilon_1(2\tilde{R}\cdot\tilde{Y}_i - 3\tilde{Y}_i^2) - \varepsilon_2\right\}y.$$

Here, $\lambda_Y = \exp\left(-\mu_Y^o/RT\right)$.

In the stationary state at $\tilde{Y}_1 = 0$, this equation turns to

$$\lambda_Y \frac{dy}{dt} = -\varepsilon_2 y.$$

While $\varepsilon_2 > 0$, then the stationary state $\tilde{Y}_1$ is stable at any $\tilde{R}$.

In the stationary states at $\tilde{Y}_{2,3} = \frac{1}{2}\tilde{R} \mp \sqrt{\frac{1}{4}\tilde{R}^2 - \frac{\varepsilon_2}{\varepsilon_1}}$, the kinetics of changing y obey the equation

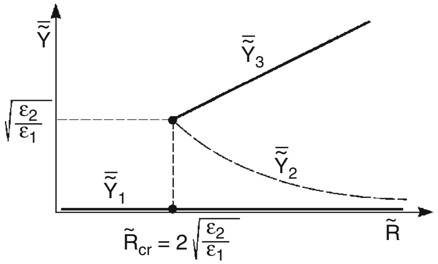

Figure 3.2 The stationary thermodynamic rushes of intermediate Y in the autocatalytic Schloegl scheme in respect to the value of controlling parameter $\tilde{R}$. See the text for the explanation.

$$\lambda_y \frac{dy}{dt} = \left[\varepsilon_1 \left(\frac{1}{2}\tilde{R} \mp \sqrt{\frac{1}{4}\tilde{R}^2 \quad \frac{\varepsilon_2}{\varepsilon_1}}\right)\left(\frac{1}{2}\tilde{R} \pm 3\sqrt{\frac{1}{4}\tilde{R}^2 \quad \frac{\varepsilon_2}{\varepsilon_1}}\right) \quad \varepsilon_2\right]$$

$$y = \varepsilon_1 \left(\sqrt{\frac{1}{4}\tilde{R}^2 \quad \frac{\varepsilon_2}{\varepsilon_1}}\right)\left(\sqrt{\frac{1}{4}\tilde{R}^2 \quad \frac{\varepsilon_2}{\varepsilon_1}} \pm \frac{1}{2}\tilde{R}\right) y \equiv \varphi_{2,3} y.$$

Obviously, $\varphi_3 < 0$ for $\tilde{Y}_3$ at $\tilde{R} > 2\sqrt{\frac{\varepsilon_2}{\varepsilon_1}}$ that is, $\tilde{Y}_3$ belongs to the stable stationary state. At the same time, inequality $\varphi_2 > 0$ is true for $\tilde{Y}_2$ at $\tilde{R} > 2\sqrt{\frac{\varepsilon_2}{\varepsilon_1}}$ that is, $\tilde{Y}_2$ belongs to the unstable stationary state.

Thus, the system, once it reaches the stationary state of the branch $\tilde{Y}_2$, turns out to be unstable, and any minor fluctuation makes $\tilde{Y}$ transfer to either branch $\tilde{Y}_1$ or branch $\tilde{Y}_3$. Such behavior resembles an electronic switch (trigger), and, for this reason, the system under discussion is referred to as "trigger" system. A thermodynamic rush of initial reactant R may be taken here, similar to Example 7, as the controlling parameter.

Example 10 Multiplicity of stable stationary states at the S shaped kinetic characteristics of stepwise transformations

When the stationary rate of stepwise transformations is described by an S-shaped dependence, the affinity $A_{r\Sigma}$ of the stepwise reaction (Figure 3.3) the properties of the reactive system can be inspected in the similar way. Like Example 9, in the system there may exist two stable stationary states at certain values of the affinity $A_{r\Sigma}$ and the

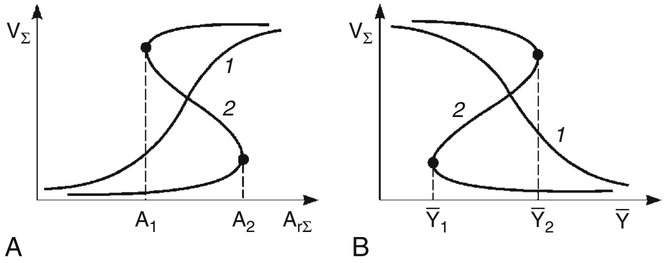

Figure 3.3 An example of the system with the S-type characteristics, which is capable of the "trigger" transitions; the plots are given in coordinates $v_\Sigma \leftrightarrow A_{r\Sigma}$ (A) and $v_\Sigma \leftrightarrow \Upsilon$ (B). Curves 1 and 2 are plotted with the stationary magnitude of an internal parameter Υ running throughout the whole range of allowed values and that correspond to different magnitudes of controlling parameter α.

actual state of the system is capable of jumping between these two stationary states in other words, the system features the “trigger” properties.

Let us say that the system has only one independent variable Y for example, the concentration (thermodynamic rush) of some intermediate. In this case, the evolution criterion $d_x\boldsymbol{P} < 0$ can be expressed in the form of total differential (3.4)

$$d_x\boldsymbol{P} = v_{\boldsymbol{\Sigma}} dA_{r\boldsymbol{\Sigma}},$$

where $v_{\boldsymbol{\Sigma}}$ is the rate of the stepwise process, $A_{r\boldsymbol{\Sigma}}$ is its affinity, and parameters $v_{\boldsymbol{\Sigma}}$ and $A_{r\boldsymbol{\Sigma}}$ are interrelated due to their dependence on a common variable Y (see Section 3.2). Let the rate of the parameter Y change be described by the initial differential equation written in a general form as

$$dY/dt = v_Y(Y, A_{r\boldsymbol{\Sigma}}, \alpha),$$

where α is the parameter controlling the shape of curves in Figure 3.3A. The stationary values of $Y = Y(A_{r\boldsymbol{\Sigma}}, \alpha)$ are determined by the equation

$$v_y(Y, A_{r\boldsymbol{\Sigma}}, \alpha) = 0.$$

Now let us say that at a given value of controlling parameter α, the stationary rate $v_{\boldsymbol{\Sigma}}$ of the stepwise process is symbate to parameter $A_{r\boldsymbol{\Sigma}}$ (curve *1* in Figure 3.3) through the entire range of parameter Y variations. In this situation, the differential $d_x\boldsymbol{P}$ is positive, which means the stability of the state under consideration for all Y.

As the stationary value of $V_{\boldsymbol{\Sigma}}$ stops being symbate to $A_{r\boldsymbol{\Sigma}}$ at another value of parameter (the segment of curve *2* between points Y_1 and Y_2 or A_1 and A_2 in Figure 3.4). Here, if Y_1 corresponds to point A_1 and Y_2 corresponds to point A_2, then the system stops being stable at the Y interval from Y_1 to Y_2 at $v_{\boldsymbol{\Sigma}}$ falling into the “antibate” range of curve 2. At the same time, the stable stationary states exist at $Y < Y_1$ in the upper segment of curve 2 in Figure 3.3 and $Y > Y_2$ in its bottom segment. Hence, when affinity of the stepwise process lies in the interval $A_2 < A_{r\boldsymbol{\Sigma}} < A_1$, the system has a multiplicity of the stable stationary states (two in the case under consideration).

In points A_1 and A_2 of curve 2 in Figure 3.3, derivative $dv_{\boldsymbol{\Sigma}}/dA_{r\boldsymbol{\Sigma}}$ turns to infinity. Hence, derivative $dv_{\boldsymbol{\Sigma}}/dA_{r\boldsymbol{\Sigma}}$ also must turn to infinity in points Y_1 and Y_2 in the case of a smooth dependence $Y = Y(A_{r\boldsymbol{\Sigma}}, \alpha)$.

In terms of thermodynamics, the energy dissipation $\boldsymbol{P}$ (or the positively defined Lyapunov function $\boldsymbol{\Phi}$) has its local minimums in the stable stationary points, and spontaneous jumping between stable stationary states in the system is only allowed when the identical “input” parameters are inherent in two states; this may be, for example, common affinity $A_{r\boldsymbol{\Sigma}}$ which is given from outside and provides the process. Therefore, we can consider these transitions as related to overcoming some dynamic “potential” barrier (see following).

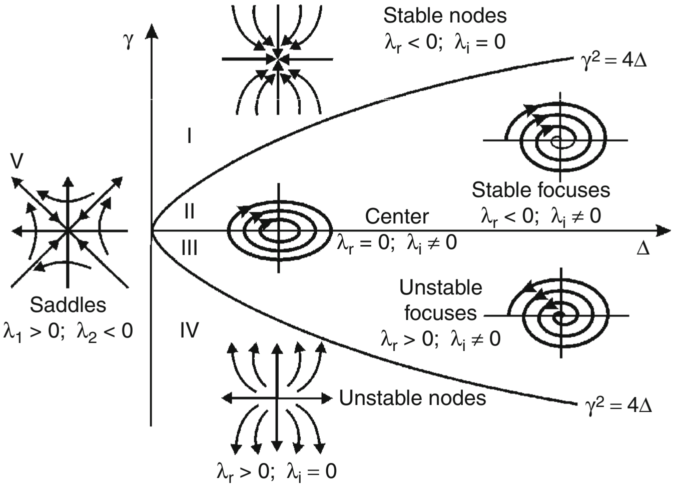

Figure 3.4 Stability types of particular points in the system of linear differential equations dy/dt = ay + bz; dz/dt = cy + dz in coordinates (Δ, γ) (according to A. M. Lyapunov).

3.5.2. Schemes of Transformations with Several Intermediates and Their Stability According to Lyapunov

Consider an algorithm of the kinetic schemes of analysis in respect to stability of the stationary states for a general case when the system has more than one internal variable. Let us say that the system has two internal parameters, Y and Z, and the evolution of these parameters is described by a set of differential equations:

$$\begin{aligned} dY/dt &= P(Y, Z, \alpha), \\ dZ/dt &= Q(Y, Z, \alpha). \end{aligned} \qquad (3.26)$$

Here, P and Q are some functions, while α is an external "controlling" param eter (for example, affinity of the stepwise process, temperature, pressure, etc.) that characterizes the distance of point (Y, Z) from the equilibrium.

Let the system be initially in the stationary state (Y, Z) and then escape this state. The system evolution ("phase trajectories") near the stationary state (Y, Z) can be determined with an assumption that $Y = Y + y$ and $Z = Z + z$ by linearizing equation (3.26) for infinitesimal parameters y and z into the set of characteristic equations

$$\mathrm{dy/dt = ay + bz},$$

$$\mathrm{dz/dt = cy + dz},$$

where $a = \frac{\partial P}{\partial y}\big|_{\bar{Y},\bar{Z}}$, $b = \frac{\partial P}{\partial z}\big|_{\bar{Y},\bar{Z}}$, $c = \frac{\partial Q}{\partial y}\big|_{\bar{Y},\bar{Z}}$, $d = \frac{\partial Q}{\partial z}\big|_{\bar{Y},\bar{Z}}$. The controlling parameter α influences parameters a, b, c, and d and is capable of changing them.

The general solution of this equation set can be written as

$$\begin{pmatrix} y \\ z \end{pmatrix} = \begin{pmatrix} y_1 \\ z_1 \end{pmatrix} e^{\lambda_1 t} + \begin{pmatrix} y_2 \\ z_2 \end{pmatrix} e^{\lambda_2 t}. \tag{3.27}$$

Here, (y_i, z_i) are eigenvectors in this equation set, while λ_1 and λ_2 are the characteristic numbers of the eigenvalue equation given by the determinant

$$\begin{vmatrix} a-\lambda & b \\ c & d-\lambda \end{vmatrix} = 0.$$

Expansion of the determinant gives

$$\lambda^2 - (a+d)\lambda + ad - bc = 0$$

or

$$\lambda^2 + \gamma\lambda + \Delta = 0$$

where $\gamma = -(a + d)$, $\Delta = ad - bc$.

It is evident that

$$\lambda_{1,2} = \frac{1}{2}\left(-\gamma \pm \sqrt{\gamma^2 - 4\Delta}\right),$$

The stable solutions are characterized by turning the solution back to the initial stationary point in the course of time. The type of solution stability depends on the characteristic numbers and is shown in Figure 3.4, plotted in the γ, Δ coordinates. Five regions, I–V, are identified in Figure 3.4, which are characterized by different types of the solution stability.

Let λ_r be the real and λ_{ir} the virtual parts of the characteristics number. The stable points are characterized by the negative real part of numbers

λ ($\lambda_r < 0$) and reside in regions I and II ($\gamma > 0$, $\Delta > 0$), which are separated by parabola $\gamma^2/4 = \Delta$. In region I, the inequality $\gamma^2 - 4\Delta > 0$ is additionally fulfilled and, consequently, $\lambda_{ir} = 0$. For this reason, a minor deviation of the system from the initial point is inevitably followed by turning the system back (evolution) to the same point along curves plotted schematically in Figure 3.4. According to A. M. Lyapunov's definition, region I relates to stable nodes.

In region II, $\gamma^2/4 < \Delta$, and therefore $\lambda_r < 0$, but $\lambda_{ir} \neq 0$. This region relates to stable focuses where the system evolution toward the initial point is described by a spiral curve. Unstable focuses and nodes are arranged in regions III and IV ($\lambda_r > 0$), respectively, and also are separated by curve $\gamma^2/4 = \Delta$. On axis $\gamma = 0$, there are center type points for which $\lambda_r = 0$, $\lambda_{ir} \neq 0$, and $\lambda_{1,2} = \pm i\lambda_{ir}$. Region V relates to unstable exceptional points of the saddle type. Here, $\lambda_i = 0$ and λ_r have different signs ($\lambda_1 > 0$, $\lambda_2 < 0$).

The points of stable thermodynamic equilibrium in the system always fall into region I. A variation in the value of controlling parameter α may cause changes in coefficients of the characteristic equation that describes the system behavior after it escapes the equilibrium and, consequently, in the value of parameters λ_1 and λ_2 (see Figure 3.4). Such a change may result not only in changing the coordinates of the exceptional point stable node but also in changing the stability type of the stationary state if the system escapes region I of stable nodes.

Note that the preceding considerations lead us to conclude as well that the necessary (but not sufficient) condition for emergence of oscillations in the evolution of the intermediate concentrations (i.e., the presence of a virtual part in the exponent via parameter λ) is the existence of no less than two intermediates; this is an important addition to the necessary conditions for the emergence of instability of the stationary state.

Systems with more than two independent variables can be analyzed in a similar way. The stable points in the phase diagram for such systems also are classified on the basis of characteristic solutions of the relevant eigenvalue equation. Lately, the positions of stable and "attracting" states of the dynamic system have been referred to as "attractors."

Transitions between the stability regions I–V of the exceptional points location can correlate with variations in the value of controlling parameter α. In a typical diagram (Figure 3.5A), the coordinates of stationary point y are plotted along the axis and controlling parameter α (the system remoteness from the initial equilibrium) is plotted along the abscissa.

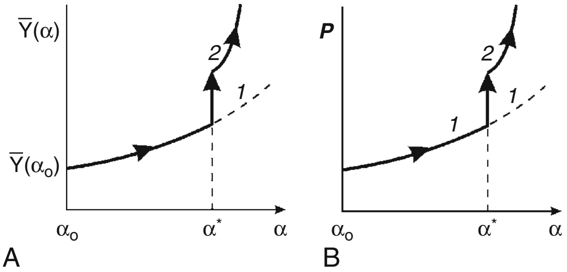

Figure 3.5 Typical diagrams of the stationary magnitude of some internal parameter Y (e.g., the concentration or thermodynamic rush of an intermediate) (A) and corresponding changes in the energy dissipation rate ***P*** (B) as the functions of a controlling parameter α upon deviation from point $Y(\alpha_o)$ of the initial stable stationary state and upon crossing the bifurcation point α^*: 1 is the "thermodynamic" branch, and 2 is the "nonthermodynamic" branch.

Let α increase as the system goes away from equilibrium. Assume that initial $\alpha = \alpha_0$ relates to the stationary point "stable node" of system (3.26) near its equilibrium and thus is located in region I in Figure 3.4. As α increases, we go along a certain branch of stationary states $Y = Y(\alpha)$. This "thermodynamic" branch (fragment *1* of the curve) describes the stable states—that is, it includes stable stationary points until α reaches the bifurcation value α^*. When $\alpha = \alpha^*$, the system loses its stability (for example, because the Lyapunov function under discussion in Section 3.4.1 stops being positively defined). In Figure 3.4, as the characteristic parameters vary continuously, this implies the transfer of the system from region I of stable nodes to another region (either II or V) with the differing stability characteristics. The further increase of α makes the system running along a "nonthermodynamic" branch (fragment 2 of curve $Y(\alpha)$), where transitions between instability regions are also allowed. The critical moment of variations in the system properties is reaching the bifurcation value $\alpha = \alpha^*$, when the system loses the stability. It is important that the rate of energy dissipation ***P*** also steps on transferring to its new state (see Figure 3.5B), since it usually increases when transferring to the nonthermodynamic branch.

The stationary states that fall into fragment *1* of the curve (Figure 3.5) are stable at minor deviations of α from α_0 in virtue of the theorem on the minimal rates of entropy production in these states. On further running away from the point $\alpha = \alpha_0$, we may fall outside the region of applicability of nonlinear thermodynamics while remaining in the "thermodynamic" branch, which is described, for example, by a "stationary state functional" as a kind of positively defined Lyapunov function (see Section 3.4.1). When this happens, the thermodynamic analysis of the state stability must apply the criterion of the stationary state's stability (3.5) as related to the positive behavior of excess energy dissipation $\delta \boldsymbol{P}$ at a potential fluctuation in the system. According to the criterion, all of the states in the thermodynamic fragment *1* of curve $\mathrm{Y}(\alpha)$ are stable until the bifurcation point α^* ($\alpha_0 < \alpha < \alpha^*$) and

$$\delta \boldsymbol{P} > 0. \tag{3.28}$$

The loss of stability and transfer to the so called "nonthermodynamic" (i.e., described by deterministic kinetic or other dynamic equations) branch happens at $\alpha = \alpha^*$, when, for example, the excess energy dissipation at $\alpha > \alpha^*$ turns negative:

$$\delta \boldsymbol{P} < 0. \tag{3.29}$$

The bifurcation point $\alpha = \alpha^*$ corresponds to the thermodynamic threshold of the emergence of instability. In this point, the system occurs at the stability boundary, and the excess energy dissipation turns to zero on small fluctuations of internal parameters:

$$\delta \boldsymbol{P} = 0.$$

In the "nonthermodynamic" branch at the region of unstable stationary states, the system properties depend on the particular form of differential equations to describe its dynamic behavior when the parameters are behind the bifurcation point. For example, the system behavior may be like a "chemical machine," which is strongly deterministic by starting conditions, or it may correspond to the so called "chaos" when any infinitesimal fluctuations cause heavy and irregular changes in the system states.

The instability arises and evolves owing to thermodynamic fluctuation (3.29). Such a fluctuation may cause complete system state decay (see, e.g., region V of "unstable saddles" in Figure 3.4). However, it may also happen that the arising instability creates a new state of the system to be stabilized in time and space. An example is the formation of the "limit (restricted) cycle" in a system that involves the exceptional point of the "unstable focus" type. The orbital stability of such a system means exactly the existence of certain time stabilized variations in the thermodynamic parameters (for example, the concentrations of reactants) that are sustained due to continuous energy and matter exchange with the surrounding medium (see the Lotka Volterra model in Example 11).

In a system that has two independent variables and is located initially in region I of the stable nodes (see Figure 3.4), changes in parameter α enable two types of transitions: (1) transition to saddle region V to lose totally the stability when one of the real roots of the eigenvalue equation turns to zero, and (2) transition to region II of stable focuses to generate oscillating solutions when the roots become complex conjugate numbers. It is obvious that the transition I → V to lose the total stability $\lambda_2 < 0$, $\lambda_1 > 0$ must be accompanied by disordering of the "thermodynamic" stability of the stationary states. For this reason, it may happen behind the bifurcation point $\alpha = \alpha^*$ and couple with the system transfer to the "nonthermodynamic" branch. On the other hand, the transition I → II does not cause the stability loss but is coupled with the violation of the condition of monotonicity (aperiodicity) of relaxation processes when the system approaches the stationary position. Hence, transitions with the violated aperiodicity condition can occur on increasing α at $\alpha < \alpha^*$ before attaining the bifurcation point α^*—that is, in the "thermodynamic" branch without violation of the stability criterion (3.28) (see Example 12). As α increases further, the system can lose stability in point α^* and transfer to region III of unstable focuses.

Thus, an increase in the value of the controlling parameter α can result either in the violation of the condition of aperiodicity in relaxation processes at the preserved total stability of the system or, vice versa, in the violation of the condition of stationary state stability by which the system is transferred to the "nonthermodynamic" branch. It is important that the properties of the system state change jumpwise when passing through the bifurcation point, and thus these changes are called sometimes the kinetic phase transitions.

In real systems, especially in heterogeneous catalytic and biological systems, the reactants are often arranged irregularly in space. Therefore, an arising instability may cause simultaneous diffusion of substances from one point to another inside the system to make the reactant concentration oscillations arranged in a certain manner in space during the occurrence of "nonlinear" chemical transformations. As a result, a new "dissipative" structure arises with a spatially nonuniform distribution of certain reactants. This is a consequence of the interaction between the process of diffusion, which tends to create uniformity of the system composition, and local processes of the concentration variations in the course of nonlinear

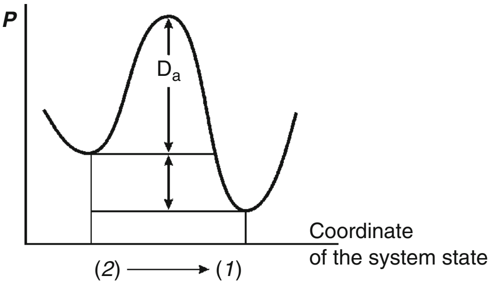

Figure 3.6 Variations in the magnitude of energy dissipation ***P*** upon transfer between locally stable stationary states *1* and *2* (see also Figure 3.5).

kinetic reactions. The emergence of such a dissipative structure is also preceded by violation of the conditions of thermodynamic stability far from equilibrium in the bifurcation point α^* and by the transition to an unstable state to the "nonthermodynamic" branch.

Obviously, the system cannot escape spontaneously the "local" stable stationary state unless it suffers from an external impact such as, for example, concentrated input (or output) of some power larger than D_a (Figure 3.6). In addition, while the heat motion inside the system may have the same result, the condition $D_a \gg RT\nu$, where ν is the frequency of a process capable of pushing the system from the stable stationary state, must be met for preventing such an event.

Example 11 The simplest system with stable oscillation: the Lotka Volterra model

The simplest example of the kinetic scheme with stable oscillation around a stationary state (the "center" situation by Lyapunov) is the autocatalytic Lotka-Volterra scheme with two intermediates. The scheme was first described in the beginning of the past century. Consider the stability of the stationary state of the stepwise process

$$R \rightarrow P,$$

which follows the scheme with two intermediates Y and Z and two elementary autocatalytic reactions, all elementary reactions a priori going far from equilibrium:

$$\begin{aligned} R + Y &\xrightarrow{\varepsilon_1} 2Y, \\ Y + Z &\xrightarrow{\varepsilon_2} 2Z, \\ Z &\xrightarrow{\varepsilon_3} P. \end{aligned} \tag{3.30}$$

This Lotka-Volterra scheme is used to describe, for example, interdependent evolution of populations of herbivorous animals ("hares" intermediate Y) and predators ("wolves" intermediate Z) that consume "hares."

The kinetics of variations in the intermediate concentrations in scheme (3.30) are described by coupled differential equations:

$$\frac{d[Y]}{dt} = \varepsilon_1 \tilde{R} \cdot \tilde{Y} \quad \varepsilon_2 \tilde{Y} \cdot \tilde{Z},$$
$$\frac{d[Z]}{dt} = \varepsilon_2 \tilde{Y} \cdot \tilde{Z} \quad \varepsilon_3 \tilde{Z}.$$

The sole nonzero stationary solution of this equation set is

$$\tilde{Y} = \varepsilon_3/\varepsilon_2,$$
$$\tilde{Z} = \varepsilon_1 \tilde{R}/\varepsilon_2. \tag{3.31}$$

Evolution of a minor fluctuation (y,z) around the stationary point $(\tilde{Y}, \tilde{Z})$ is described by the equation set

$$\lambda_Y \frac{d}{dt} y = (\varepsilon_1 \tilde{R} \quad \varepsilon_2 \tilde{Z})y \quad \varepsilon_2 \tilde{Y} \cdot z = \quad \varepsilon_3 z,$$
$$\lambda_Z \frac{d}{dt} z = \varepsilon_2 \tilde{Z} \cdot e + (\varepsilon_2 \tilde{Y} \quad \varepsilon_3)z = \varepsilon_2 \tilde{Z} \cdot y = \varepsilon_1 \tilde{R} \cdot y, \tag{3.32}$$

where $\lambda_Y = \exp(\quad \mu_Y^o/RT)$, $\lambda_Z = \exp(\quad \mu_Z^o/RT)$. For simplicity, we shall assume $\lambda_Y = \lambda_Z = 1$.

It was shown previously that the solution of equation set (3.32) can be written in the form

$$\begin{pmatrix} y \\ z \end{pmatrix} = \begin{pmatrix} y_1 \\ z_1 \end{pmatrix} e^{\lambda_1 t} + \begin{pmatrix} y_2 \\ z_2 \end{pmatrix} e^{\lambda_2 t},$$

where vectors (y_1,z_1) and (y_2,z_2) are determined by the starting conditions, while λ_1 and λ_2 are the roots of the eigenvalue equation

$$\begin{vmatrix} 0 \quad \lambda & \quad \varepsilon_3 \\ \varepsilon_1 \tilde{R} & 0 \quad \lambda \end{vmatrix} = 0. \tag{3.33}$$

From the last equation:

$$\lambda_{1,2} = \pm i \sqrt{\varepsilon_1 \varepsilon_3 \tilde{R}}.$$

This corresponds to the situation "center" by Lyapunov (see Figure 3.4) and to a solution with the thermodynamic rushes (concentrations) of intermediates Y and Z oscillating

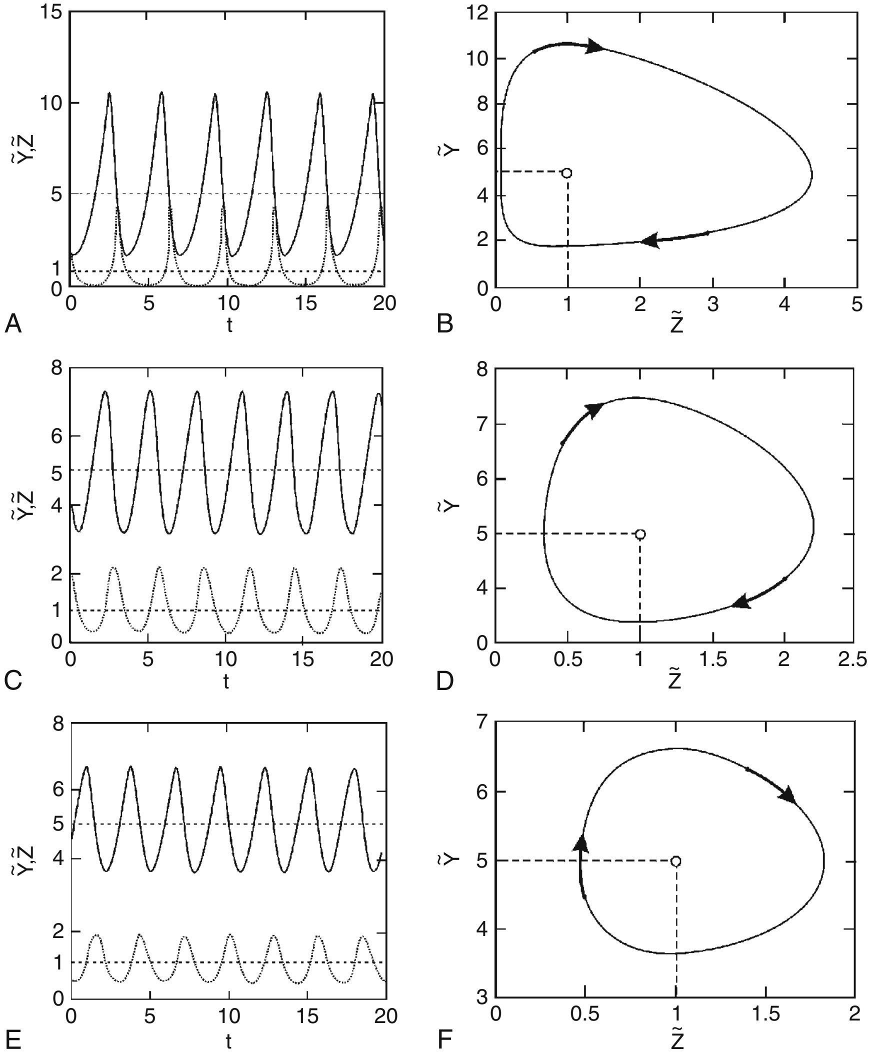

Figure 3.7 Typical kinetic curves (A, C, E) and the corresponding phase trajectories (B, D, F) of the evolution of thermodynamic rushes of intermediates Y (solid line) and Z (dashed line) in the the Lotka-Volterra scheme (3.30). The calculations are given for the cases of constant values $\tilde{R} = 1$, $\varepsilon_1 = \varepsilon_2 = 1$, and $\varepsilon_3 = 5$ at different initial system deviations from the stationary state. The starting conditions: $\tilde{Y}_o = 2$, $\tilde{Z}_o = 2$ (A and B); $\tilde{Y}_o = 4$, $\tilde{Z}_o = 2$ (C and D): and $\tilde{Y}_o = 4.5$, $\tilde{Z}_o = 0.5$ (E and F). In all of the cases, the phase trajectories are closed curves (periodical oscillations) around the same attractor : point of stationary state $\tilde{Y} = 5$, $\tilde{Z} = 1$. In the case of a considerable initial deviation from the stationary state (curves in B and D), the closed curves may differ in shape from a regular circle.

around the stationary state (3.31) with the frequency $\omega = \sqrt{\varepsilon_1 \varepsilon_3 \tilde{R}}$. Thus, the thermodynamic rush (concentration) of initial substrate $\tilde{R}$ can be considered, indeed, as the controlling parameter of the system under consideration. Evidently, the kinetics of the evolution of full solution (in assumption that y and z are infinitesimals) can be expressed by sinusoidal oscillations at equal frequencies but displaced in phase φ:

$$\begin{aligned} \tilde{Y} &= \tilde{Y} + y' \cdot \sin(\omega t + \varphi_Y) \\ \tilde{Z} &= \tilde{Z} + z' \cdot \sin(\omega t + \varphi_Z). \end{aligned} \tag{3.34}$$

Here, y' and z', as well as phases φ_Y and φ_Z, depend on the starting conditions of the relevant minor fluctuation (see Figure 3.7).

The given sustained thermodynamic solution can be considered as the appearance of a temporary dissipative system. Emphasize that $\tilde{Y}$ and $\tilde{Z}$ always remain localized around point $\tilde{Y}, \tilde{Z}$. This behavior of the dynamic system is commonly considered as a manifestation of an attractor that is, the point of "attraction" of even unstable solutions.

Indeed, one can analyze in the same manner the evolution of the system under consideration under conditions of reversibility of all of the elementary reactions in scheme (3.30). Unfortunately, in this situation the analytic solution of the eigenvalue equation in respect to parameter λ appears unreasonably awkward. However, if the kinetic irreversibility of both nonlinear steps are a priori assumed, it is easy to find stationary valued ($\tilde{Y}_i$, $\tilde{Z}_i$), and we come to the preceding oscillating solution. At the same time, near thermodynamic equilibrium (i.e., at $\tilde{R} \approx \tilde{P}$), there exits only a sole and stable stationary state of the system with ($\tilde{Y} \approx \tilde{Z} \approx \tilde{R}$).

Example 12 The simplest system with time fading auto oscillations: the scheme with an autocatalytic reaction and one "buffer" intermediate

Consider a kinetically irreversible stepwise reaction

$$R \rightarrow P$$

that follows the scheme including a "buffer" step of the formation of reaction intermediate Y followed by the autocatalytic step of the interaction between Y and intermediate-autocatalyst Z in the a priori assumption of kinetic irreversibility of two steps:

$$\begin{gathered} R \xrightarrow{\varepsilon_1} Y \\ Y + Z \overset{\varepsilon_2}{\rightleftarrows} 2Z \\ Z \xrightarrow{\varepsilon_3} P. \end{gathered} \tag{3.35}$$

A model that is very similar to this simplest kinetic scheme was suggested by A. Lotka in 1910 [1]. At certain relationships between external parameters $\tilde{R}$ and ε_i, scheme (3.35) describes the relaxation fading auto-oscillations. Let us demonstrate this.

As usual, let us determine the stationary $\tilde{Y}$ and $\tilde{Z}$ values via solving the kinetic equations set:

$$\frac{d[Y]}{dt} = \varepsilon_1\tilde{R} \quad \varepsilon_2\left(\tilde{Y}\cdot\tilde{Z} \quad \tilde{Z}^2\right) = 0$$

$$\frac{d[Z]}{dt} = \varepsilon_2\left(\tilde{Y}\cdot\tilde{Z} \quad \tilde{Z}^2\right) \quad \varepsilon_3\tilde{Z} = 0.$$

It follows from the second equation that intermediate Z may have two stationary states:

$$\tilde{Z}_1 = 0$$

and

$$\tilde{Z}_2 = \tilde{Y} \quad \frac{\varepsilon_3}{\varepsilon_2} \tag{3.36}$$

(see the solution in Example 7).

It is evident that the formal stationary solution $\tilde{Z}_1 = 0$ is not applicable to describe the stationary state of the system in respect of the second internal variable $\tilde{Y}$ ($\varepsilon_1\tilde{R}$ cannot be equal to zero). Therefore, we find the stationary value $\tilde{Y}_2$ at the nonzero $\tilde{Z}_2$ by inserting equation (3.36) into the equation for the rate of changing the concentration of Y:

$$\varepsilon_1\tilde{R} \quad \varepsilon_2\left\{\tilde{Y}_2\cdot\left(\tilde{Y}_2 \quad \frac{\varepsilon_3}{\varepsilon_2}\right) \quad \left(\tilde{Y}_2 \quad \frac{\varepsilon_3}{\varepsilon_2}\right)^2\right\} = 0,$$

where

$$\tilde{Y}_2 = \frac{\varepsilon_1}{\varepsilon_3}\tilde{R} + \frac{\varepsilon_3}{\varepsilon_2}.$$

Hence, the nonzero stationary value $\tilde{Z}_2$ is

$$\tilde{Z}_2 = \frac{\varepsilon_1}{\varepsilon_3}\cdot\tilde{R}.$$

Examine the stability of this stationary state $\{\tilde{Y}_2, \tilde{Z}_2\}$ by considering the evolution of independent minor fluctuations y and z of stationary values $\tilde{Y}_2$ and $\tilde{Z}_2$:

$$\lambda_Y \frac{dy}{dt} = \quad \varepsilon_2\left(y\cdot\tilde{Z}_2 + z\cdot\tilde{Y}_2 \quad 2z\cdot\tilde{Z}_2\right) = \quad \varepsilon_2\frac{\varepsilon_1}{\varepsilon_3}\tilde{R}\cdot y \quad \varepsilon_2\left(\quad \frac{\varepsilon_1}{\varepsilon_3}\tilde{R} + \frac{\varepsilon_3}{\varepsilon_2}\right)\cdot z$$

$$\lambda_Z \frac{dz}{dt} = \varepsilon_2\left(y\cdot\tilde{Z}_2 + z\cdot\tilde{Y}_2 \quad 2z\cdot\tilde{Z}_2\right)\varepsilon_3 z = \varepsilon_2\frac{\varepsilon_1}{\varepsilon_3}\tilde{R}\cdot y + \varepsilon_2\left(\quad \frac{\varepsilon_1}{\varepsilon_3}\tilde{R}\right)\cdot z.$$

Here, $\lambda_Y = \exp\left(\quad \mu_Y^o/RT\right)$, and $\lambda_Z = \exp\left(\quad \mu_Z^o/RT\right)$.

If we assume for simplicity that $\lambda_Y = \lambda_Z = 1$, we shall have the eigenvalue equation for determining powers of the time-dependent exponents in the time-dependent solution:

$$\begin{vmatrix} \frac{\varepsilon_1\varepsilon_2}{\varepsilon_3}\tilde{R} \quad \lambda & \frac{\varepsilon_1\varepsilon_2}{\varepsilon_3}\tilde{R} \quad \varepsilon_3 \\ \frac{\varepsilon_1\varepsilon_2}{\varepsilon_3}\tilde{R} & \frac{\varepsilon_1\varepsilon_2}{\varepsilon_3}\tilde{R} \quad \lambda \end{vmatrix} = 0$$

or

$$\begin{vmatrix} A \quad \lambda & A \quad \varepsilon_3 \\ A & A \quad \lambda \end{vmatrix} = 0,$$

where $A \equiv \frac{\varepsilon_1\varepsilon_2}{\varepsilon_3}\tilde{R}$ and ε_3 are positives.

Herein:

$$\lambda_{1,2} = \quad A \pm \sqrt{A(A \quad \varepsilon_3)}.$$

It is obvious that at $A \equiv \frac{\varepsilon_1\varepsilon_2}{\varepsilon_3}\tilde{R} > \varepsilon_3$, both values λ_1 and λ_2 are real and negative that is, the stationary state $\left(\tilde{Y}_2, \tilde{Z}_2\right)$ is attributed to a stable node (see Figure 3.4).

At $A \equiv \frac{\varepsilon_1\varepsilon_2}{\varepsilon_3}\tilde{R} < \varepsilon_3$, the parameters λ_1 and λ_2 are characterized by a negative real part and existence of a virtual component. This corresponds to the stable focus that is, the time-fading (relaxation) oscillating solution. On variations in the controlling parameter $\tilde{R}$, point $\tilde{R}_{cr} = \frac{\varepsilon_3^2}{\varepsilon_1\varepsilon_2}$ appears to be the bifurcation point for the stability of the stationary state (see Figure 3.8), and the oscillation frequency ω equals

$$\omega = \lambda_{ir} = \sqrt{A(A \quad \varepsilon_3)} = \sqrt{\frac{\varepsilon_3^2}{\varepsilon_1\varepsilon_2}\tilde{R}\left(\frac{\varepsilon_3^2\tilde{R}}{\varepsilon_1\varepsilon_2} \quad \varepsilon_3\right)}.$$

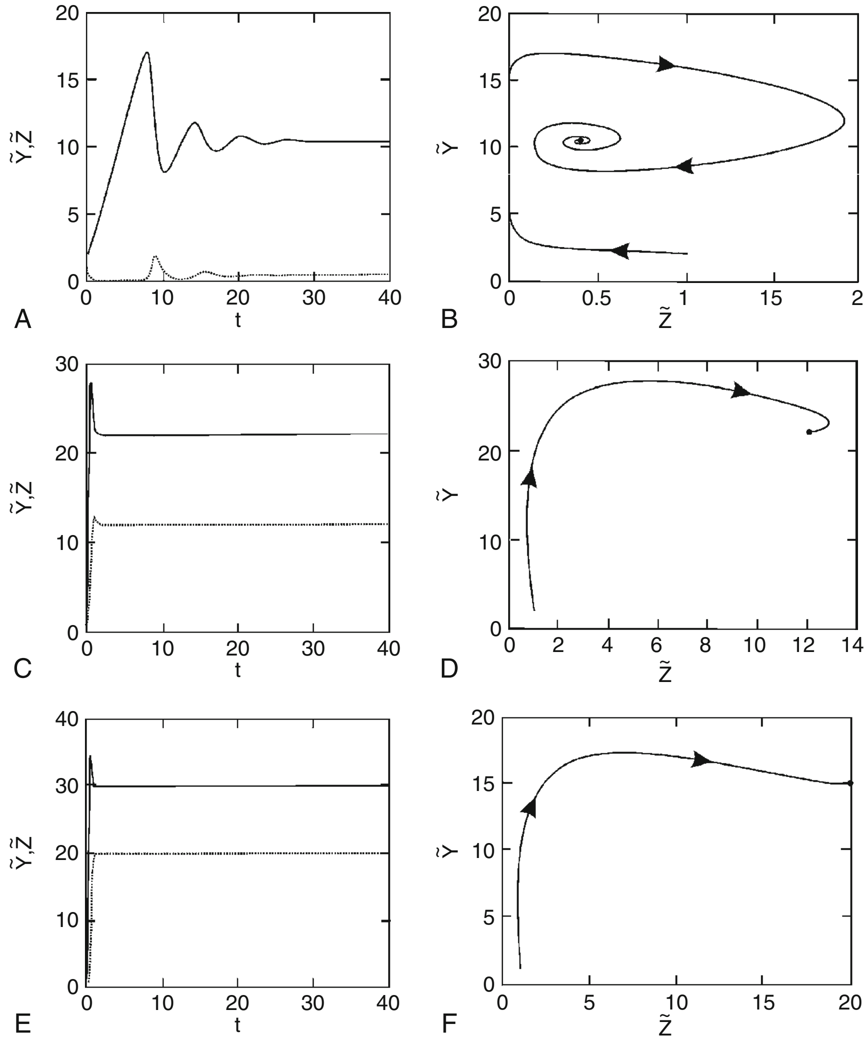

Figure 3.8 Typical kinetic curves (A, C, E) and the corresponding phase trajectories (B, D, F) of the evolution of thermodynamic rushes of intermediates Y (solid line) and Z (dash line) in scheme (3.35) with damped oscillations. Calculations are given for the cases of constant values $\varepsilon_1 = 2$, $\varepsilon_2 = 0.5$, and $\varepsilon_3 = 5$ and starting condition $\tilde{Y}_o = 2$, $\tilde{Z}_o = 1$ at different values of the controlling parameters $\tilde{R}$: $\tilde{R} = 1$ in diagrams A and B (stationary state at $\tilde{Y} = 10.4$, $\tilde{Z} = 0.4$); $\tilde{R} = 30$ in diagrams C and D (stationary state at $\tilde{Y} = 22$, $\tilde{Z} = 12$), and $\tilde{R} = 50$ in diagrams E and F (stationary state $\tilde{Y} = 30$, $\tilde{Z} = 20$). There is a bifurcation value of the controlling parameter $\tilde{R} = 25$ for all the other external parameters.

3.6. PHYSICOCHEMICAL BEHAVIOR OF DISSIPATIVE STRUCTURES

Typical higher ordered dissipative structures are living organisms. They exist only far from equilibrium and under conditions of large flows of matter (food) and/or energy (light for photosynthesizing bacteria and plants). However, there are much simpler abiogenic dissipative structures. In the case of chemically reactive systems, these structures are most often observed in the systems with catalytic transformations, both homogeneous and heterogeneous. Chapter 4 discusses these systems in more detail, but here we shall limit ourselves to some of the typical dissipative structures that develop without chemical transformations.

3.6.1. Spatial Dissipative Structures

The simplest spatial dissipative structures were described by French researcher Henri Benard in 1900. These structures can be observed by anyone who uses a frying pan for cooking. When a thin layer of a fluid is heated in the pan, a temperature difference $\Delta T = T_2 \quad T_1 > 0$ between the bottom and upper surfaces of the field is created (Figure 3.9A). While ΔT does not exceed some critical value ΔT_{cr}, the heat supplied from the pan's bottom expands upward owing to heat conductance, and the fluid in the pan remains immovable. However, as soon as ΔT exceeds ΔT_{cr}, a spontaneous convection of the fluid begins: The cold fluid comes down while the heated fluid comes up. The distribution of these concurrent streams appears self organized in 3D space (see Figure 3.9A) to give rise to a system of regular hexagonal Benard convection cells (Figure 3.9B). The upstream is centered in the cell, and the downstream is peripheral.

Figure 3.10 illustrates a qualitative dependence of the overall heat flux J_Q from the bottom to the upper surface on the temperature difference ΔT.

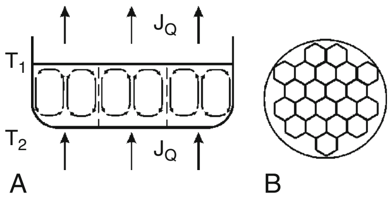

Figure 3.9 The Benard cells in a flat vessel of liquid: (A) a schematic of the cell formation due to the self-organized convection of a heated liquid, and (B) the top view of the cells. The convective vertical downstream is centered in the hexagons.

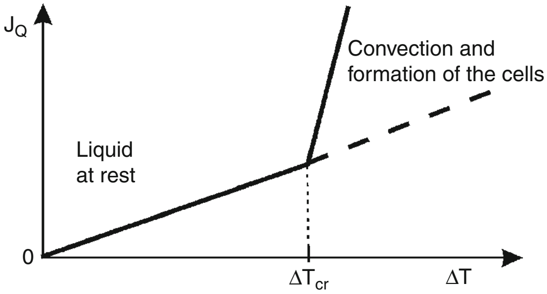

Figure 3.10 Dependence of the total vertical heat flux J_Q (see Figure 3.9) on the temperature difference $\Delta T = T_2 - T_1$ between the bottom and top liquid layers. Point ΔT_{cr} is the bifurcation.

At $\Delta T > \Delta T_{cr}$, the immovable heat conducting fluid becomes unstable (dashed line in Fig. 3.10) but another mode in the form of the Benard convection cells becomes stable instead. This is because the resting fluid is no longer capable of providing the transfer of the increased amount of heat, and a new convection mode is forced to arise in order to ensure the required heat transfer due to the ordered motion of large portions of the fluid.

Obviously, the heat transfer is the conjugating process here with respect to establishing the conjugate convection process. The controlling parameter is obviously the differential temperature ΔT, while point ΔT_{cr} behaves as the bifurcation point of the potential stationary states of the system.

In transferring from the precritical to the supracritical modes, the system symmetry changes spontaneously by analogy with thermodynamic phase transitions. This is why the transitions to form spatial dissipative structures in nonequilibrium systems are sometimes referred to as kinetic phase transitions.

Dissipative structures arise only in strongly nonequilibrium systems, with the states described by nonlinear equations for internal macro parameters. The emergence of the Benard cells in fluids can be described using nonlinear differential equations of hydrodynamics coupled with Lyapunov's analysis of the instability of the respective solutions. It is shown that the solution of hydrodynamic equations related to a resting fluid and normal heat transfer becomes unstable at $\Delta T \geq \Delta T_{cr}$, and a new stable convection mode is established in the fluid.

Recently, it has been discovered that phenomena similar to the preceding ones are even responsible for the geodynamics of continents on Earth. The tectonic plates of the continents "float" over the surface of molten magma and are involved in a continuous horizontal motion caused by vertical "plumes" of viscous magma. The tectonic plates collide in the downstreams to form the continents.

A commonly known example of stable dissipative structures is the turbulence (the generation of internal vortices) in quickly flowing gas or fluid. The stream, which is laminar at low velocities, jumps to the turbulent state when passing through the bifurcation point, which is determined by the Reynolds number dependent on a combination of kinetic and viscous parameters of the fluid medium. Tornadoes and storms that can be seen from space are amplitudinous phenomena of dissipative structures that can arise in the strongly non equilibrium atmosphere.

A classic example of spatial dissipative structures is the so called vacancy pore lattice. J. Evans discovered it experimentally in 1970 when studying microstructure of molybdenum crystals under their irradiation by fast nitrogen ions. The metal irradiation by ionizing particles (neutrons, high energy ions) is known to result in the formation of point defects (vacancies and interstitial atoms) in the crystal lattice. At elevated temperatures, these vacancies transfer inside the crystal to form complex clusters of defects in the form of vocational pores and flat dislocation loops. Usually these clusters build a kind of spatially uniform system, but in certain irradiation conditions, the vocational pores are arranged as regular "superlattices" that match the crystal lattice of the metal, but their lattice constants exceed those of the maternal crystal by several orders of magnitude. The formation of these ordered structures of vocational pores results from the nonlinear dynamic interaction between the point defects and the small vacation clusters and involves the diffusion between the pores.

A similar spatial structurization can be seen in dusted plasma when strongly ionized solid nanoparticles form a stable crystal like body that is "hanging" in space (see Figure 3.11). Supposedly, sleeves of spiral galaxies, the rings which surround Saturn and some other large planets, are also spatial dissipative structures (astrologists can see more than 90 rings around Saturn). In the early stages of formation of the solar system, Earth and some other planets were condensed from such sleeves of the initial gas dust cloud. The formation of these structures is accounted for by gravitational nonequilibricity of disperse matter that rotates around the planet and its attraction to the central massive body, while individual particles interact with one another.

For the last century, numerous phenomena of the formation of dissipative structures have been observed by chemists, too. One classic and

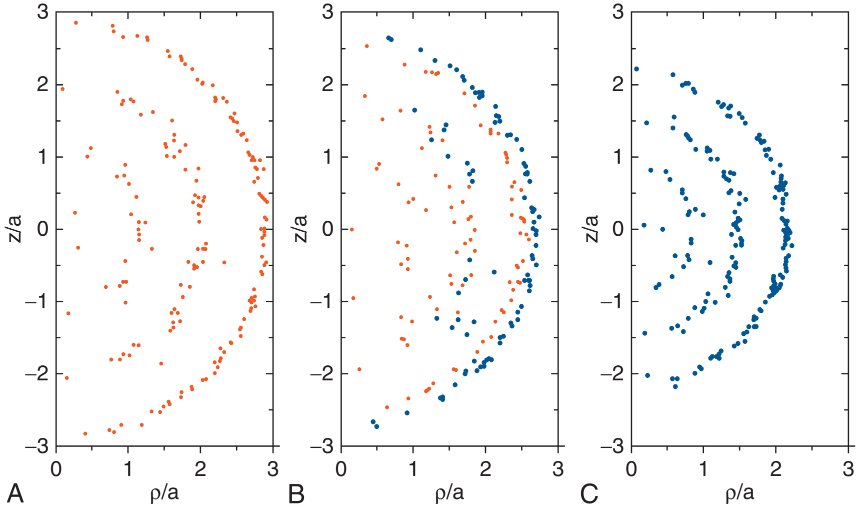

Figure 3.11 Location of particles in dusty plasma in a so-called Coulomb ball (according to calculations done at certain conditions in [3]); (A) and (C) are plasma containing dust particles of uniform size (small and large, respectively); (B) is plasma containing a mixture of particles of the two mentioned sizes. (Courtesy of S. G. Psakhie [3])

well recognized structure is the "self oscillating reaction," most of which are catalytic in nature. The modern in situ technique allows the detection of the catalyst state directly in the course of the reaction. The observed isothermal oscillations of the rate of catalytic reactions and, often, the generation of "chemical waves" should be classified as temporal and space temporal dissipative structures. Both types of structures are observed in homogeneous and heterogeneous catalytic systems (see Section 4.8). The time stable spatial dissipative structures are still not well understood in catalysis due to difficulties in their experimental discrimination against, for example, "equilibrium" reconstruction of the catalyst surface under the action of the reaction medium.

3.7. CHAPTER EXERCISES

1. What does the term *dissipative structures* include? What is the difference between an ordinary stationary state and a dissipative structure?
2. A gas phase stepwise reaction $H_2 + Cl_2 \rightleftarrows 2HCl$ follows the unbranched chain mechanism that involves atomic H and Cl as active intermediates:

$$Cl_2 \rightleftarrows 2\,Cl \tag{1}$$

$$Cl + H_2 \rightleftarrows HCl + H \tag{2}$$

$$H + Cl_2 \rightleftarrows HCl + Cl \tag{3}$$

$$H_2 \rightleftarrows 2\,H \tag{4}$$

Plot a diagram of chemical potentials for intermediates of this reaction. Is the stationary state of this reaction stable when the reaction proceeds at 400 K and the partial pressures $p(Cl_2) = p(H_2) = 10$ bar, $p(HCl) = 0.2$ bar? The following is known from the literature:

Compound	$\Delta_f H^o_{298}$, ***kJ/mol***	S^o_{298}, ***J/mol·K***	$C^o_{p,298}$, ***J/mol·K***
H_2	0	130,52	29,13
Cl_2	0	222,9	34,94
HCl	–92,3	186,8	29,13

3. A kinetically irreversible stepwise reaction

$$R \rightarrow P$$

follows the scheme

$$R + Y \overset{\varepsilon_1}{\rightleftarrows} 2Y$$

$$Y \overset{\varepsilon_2}{\rightleftarrows} Z$$

$$Y \overset{\varepsilon_3}{\rightarrow} P,$$

where Y and Z are intermediates. Find the stationary state of this process in respect to the intermediates and examine its stability.

3. What is the condition of existence of more than two stationary states?

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CHAPTER 4

Catalytic Processes and the Thermodynamics of Operating Catalysts

Contents

4.1. OPERATING CATALYSTS AS OBJECTS OF THE THERMODYNAMICS

The phenomenon of chemical catalysis is identified as the acceleration of chemical processes along a required route under the action of a noncon sumed catalyst matter. Catalysis is of great practical importance to a variety of aspects of human life and embraces numerous chemical manifestations from metabolism processes in living objects to large scale chemical indus tries. In the mid twentieth century, catalysis was unambiguously shown to be a pure chemical phenomenon that occurs under the control of particu lar and diversified intermediate chemical interactions between the reactants and the catalyst. Therefore, by definition, a catalyst is a substance capable of accelerating or initiating a chemical transformation by means of entering some intermediate chemical interactions with the transformation partici pants and of regenerating to its initial state after accomplishing the total transformation cycle. Thus, the principal distinguishing feature of catalysis as a physicochemical phenomenon implies the existence of some cyclic processes of the formation and transformation of chemical intermediates of the catalyzed stepwise reaction. It was shown in Section 1.2.4 that the catalyzed stepwise reaction is obviously conjugating to its conjugate cycle of catalytic intermediates' transformations, the substance of the catalyst active component being in a nonequilibrium state.

The last decades were particularly successful in understanding the phe nomenon of chemical catalysis owing to the widespread application of direct physical methods for in situ (i.e., directly during the catalysts opera tion) studies of elementary catalytic processes. The studies ensured the understanding of intimate mechanisms of the catalytic action in numerous model and real homogeneous and heterogeneous systems. However, it is important to note that many of studies in the field were reduced mainly to searching for the nature of the most probable intermediates of the cata lytic processes and the relevant kinetic schemes of the intermediate trans formations, rather than revealing the driving forces of the involved catalytic transformations. As a consequence, despite considerable progress in physicochemical modeling of some catalytic systems using the "pure" kinetic approach, the obtained results are usually difficult to generalize and to extend to different type systems of the reactions or catalysts; that is, their applicability is limited to the particular investigated objects only. Incredible as it may seem that the very powerful analytic tools of modern chemical thermodynamics have been until recently applied to the catalyzed process only but not to the state of the catalyst per se.

Eventually, the current catalysis science usually leave behind serious numerous physicochemical factors that affect the composition and size of particles of a heterogeneous catalyst at the stage of its preparation, even though the catalyst preparation often comprises hydrothermal processes that were well understood in equilibrium thermodynamics of geochemical processes. Even thermodynamic factors such as those that affect the surface state of the operating catalyst, its chemical composition, and potential surface "reconstruction" under the action of the reaction medium are not well understood. All of these include the phenomena that control the most important properties of the catalyst in the course of the reaction it catalyzes.

Therefore, the consideration of basic principles of the catalytic action via the insight into catalysis as a particular but rather common physicochemical phenomenon has remained important since the mid twentieth century, which was the period of rapid development of general ideas on the physicochemical nature of catalysis.

Georgii Boreskov, an eminent Soviet scientist in catalysis, devoted his research to the creation of an adequate physicochemical language for describing the phenomenon of heterogeneous catalysis, and he considered thermodynamics the fundamentals for the description. His analysis of the thermodynamic bases of catalytic processes produced the commonly accepted and experimentally proved Boreskov's rule on the approximate constancy of the specific catalytic activity:

Solid catalysts change their chemical composition, surface structure, and catalytic properties under the action of the reaction medium. A specific state of the catalyst which is independent of its initial state is characteristic of each particular composition of the reaction mixture and temperature.

This rule is based on a thermodynamic examination of catalytic systems and, as a natural consequence, an assumption on the relationship between the composition (and, as a result, the properties of the catalyst surface) and external conditions brought about by the reaction medium. The validity of the Boreskov rule for a large variety of catalytic systems indicates that the structural and chemical transformations of the catalyst surface induced by the reaction medium are indispensable indeed to heterogeneous catalysis.

Along with the Boreskov rule, other thermodynamic generalizations are applied when considering the catalytic processes. One is the commonly known trivial postulate that the catalyst is not capable of changing the thermodynamic equilibrium between reactants and the products of the catalyzed reaction. Another thermodynamic principle is expressed by the Horiuti Boreskov relations to determine the rate of a catalytic reaction as the difference between the rates of the direct and back stepwise transfor mation (see Section 1.3.2).

In addition, a variety of correlations often are used in the catalysis sci ence, which relate to the reaction rates and energies of the reaction inter mediates formation upon interaction of the catalyst with the initial reactants and transformation products. Many of these relations are known as the Broensted Polanyi relations.

Thermodynamic inspection of the states of operating catalysts is aimed mainly at the prediction of both the evolution course and properties of the catalyst active sites, as well as at elucidating the influence of thermo dynamic parameters on the rates of catalytic processes. The combined kinetic and thermodynamic analysis that was considered in the previous chapters can be used efficiently to reveal some specific features of the operating catalyst state and, in particular, to answer the following important questions:

1. How do the thermodynamic and kinetic parameters of elementary steps affect the most important parameters of a catalyst that is the rate of the catalytic reaction with the given transformation scheme? Is it possible to apply a single kinetic equation in the case of multiplicity of the allowed reaction pathways in the presence of the catalyst?
2. What are the rate limiting and rate controlling steps of a particular cat alytic process? What are the rate affecting parameters of the operating system?
3. What is the dependence of the most important parameter of a cata lytic process, which is its apparent activation energy at the stationary occurrence of the catalytic process, on the standard thermodynamic parameters of the system?
4. How do you know if the stationary state of the catalyst is stable?
5. Is there any sufficient reconstruction of the catalyst (surface)? What are the driving forces of this reconstruction?
6. Is there a correlation between the rates of catalytic transformations via different channels (routes) of the transformations when the catalyst is not selective?

Any stoichiometric catalytic process is a stoichiometric stepwise reaction that is intermediated by the chemical interaction of the reactants with the active centers of the catalyst to form some intermediate compounds (complexes of the reactants and active sites of the catalyst). Let us define some of the terms that are used in discussing the catalytic processes.

The *active center* of a catalyst is a chemical compound (one or a group of atoms of the catalyst) that makes it possible for the said intermediates to form. So, for operating catalysts, the active centers can exist in different forms (unoccupied or occupied by some catalytic intermediates). In heterogeneous catalysts, the active centers reside typically on the surface of the *active component* or active phase. In the anchored catalysts, the active centers are immobilized on the support. In an ideal case, the support can be considered as a catalytically inert substance.

A specific feature of most heterogeneous catalysts is obviously the diversity of simultaneously operating active centers, which differ from one another by their physicochemical properties (activity, etc.) and, as a consequence, the feasibility of diversified routes of catalytic transformations. In a majority of homogeneous, heterogeneous, and enzymatic processes, the total number of active centers is preserved in the course of the reaction and, therefore, a balance exists for the amount of all of the species in the active center. There are, however, exceptions to the rule—for example, one specific acid catalysis where the number of active centers depends on the content of H_3O^+ ions, which is controlled by the pH of the medium.

With the balance for the number of available forms of active centers of a catalyst, the concentrations and, correspondingly, the thermodynamic rushes of the reaction complexes (*catalytic intermediates*)—that is, the thermalized intermediate compounds of the reactant molecule (or molecular fragment) with the active center—appear interrelated through these balance relations in respect of each type of active center. The balance is of primary importance to the kinetics of the stepwise transformations and causes a number of peculiarities of the stationary kinetics of the stepwise processes. This makes the kinetic description of the catalytic transformations differ considerably from the description of the preceding schemes of noncatalytic reactions. For example, in the simplest catalytic stepwise transformation of substance R to substance P,

$$\mathrm{R} \rightleftarrows \mathrm{P},$$

which follows the mechanism

$$\mathrm{R} + \mathrm{K} \rightleftarrows \{\mathrm{K_i}\} \rightleftarrows \mathrm{K} + \mathrm{P},$$

where K is a "free" form of the active center, $\{K_i\}$ (i = 1, . . . , N) is an ensemble of the mutually interconverting catalytic intermediates, the preceding balance is expressed as

$$[K]_o = [K] + \sum_{i=1}^{N} [K_i], \quad (4.1)$$

where $[K]_o$ is a total of the active center concentration.

In some cases, the chemical composition and the number of active cen ters may evolve in time under the action of the reaction medium, the number of active centers being, in general, capable of both decreasing (for example, due to their irreversible poisoning) and increasing (like the development or multiplication of living organisms, etc.).

The *evolution*—the spontaneous transformations—of catalytic inter mediates are evidently determinative for the catalyst properties. Thus, the diversity of catalytic intermediates generates the diversity as well as the kinetic or thermodynamic particularity of catalytic reactions. Figure 4.1 illustrates a cycle of the simplest catalytic reaction described by the Michaelis Menten scheme (1.23)–(1.24) (see also (4.3)–(4.4)) and the rel evant energy diagram of the transformations expressed via chemical poten tials of the initial and final reactants, reaction intermediate K_1, and the free state of active center K. The diagram makes it obvious that the left to right reaction route needs the chemical potential μ_{K_1} of the intermedi ate falling between chemical potential of the initial and final reactant groups:

$$(\mu_R + \mu_K) > \mu_{K_1} > (\mu_P + \mu_K). \quad (4.2)$$

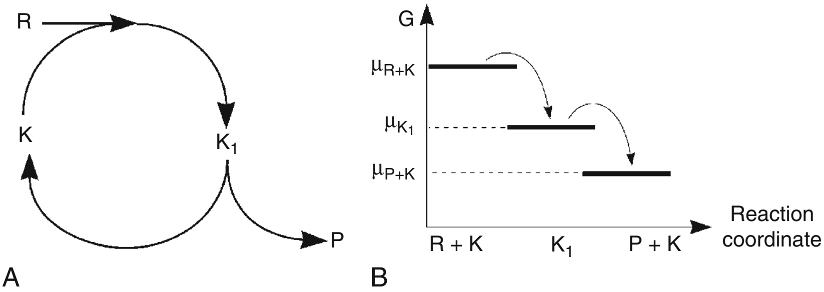


Figure 4.1 The cyclic transformations (A) and Gibbs energy (B) diagrams of the simplest catalytic reaction described by the Michaelis-Menten scheme (1.23)–(1.24).

Hence, the current value of chemical potential of the catalytic intermediate must be determined by the chemical potentials of the reactants, while the intermediate chemical interactions between the reactants and the catalyst are coupled with the main catalyzed reaction.

Thus, in the course of any catalytic transformation, the active component exists necessarily in a thermodynamically nonequilibrium state (stationary or other) that is governed by thermodynamic forces that exist in the nonequilibrium system—that is, by current affinities of all of the involved elementary chemical transformations.

Apart from the preceding dynamic nonequilibricity of the active component during its operation, there may exists a static nonequilibricity of the active centers as well. The latter may be caused by their "biography"—that is, the prehistory of the catalyst preparation or activation. Nonequilibricity can result, for example, from fast cooling ("quenching") of a solid catalyst during its preparation or nonequilibricity of coordinatively unsaturated compounds produced by the partial etching (dissolution) of the matrix that bears preinserted precursors of active centers. Many types of the biographic nonequilibricity can be even resistant to long operations of the catalyst in the real reaction medium.

The catalytic process per se, or at least some of its steps, can be considered here as stationary in respect to the catalytic intermediates. Thermodynamics of nonequilibrium processes usually treat the concentrations and chemical potentials of catalytic intermediates as internal parameters, while those of the stepwise reaction products treat them as external parameters.

4.2. "MICROKINETIC" DESCRIPTIONS OF STATIONARY CATALYTIC REACTIONS

The potential diversity of types (nonuniformity) of active centers and, therefore, pathways of real catalytic reactions (especially heterogeneous catalytic reactions) makes it necessary to consider the whole set of possible channels (routes) of the process and the evolution of the whole body of possible catalytic intermediates. We saw in Section 1.3 that the tools of nonequilibrium thermodynamics allow the course of these processes with an unknown or poorly understood mechanism to be inspected by combining kinetic and thermodynamic analysis in terms of the thermodynamic driving forces of the process.

Generally, a catalytic reaction that involves a large number of catalytic intermediates can be visualized as a water stream in the system of “mountains” of transition states that are separated by “lakes” of thermalized intermediates, with the “water” levels described by the stationary chemical potentials of the intermediates (see Figure 1.5). Evidently, the “water” stream in such a system does not necessarily follow a single route only. Since numerous routes can exist, the contribution of them to the overall stream is dependent on the “water” level in the “lake.”

As applied to catalysis, the *microkinetic* analysis of catalytic reactions is used most often. This is an instrument of an idealized description of complex catalytic processes without consideration of the mass transfer that can affect considerably the observed kinetics of the catalytic transformations. The microkinetic analysis with the necessary consideration of the active sites balance for all types of active centers of the catalyst, even though it has several drawbacks, can provide important information about the potential influence of the very different thermodynamic factors.

4.2.1. Stationary Catalytic Reactions

Some specific features of catalytic reactions, which are identified via the microkinetic analysis and are what make catalytic and noncatalytic reactions qualitatively different, are discussed following. One is possible noncoincidence of the rate limiting steps (the process “bottleneck”) and rate determining steps, the parameters of the latter being directly present in the expressions that describe the stationary rate of the stepwise process.

Again, while the stationary rate of stepwise noncatalytic reactions is independent of the standard thermodynamic parameters of thermalized intermediates, the rate determining parameters of catalytic reactions may depend on the standard thermodynamic parameters of thermalized catalytic intermediates and, as a consequence, influence considerably the apparent activation energy of the overall process.

We analyze a few of the simplest catalytic systems following. In the systems under consideration, the constituent elementary transformations usually are linear in respect to the concentrations of catalytic intermediates. Generally speaking, the results of this kind of analysis are only applicable when the interaction between the active centers, whether identical or different, of the catalyst can be ignored. This is the case mainly for homogeneous and enzymatic rather than heterogeneous catalysis. However, in some cases, the conclusions can be extended to more complex catalytic systems operating in the steady stationary states even with the lateral interaction between the active centers.

The expressions of the derived type (4.10) are valid for the intermediate linear schemes of catalytic stepwise reactions over a wide range of condi tions. Therefore, the stationary rate v_Σ of the overall stepwise process can be treated here as proportional to the difference of thermodynamic rushes of the initial reactants and final products of the catalytic reaction. This is in line with the Horiuti Boreskov relation (1.36) (see Section 1.3.2) that describes the dependence of the stationary rates of many catalytic processes on the degree of their thermodynamic nonequilibricity.

When any complex catalytic system, even those that include inter mediate nonlinear steps, is close to its thermodynamic equilibrium, the stationary rate of the catalytic stepwise process is necessarily proportional to the affinity of the conjugating—that is, catalyzed—reaction as it was shown for non catalytic reaction in examples of Section 1.3.2.

The current or stationary values of chemical potentials of catalytic inter mediates are of principal importance for analyzing the role of the inter mediates in catalytic processes. For example, in the stationary mode of catalytic reactions, the relevant chemical transformations, the "reactant–active center" complexes—should be described as transitions between the stationary chemical potentials rather than the traditionally considered minimums of potential energy that relate to the standard state of the parti cipants of the stepwise transformation (see, for example, Figure 4.1).

4.2.2. Stationary Microkinetics and Rate-Determining Parameters of the Simplest Intermediate-Linear Catalytic Reactions

As we just saw, the balance of all of the species bearing potentially the catalytic active centers should be taken into account for calculating the stationary rates of most of the typical schemes of catalytic transforma tions. We shall consider a few typical examples of the simplest catalytic reactions.

Example 1 The simplest catalytic reaction with one catalytic intermediate (the Michaelis Menten scheme)

Let us identify the rate-determining parameters of the stationary catalytic transformation of substance R to substance P

$$R \rightleftarrows P, \qquad (4.3)$$

which follows the simplest so-called Michaelis-Menten scheme

$$\begin{aligned} &\mathrm{R} + \mathrm{K} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1, \\ &\mathrm{K}_1 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{P} + \mathrm{K}, \end{aligned} \tag{4.4}$$

where K is a free form of the active center, and K_1 is the catalytic intermediate. We shall consider the overall stepwise process going left to right: $\tilde{R} > \tilde{P}$.

Obviously, the true initial and final reaction groups of stepwise reaction (4.3) are the groups comprising free states of the active center: R + K and P + K. Therefore, one should expect that due to the linearity of scheme (4.4) in respect to intermediate K_1, the final expression for the reaction rate v_Σ is

$$v_\Sigma = \varepsilon_\Sigma\left(\tilde{R} \cdot \tilde{K} - \tilde{P} \cdot \tilde{K}\right) = \varepsilon_\Sigma \tilde{K}\left(\tilde{R} - \tilde{P}\right).$$

In fact, this expression is the result of a simple mathematical operation based on the expression

$$v_\Sigma = \frac{d[P]}{dt} = \varepsilon_2\left(\tilde{K}_1 - \tilde{K} \cdot \tilde{P}\right).$$

It follows from the condition of stationarity in respect to catalytic intermediate K_1 (or, that is the same, intermediate K) that

$$\tilde{K}_1 = \tilde{K}\frac{\varepsilon_1 \tilde{R} + \varepsilon_2 \tilde{P}}{\varepsilon_1 + \varepsilon_2}. \tag{4.5}$$

Hence, in the stationary for intermediate K_1 state, the rate of the catalytic reaction is really

$$v_\Sigma = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\tilde{K}\left(\tilde{R} - \tilde{P}\right) \equiv \varepsilon_\Sigma \tilde{K}\left(\tilde{R} - \tilde{P}\right). \tag{4.6}$$

It is evident here that the rate-limiting stage (the reaction "bottleneck") that is the step with the largest difference of the stationary values of chemical potentials (thermodynamic rushes) of the interacting reaction groups is the one with minimal ε_i. This is identical to the case of the chain of noncatalytic transformations (1.54).

It is essential, however, that expression (4.6) comprises a dependent "internal" parameter that is the thermodynamic rush $\tilde{K}$ of the free form of the active center of the catalyst. At the same time, for making the kinetic-thermodynamic analysis, one must have only "external" parameters in the final expression for v_Σ. In the case of the active centers of a catalyst, these are their *full concentration.* Let us denote this concentration by $[K]_o$. It is easy to find the relationship between [K] and $[K]_o$ based on the balance between the different forms of active centers. In scheme (4.4), this corresponds to the simple equality

$$[K_1] + [K] = [K]_o, \tag{4.7}$$

which often is written as

$$\theta_K + \theta_{K_1} = 1, \tag{4.8}$$

where $\theta_{K_1} \equiv [K_1]/[K]_o$ is the occupation (or coverage) of the active center by reaction intermediate K_1, $\theta_K \equiv [K]/[K]_o$ is the fraction of the free (nonoccupied) form of the active centers.

While in the thermodynamically ideal systems

$$\tilde{A}_\alpha = \exp\left(\frac{\mu_\alpha}{RT}\right) = [A_\alpha]\exp\left(\frac{\mu^o_\alpha}{RT}\right),$$

the relationship (4.7) is identical to equality

$$\tilde{K}_1 \exp\left(\quad \frac{\mu^o_{K_1}}{RT}\right) + \tilde{K}\exp\left(\quad \frac{\mu^o_K}{RT}\right) = \tilde{K}_o \exp\left(\quad \frac{\mu^o_K}{RT}\right)$$

or

$$\tilde{K} + \lambda_{K_1}\tilde{K}_1 = \tilde{K}_o. \tag{4.9}$$

Here, $\tilde{K}_o$ is the thermodynamic rush of the free form of the active centers of the catalyst in the case when all of the active centers remain free in other words, in the state with $\theta_K = 1$, μ^o_K and $\mu^o_{K_1}$ are standard chemical potentials of the free form of active center K and that of intermediate complex K_1, respectively, $\lambda_{K_1} \equiv \exp\left[(\mu^o_K \quad \mu^o_{K_1})/RT\right]$.

Comparing (4.7) (4.9) gives

$$\begin{aligned}\theta_K &= \tilde{K}/\tilde{K}_o\\ \theta_{K_1} &= \lambda_{K_1}\tilde{K}_1/\tilde{K}_o.\end{aligned}$$

Therefore, if you take into account (4.5),

$$\frac{\theta_{K_1}}{\theta_K} = \lambda_{K_1}\frac{\tilde{K}_1}{\tilde{K}} = \lambda_{K_1}\frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}}{\varepsilon_1 + \varepsilon_2} \equiv \frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}}{\varepsilon_1 + \varepsilon_2}\exp\left[\left(\mu^o_K \quad \mu^o_{K_1}\right)\Big/RT\right]$$

and

$$\tilde{K} = \theta_K \cdot \tilde{K}_o = \frac{\tilde{K}_o}{1 + \dfrac{\theta_{K_1}}{\theta_K}} = \frac{\tilde{K}_o}{1 + \lambda_{K_1}\left(\dfrac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}}{\varepsilon_1 + \varepsilon_2}\right)}$$

Hence,

$$v_{\Sigma} = \varepsilon_{\Sigma}\frac{\tilde{K}_o}{1+\dfrac{\theta_{K_1}}{\theta_K}}(\tilde{R} \quad \tilde{P}) \equiv \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\frac{\tilde{K}_o}{1+\lambda_{K_1}\left(\dfrac{\varepsilon_1\tilde{R}+\varepsilon_2\tilde{P}}{\varepsilon_1+\varepsilon_2}\right)}(\tilde{R} \quad \tilde{P}) \tag{4.10}$$

Note that v_{Σ}, when divided by the total concentration of active centers $[K]_o$, gives the very important catalyst parameter of the catalyst activity that is the turnover frequency of the active center, TOF:

$$\mathrm{TOF} = v_{\Sigma}/[K]_o = \left(v_{\Sigma}/\tilde{K}_o\right)\cdot\exp\left(\frac{\mu_K^o}{RT}\right) = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\frac{(\tilde{R} \quad \tilde{P})\exp\left(\dfrac{\mu_K^o}{RT}\right)}{1+\lambda_{K_1}\left(\dfrac{\varepsilon_1\tilde{R}+\varepsilon_2\tilde{P}}{\varepsilon_1+\varepsilon_2}\right)}. \tag{4.11}$$

The balance equations of type (4.9) can be obtained for the thermodynamically nonideal systems as well. In this case, the thermodynamic nonideality is taken into account through the equality

$$\frac{\tilde{K}_o}{\gamma_{K_o}} = \frac{\tilde{K}}{\gamma_K} + \frac{\lambda_{K_1}\tilde{K}_1}{\gamma_{K_1}},$$

where γ_{K_o}, γ_K, and γ_{K_1} are the activity coefficients of the relevant forms and states of the active center, which usually depend on θ_K and θ_{K_1}. Hence,

$$\tilde{K} = \frac{\tilde{K}_o}{\dfrac{\gamma_{K_o}}{\gamma_K}\left\{1+\dfrac{\theta_{K_1}}{\theta_K}\right\}} = \frac{\tilde{K}_o}{\dfrac{\gamma_{K_o}}{\gamma_K}\left\{1+\lambda_{K_1}\dfrac{\gamma_K}{\gamma_{K_1}}\left(\dfrac{\varepsilon_1\tilde{R}+\varepsilon_2\tilde{P}}{\varepsilon_1+\varepsilon_2}\right)\right\}},$$

that can be used for a further analysis of stationary properties of the system. For example,

$$v_{\Sigma} = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\frac{\tilde{K}_o(\tilde{R} \quad \tilde{P})}{\dfrac{\gamma_K}{\gamma_{K_1}}\left\{1+\lambda_{K_1}\dfrac{\gamma_K}{\gamma_{K_1}}\left(\dfrac{\varepsilon_1\tilde{R}+\varepsilon_2\tilde{P}}{\varepsilon_1+\varepsilon_2}\right)\right\}}.$$

To facilitate the consideration of model catalytic systems, we shall limit it, as before, to the thermodynamically ideal systems with $\gamma_i = 1$. Parameters ε_i and, therefore, the effective value in equation (4.10) does not depend on standard chemical potentials of the interacting reactants. However, the existence of the balance relationship (4.7) makes the catalytic stepwise reactions different from noncatalytic reactions in that v_{Σ} of the catalytic reactions may be dependent on standard characteristics of catalytic intermediates. We shall illustrate this conclusion by inspecting separately the cases of low and high occupation of the active center by catalytic intermediate K_1.

The case of low occupation of the active center by intermediate K_1: At low occupation of the active center by the intermediate, $\theta_{K_1} \ll 1$ or, that is the same, $\theta_{K_1}/\theta_K \ll 1$. When so, equation (4.10) gives

$$v_\Sigma = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \tilde{K}_o \left(\tilde{R} - \tilde{P} \right)$$

Hence, at low coverage of the active centers by the intermediate, the stationary rate, v, of the catalytic reaction under consideration, like that of noncatalytic transformations, is independent of the standard thermodynamic parameters of the thermalized intermediate. In addition to the linear dependence of the stationary rate on the difference between thermodynamic rushes of the initial reactant and the final product, there is also proportionality of the rate on the thermodynamic rush of the free form of the active center and the dependence on the standard thermodynamic parameters of transition states of the elementary reactions in scheme (4.4).

In the case under consideration, the rate-determining and rate-limiting steps of the overall catalytic process are identical, since both are steps with minimal ε_i. Like the case of noncatalytic transformations (see Section 1.4), the apparent activation energy, $E_{a\Sigma}$, of the catalytic stepwise reaction (4.3) is easy to determine when the stepwise process is kinetically irreversible: $\tilde{R} \gg \tilde{P}$. Evidently,

$$E_{a\Sigma} = \Delta_f H_{\text{lim}}^{/o} - \Delta_f H_K^o - \Delta_f H_R^o + RT,$$

where $\Delta_f H_{\text{lim}}^{/o}$ is the standard enthalpy of formation of the transition state in the rate-limiting step. Note that this value follows the statement of Section 1.4.5 on the apparent activation energy of a noncatalytic consecutive process being equal to the activation energy of the rate-limiting step minus the sum of heat of the preceding step.

The case of high occupation of the active center by intermediate K_1: In this case, $\theta_{K_1} \approx 1$ that is identical to inequality $\theta_{K_1}/\theta_K \gg 1$. Therefore,

$$v_\Sigma = \frac{\varepsilon_1 \cdot \varepsilon_2}{\left(\varepsilon_1 \tilde{R} + \varepsilon_2 \tilde{P} \right) \cdot \lambda_{K_1}} \tilde{K}_o \left(\tilde{R} - \tilde{P} \right). \tag{4.12}$$

Equation (4.12) can be analyzed by considering two limiting cases for the parenthesized expression in the denominator.

Case *a*:

$$\varepsilon_1 \tilde{R} \gg \varepsilon_2 \tilde{P}, \tag{4.13}$$

implies that the active center occupation with intermediate K_1 is controlled by initial reactant R.

Case *b*:

$$\varepsilon_1\tilde{R} \ll \varepsilon_2\tilde{P}, \tag{4.14}$$

indicates the control of the active center occupation with the intermediate by the final product P. Remember that the condition $\tilde{R} > \tilde{P}$ is met when the process goes left to right. Hence, Case *b* also relates to the situation $\varepsilon_1 \ll \varepsilon_2$ that is, step 1 of scheme (4.4) is the rate-limiting one.

In Case *a,*

$$v_\Sigma = \varepsilon_2 \frac{\tilde{K}_o(\tilde{R} - \tilde{P})}{\lambda_{K_1}\tilde{R}} = \varepsilon_2 \frac{\tilde{K}_o(\tilde{R} - \tilde{P})}{\tilde{R}} \exp\left[\left(\mu^o_{K_1} - \mu^o_K\right)/RT\right].$$

It is evident that here the rate-determining stage is step 2 in scheme (4.4) that is, the desorption (elimination) of the final product from intermediate K_1. The given expression for stationary rate v_Σ depends on the standard values not only of the Gibbs potential of the formation of the transition state in elementary reaction 2 but also of the Gibbs potential of the formation of intermediate K_1.

We must emphasize that the condition $\tilde{R} > \tilde{P}$ satisfies inequality (4.13) at both $\varepsilon_1 \gg \varepsilon_2$ and $\varepsilon_1 \ll \varepsilon_2$, which means that the rate-determining stage in Case *a* appears to be step 2, no matter which step of the stepwise process is the actual rate-limiting one (the "bottleneck")!

When the catalyzed reaction is kinetically irreversible, $\tilde{R} \gg \tilde{P}$ and, therefore,

$$v_\Sigma \approx \varepsilon_2\tilde{K}_o \exp\left[\left(\mu^o_{K_1} - \mu^o_K\right)/RT\right] = \varepsilon_2 \cdot [K]_o \exp\left(\mu^o_{K_1}/RT\right). \tag{4.15}$$

The apparent activation energy of the stepwise reaction here is

$$E_{a\Sigma} = \Delta_f H_2^{o/} - \Delta_f H^o_{K_1} + RT \equiv E_{a2}. \tag{4.16}$$

This corresponds to the activation energy E_{a2} of the elementary step of the product P elimination from intermediate K_1 and equals approximately (to an accuracy of RT) the heat of the formation of the transition state of elementary reaction 2 from the standard state of intermediate K_1 (Figure 4.2A). Note that here and in other examples of catalytic reaction schemes with the high occupation of the active center with intermediates the value of the apparent activation energy does not follow the statement in Section 1.4.5 on the apparent activation energies of noncatalytic consecutive processes.

In Case *b,*

$$v_\Sigma = \varepsilon_1\tilde{K}_o(\tilde{R} - \tilde{P})\tilde{P}\exp\left[\left(\mu^o_{K_1} - \mu^o_K\right)/RT\right];$$

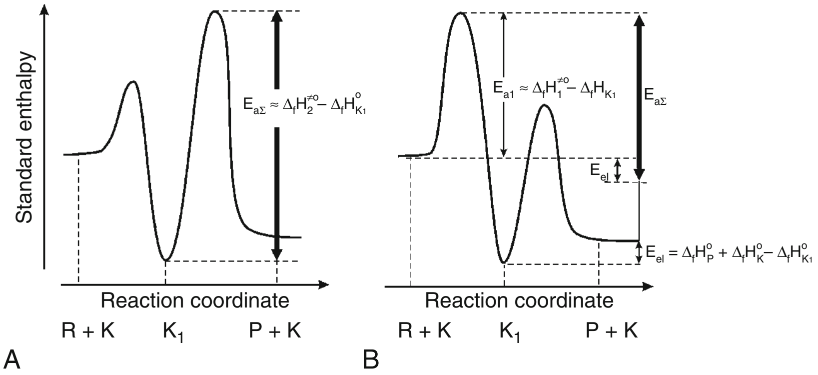


Figure 4.2 A graphical interpretation of the apparent activation energy $E_{a\Sigma}$ of the simplest catalytic reaction in the case of considerable coverage of the active center with intermediate K_1 (see the text for details).

that is, the rate is determined by ε_1, and, consequently, the rate-determining and rate-limiting steps are identical.

When $\tilde{R} \gg \tilde{P}$ and all thermalized participants of the transformation are thermodynamically ideal, then

$$v_\Sigma \approx \varepsilon_1 \tilde{K}_o \frac{\tilde{R}}{\tilde{P}} \exp\left[\left(\mu^o_{K_1} \quad \mu^o_K\right)/RT\right] = \varepsilon_1 [K]_o \frac{[R]}{[P]} \exp\left[(\mu^o_R \quad \mu^o_P + \mu^o_{K_1})/RT\right].$$

Thus, the rate-determining parameters here are the standard Gibbs energy of the formation of the transition state in elementary reaction 1 (scheme 4.4) and the standard Gibbs potentials of the formation of "external" reactants R as well as of P and intermediate K_1. The apparent activation energy of the stepwise reaction is

$$\begin{gathered} E_{a\Sigma} \approx \Delta_f H_1^{/o} \quad \Delta_f H^o_R + \Delta_f H^o_P \quad \Delta_f H^o_{K_1} + RT \\ \left(\Delta_f H_1^{/o} \quad \Delta_f H^o_R \quad \Delta_f H^o_K + RT\right) + \left(\Delta_f H^o_P + \Delta_f H^o_K \quad \Delta_f H^o_{K_1}\right) \quad E_{a1} + \Delta_r H^o_2, \end{gathered} \tag{4.17}$$

which means that it equals the activation energy E_{a1} of the first step plus the standard enthalpy of desorption (elimination) of product P from intermediate K_1 (Figure 4.2B).

In catalytic stepwise reactions, which involve more complex elementary transformations than scheme (4.4), the rate-determining parameters can be identified through similar considerations. Several examples of simple model schemes of catalytic transformations are given following. These schemes often are used for the microkinetic analysis of particular catalytic transformations and help to reveal the influence of various factors.

Example 2 The catalytic process through consecutive transformations of two catalytic intermediates

Compared to the previous simplest scheme (4.4) of the catalyzed reaction,

$$\mathrm{R} \rightleftarrows \mathrm{P},$$

it is much more realistic to use the scheme that includes the consecutive formation of two catalytic intermediates K_1 and K_2:

$$\mathrm{R} + \mathrm{K} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1, \tag{4.18}$$

$$\mathrm{K}_1 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{K}_2, \tag{4.19}$$

$$\mathrm{K}_2 \overset{\varepsilon_3}{\rightleftarrows} \mathrm{P} + \mathrm{K}. \tag{4.20}$$

As before, symbol K relates to the free form of the active center.

Schemes (4.18)–(4.20) can be interpreted as the preadsorption of initial reactant R to form a K_1 sorbate, followed by its transformation to intermediate K_2 as an adsorbed form of product P. The last step is the desorption (elimination) of product P from intermediate K_2 to form the free form of the active center. When the reaction is stationary in respect to both intermediates, the following equalities are valid:

$$\frac{d[\mathrm{K}_1]}{dt} = \varepsilon_1\left(\tilde{\mathrm{R}} \cdot \tilde{\mathrm{K}} - \tilde{\mathrm{K}}_1\right) - \varepsilon_2\left(\tilde{\mathrm{K}}_1 - \tilde{\mathrm{K}}_2\right) = 0,$$

$$\frac{d[\mathrm{K}_2]}{dt} = \varepsilon_2\left(\tilde{\mathrm{K}}_1 - \tilde{\mathrm{K}}_2\right) - \varepsilon_3\left(\tilde{\mathrm{K}}_2 - \tilde{\mathrm{P}} \cdot \tilde{\mathrm{K}}\right) = 0.$$

Therefore,

$$\tilde{\mathrm{K}}_1 = \frac{\varepsilon_1(\varepsilon_2 + \varepsilon_3)\tilde{\mathrm{R}} + \varepsilon_2\varepsilon_3\tilde{\mathrm{P}}}{\varepsilon_1\varepsilon_2 + \varepsilon_2\varepsilon_3 + \varepsilon_1\varepsilon_3}\tilde{\mathrm{K}} \equiv \delta_1\tilde{\mathrm{K}}, \tag{4.21}$$

$$\tilde{\mathrm{K}}_2 = \frac{\varepsilon_1\varepsilon_2\tilde{\mathrm{R}} + (\varepsilon_1 + \varepsilon_2)\varepsilon_3\tilde{\mathrm{P}}}{\varepsilon_1\varepsilon_2 + \varepsilon_2\varepsilon_3 + \varepsilon_1\varepsilon_3}\tilde{\mathrm{K}} \equiv \delta_2\tilde{\mathrm{K}}, \tag{4.22}$$

and eventually

$$v_{\Sigma} = \frac{d[\mathrm{P}]}{dt} = \varepsilon_3\left(\tilde{\mathrm{K}}_2 - \tilde{\mathrm{P}} \cdot \tilde{\mathrm{K}}\right) = \varepsilon_{\Sigma}\tilde{\mathrm{K}}\left(\tilde{\mathrm{R}} - \tilde{\mathrm{P}}\right),$$

where $\dfrac{1}{\varepsilon_{\Sigma}} = \dfrac{1}{\varepsilon_1} + \dfrac{1}{\varepsilon_2} + \dfrac{1}{\varepsilon_3}$.

The balance for all forms of the active center is

$$[K_1] + [K_2] + [K] = [K]_o,$$

or

$$\theta_{K_1} + \theta_{K_2} + \theta_K = 1,$$

where $\theta_{K_i} = \dfrac{[K_i]}{[K]_o}$.

This condition gives again

$$\tilde{K} = \theta_K \tilde{K}_o \equiv \tilde{K}_o \left(1 + \frac{\theta_{K_1}}{\theta_K} + \frac{\theta_{K_2}}{\theta_K}\right)^{-1} \equiv \tilde{K}_o / \boldsymbol{\Delta},$$

$$\boldsymbol{\Delta} \equiv 1 + \frac{\theta_{K_1}}{\theta_K} + \frac{\theta_{K_2}}{\theta_K} = 1 + \delta_1 \exp\left(\frac{\mu_K^o - \mu_{K_1}^o}{RT}\right) + \delta_2 \exp\left(\frac{\mu_K^o - \mu_{K_2}^o}{RT}\right),$$

where δ_1 and δ_2 are defined by relationships (4.21) and (4.22).

Let us consider the most realistic situation when step 2 of the conversion of the adsorbed reactant into the adsorbed product is the rate-limiting stage with the maximal difference between chemical potentials of the consecutive reaction groups. This situation implies satisfaction of inequalities $\varepsilon_2 \ll \varepsilon_1$ and $\varepsilon_2 \ll \varepsilon_3$; finally, $\varepsilon_{\boldsymbol{\Sigma}} \approx \varepsilon_2$. While $\tilde{R} > \tilde{P}$ during the overall catalyzed stepwise reaction from R to P, the accepted condition for the rate-limiting stage also gives $\tilde{K}_1 \approx \tilde{R} \cdot \tilde{K}$, whereas $\tilde{K}_2 \approx \left(\dfrac{\varepsilon_2}{\varepsilon_3}\tilde{R} + \tilde{P}\right)\tilde{K}$.

In the situation under consideration

$$v_{\boldsymbol{\Sigma}} \approx \frac{\varepsilon_2 \tilde{K}_o (\tilde{R} - \tilde{P})}{\boldsymbol{\Delta}},$$

where $\boldsymbol{\Delta} \equiv 1 + \dfrac{\theta_{K_1}}{\theta_K} + \dfrac{\theta_{K_2}}{\theta_K}$,

$$\frac{\theta_{K_1}}{\theta_K} = \tilde{R} \exp\left(\frac{\mu_K^o - \mu_{K_1}^o}{RT}\right), \quad \frac{\theta_{K_2}}{\theta_K} = \left(\frac{\varepsilon_2}{\varepsilon_3}\tilde{R} + \tilde{P}\right) \exp\left(\frac{\mu_{K_1}^o - \mu_{K_2}^o}{RT}\right).$$

To continue the analysis, we need to inspect potential situations with the occupation of the active center by the reaction intermediates. We shall do that for the case of the kinetic irreversibility of the overall stepwise process: at $\tilde{R} \gg \tilde{P}$. At the low occupation of the active center by intermediates K_1 and K_2, $\theta_{K_1}/\theta_K \ll 1$ and $\theta_{K_2}/\theta_K \ll 1$. When so, $\boldsymbol{\Delta} \approx 1$ and

$$v_{\boldsymbol{\Sigma}} \approx \varepsilon_2 \tilde{K}_o \cdot \tilde{R}.$$

The rate-controlling parameters here are the standard Gibbs potential of the formation of the transition state of the second (rate-limiting) step as well as the standard Gibbs potentials of the formation of the initial reactant and free active center.

The apparent activation energy, $E_{a\Sigma}$, here is

$$\begin{aligned} E_{a\Sigma} &\approx \Delta_f H_2^{\neq o} \quad \Delta_f H_K^o \quad \Delta_f H_R^o + RT \\ &= \left(\Delta_f H_2^{\neq o} \quad \Delta_f H_{K_1}^o + RT\right) \quad \left(\Delta_f H_K^o + \Delta_f H_R^o \quad \Delta_f H_{K_1}^o\right) \equiv E_{a2} + \Delta_r H_1^o. \end{aligned}$$

Thus, the apparent activation energy of the catalyzed stepwise reaction is equal to the activation energy of the rate-limiting step 2 plus the standard enthalpy of the preceding (preadsorption) step $\Delta_r H_1^o \equiv \Delta_f H_{K_1}^o \quad \Delta_f H_K^o \quad \Delta_f H_R^o$. The latter enthalpy is equal to the heat of desorption of the initial reactant R (Figure 4.3a) from the first reaction intermediate K_1.

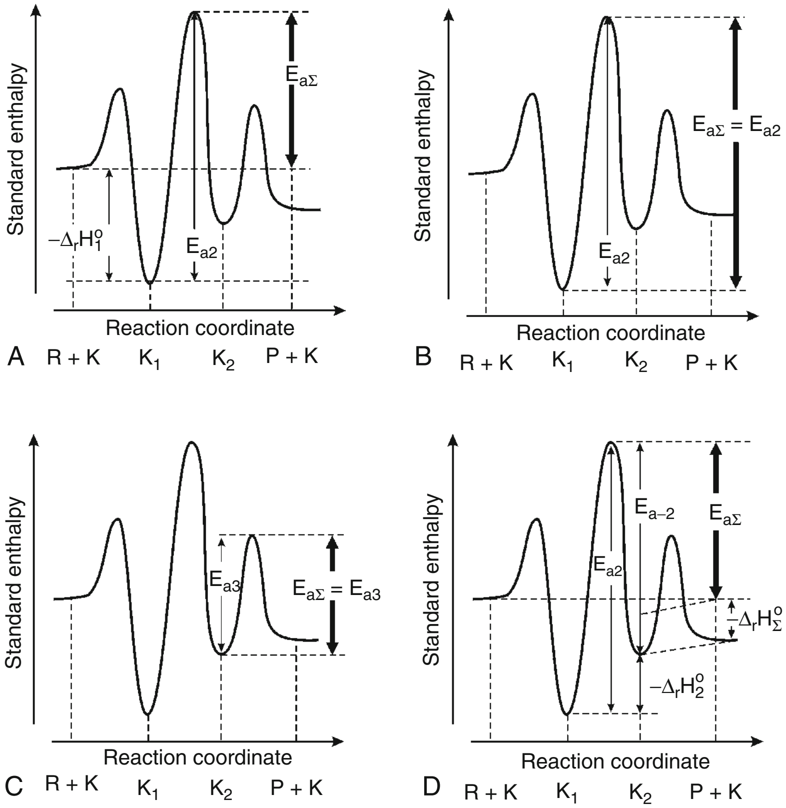


Figure 4.3 A graphical interpretation of the apparent activation energy $E_{a\Sigma}$ of a catalytic reaction with two catalytic intermediates K_1 and K_2 in few particular situations (see the text for details).

When intermediate K_1 that is, adsorbed but not yet transformed initial reactant R is the predominant form of the active center, then $\frac{\theta_{K_1}}{\theta_K} = \tilde{R} \cdot \exp\left(\frac{\mu_K^o \quad \mu_{K_1}^o}{RT}\right) \gg 1$ and $\frac{\theta_{K_1}}{\theta_K} \gg \frac{\theta_{K_2}}{\theta_K}$. In this case,

$$v_\Sigma \approx \varepsilon_2 \tilde{K}_o \exp\left(\frac{\mu_{K_1}^o \quad \mu_K^o}{RT}\right) = \varepsilon_2 [K]_o \exp\left(\frac{\mu_{K_1}^o}{RT}\right).$$

Therefore, the rate-determining parameters here are the standard Gibbs potentials of the formation of thermalized intermediate K_1 and of the transition state of the rate-limiting stage 2.

In this case, the apparent activation energy is expressed as

$$E_{a\Sigma} = \Delta_f H_2^{\neq o} \quad \Delta_f H_{K_1}^o + RT \equiv E_{a2},$$

which is identical to the activation energy, E_{a2}, of the rate-limiting step 2 (see Figure 4.3B).

When the predominating form of the active center appears to be intermediate K_2 that is, the adsorbed form of final product P then $\frac{\theta_{K_2}}{\theta_K} \equiv \left(\frac{\varepsilon_2}{\varepsilon_3}\tilde{R} + \tilde{P}\right) \cdot \exp\left(\frac{\mu_K^o \quad \mu_{K_2}^o}{RT}\right) \gg 1$ and $\frac{\theta_{K_2}}{\theta_K} \gg \frac{\theta_{K_1}}{\theta_K}$.

There may be two alternatives here:

1. If $\varepsilon_2 \tilde{R} \gg \varepsilon_3 \tilde{P}$, the occupation of the active center with intermediate K_2 is controlled by the concentration of initial reactant R and

$$v_\Sigma \approx \varepsilon_3 \tilde{K}_o \exp\left(\frac{\mu_{K_2}^o \quad \mu_K^o}{RT}\right) = \varepsilon_3 [K]_o \exp\left(\frac{\mu_{K_2}^o}{RT}\right).$$

Emphasize that in the situation under consideration, like in Example 1, the rate-determining parameter is the truncated rate constant ε_3 of elementary reaction 3 of the elimination of the final product from intermediate K_2 rather than the constant ε_2 of the real rate-limiting step 2.

The apparent activation energy here equals

$$E_{a\Sigma} = \Delta_f H_3^{\neq o} \quad \Delta_f H_{K_2}^o + RT \equiv E_{a3},$$

which corresponds to the activation energy E_{a3} of the rate-determining step 3 (see Figure 4.3C).

2. If $\varepsilon_2\tilde{R} \ll \varepsilon_3\tilde{P}$, the occupation of the active center with intermediate K_2 is controlled by the concentration of final product P and

$$v_\Sigma \approx \frac{\varepsilon_2\tilde{K}_o \cdot \tilde{R}}{\tilde{P}}\exp\left(\frac{\mu^o_{K_2} - \mu^o_K}{RT}\right) = \frac{\varepsilon_2[K]_o[R]}{[P]}\exp\left(\frac{\mu^o_{K_2} + \mu^o_R - \mu^o_P}{RT}\right).$$

The apparent activation energy here is

$$\begin{aligned} E_{a\Sigma} &= \Delta_f H_2^{/o} - \Delta_f H^o_R + \Delta_f H^o_P - \Delta_f H^o_{K_2} + RT \\ &= \left(\Delta_f H_2^{/o} - \Delta_f H^o_{K_1} + RT\right) - \left(\Delta_f H^o_{K_1} - \Delta_f H^o_R - \Delta_f H^o_K\right) \\ &\quad + \left(\Delta_f H^o_P + \Delta_f H^o_K - \Delta_f H^o_{K_2}\right) \\ &\equiv E_{a2} - \Delta_r H^o_1 + \Delta_r H^o_3. \end{aligned}$$

This expression can be interpreted, for example, as the difference of the activation energy E_{a2} of the rate-limiting transformation of intermediate K_1 to K_2 and the standard enthalpy $\Delta_r H^o_1$ of the preceding step 1 plus the standard enthalpy $\Delta_r H^o_3$ of the desorption K_2 to form product P (see Figure 4.2D).

Example 3 Catalytic reaction with the consecutive transformation of a large number of intermediates

Let us identify the rate-determining parameters of the catalytic stepwise reaction

$$R \rightleftarrows P$$

with a still more complicated mechanism described as

$$R + K \rightleftarrows \{K_i\} \rightleftarrows P + K, \tag{4.23}$$

where K is the free form of the active center species, and $\{K_i\}$ is a set of thermalized catalytic intermediates K_i ($i = 1, \ldots, Q$), which undergo an arbitrary set of monomolecular transformations.

For scheme (4.23), the stationary rate of the reaction is obviously defined as

$$v_\Sigma = \varepsilon_\Sigma\left(\tilde{R} - \tilde{P}\right)\tilde{K} = \varepsilon_\Sigma\tilde{K}_o\left(\tilde{R} - \tilde{P}\right)/\Delta, \tag{4.24}$$

where parameter ε_Σ is an algebraic combination of parameters ε_{ij} of all of the elementary steps in scheme (4.24), and denominator Δ is equal to

$$\Delta = 1 + \frac{\theta_{K_1}}{\theta_K} + \frac{\theta_{K_2}}{\theta_K} + \ldots + \frac{\theta_{K_n}}{\theta_K};$$

that is, as earlier, a simple algebraic function of parameters ε_{ij}, $\tilde{R}$, $\tilde{P}$, and $\lambda_{K_i} \equiv \exp\left(\frac{\mu_K^o \quad \mu_{K_i}^o}{RT}\right)$.

The appearance of denominator in expression (4.24) results, as before, from the balance of various forms of the active center:

$$[K] + \sum_{i \quad 1}^{n} [K_i] = [K]_o, \tag{4.25}$$

where $[K]_o$ is a total of the active center concentration.

When all forms of the active center are thermodynamically ideal, this relationship is transformed to the equality

$$\tilde{K} + \sum_{i \quad 1}^{n} \tilde{K}_i \cdot \lambda_{K_i} = \tilde{K}_o. \tag{4.26}$$

In scheme (4.23), the rate-controlling parameters can be found in the same way as before. So, at the low occupation of the active center by the catalytic intermediates, the overall stationary rate, v_Σ, of the stepwise process does not depend on the standard thermodynamic parameters of the intermediates.

A more detailed but nevertheless quite general analysis of the case of the high occupation of the active center by the intermediates can be done if the stepwise reaction goes through a series of consecutive transformations of thermalized intermediates K_i ($i = 1, \ldots, n$):

$$R + K \overset{\varepsilon_1}{\rightleftarrows} K_1 \overset{\varepsilon_2}{\rightleftarrows} \ldots \rightleftarrows K_L \overset{\varepsilon_{L+1}}{\rightleftarrows} K_{L+1} \rightleftarrows \ldots \overset{\varepsilon_n}{\rightleftarrows} K_n \overset{\varepsilon_{n+1}}{\rightleftarrows} K + P.$$

All of the intermediate transformations can be classified into two groups: the transformations before and after the rate-limiting step "L, L + 1" ("lim"), the former being characterized by the largest difference of chemical potentials and, thus, by the smallest value of $\boldsymbol{\varepsilon}_i$.

At the steps preceding the rate-limiting stage,

$$\mu_R + \mu_K \approx \mu_{K_1} \approx \mu_{K_2} \approx \ldots \approx \mu_{K_L},$$

and, therefore,

$$\tilde{R} \cdot \tilde{K} \cdot \approx \tilde{K}_1 \approx \tilde{K}_2 \approx \ldots \approx \tilde{K}_L.$$

After the rate-limiting stage, it can be roughly supposed that

$$\tilde{K}_L \approx \tilde{R} \cdot \tilde{K} \gg \tilde{K}_{L+1} > \tilde{K}_{L+2} > \ldots > \tilde{P} \cdot \tilde{K}.$$

Hence, at the low occupation of the active sites

$$\tilde{K} \approx \tilde{K}_o,$$

and

$$v_\Sigma \approx \varepsilon_{\lim} \tilde{K}_o \cdot \tilde{R}.$$

In this case,

$$\begin{aligned} E_{a\Sigma} &\approx \Delta_f H^{\neq o}_{\lim} - \Delta_f H^o_K - \Delta_f H^o_R + RT \\ &\equiv \left(\Delta_f H^{\neq o}_{\lim} - \Delta_f H^o_L + RT\right) + \left(\Delta_f H^o_L - \Delta_f H^o_K - \Delta_f H^o_R\right) \equiv E_{a\ \lim} + \Delta_r H^o_{(RK \to L)}. \end{aligned}$$

As before, the apparent activation energy is equal to the activation energy $E_{a\ \lim}$ of the rate-limiting step plus the sum of standard enthalpies $\Delta_r H^o_{(RK_L)}$ of all of the steps that precede the rate-limiting step.

When the predominant form of the active center is catalytic intermediate K_i, which is produced before the rate-limiting step, then we receive, as earlier,

$$v_\Sigma \approx \varepsilon_{\lim} \tilde{K}_o \exp\left(\frac{\mu^o_{K_i} - \mu^o_K}{RT}\right) = \varepsilon_{\lim} [K]_o \exp\left(\frac{\mu^o_{K_i}}{RT}\right)$$

and

$$\begin{aligned} E_{a\Sigma} &\approx \Delta_r H^{\neq o}_{\lim} - \Delta_f H^o_{K_i} + RT \\ &\equiv \left(\Delta_f H^{\neq o}_{\lim} - \Delta_f H^o_L + RT\right) + \left(\Delta_f H^o_L - \Delta_f H^o_{K_i}\right) \equiv E_{a\ \lim} + \Delta_r H^o_{(K_i \to L)}. \end{aligned}$$

Thus, when the surface is predominantly covered by intermediate K_i formed before the rate-limiting step, the apparent activation energy equals the activation energy of the rate-limiting step plus the standard enthalpy of the formation of intermediate K_L from intermediate K_i.

If the surface is predominantly covered by intermediate K_i formed after the rate-limiting step, the situation is more complicated for analysis, and cases must be considered individually when the concentration of K_i is determined by the concentration of initial reactant R or by the concentration of the final product P. It may happen here that the rate-limiting and rate-determining steps are not the same.

Example 4 A simple catalytic reaction in the presence of an inhibitor that forms a complex with the free form of the active center of the catalyst

Let us find the intermediate-stationary rate of the stepwise process

$$\mathrm{R} \rightleftarrows \mathrm{P},$$

which follows the scheme

$$\begin{aligned} \mathrm{R} + \mathrm{K} &\overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1 \\ \mathrm{K}_1 &\overset{\varepsilon_2}{\rightleftarrows} \mathrm{P} + \mathrm{K}, \\ \mathrm{K}_1 + \mathrm{I} &\overset{\varepsilon_3}{\rightleftarrows} \mathrm{K}_2. \end{aligned} \tag{4.27}$$

Unlike the simplest scheme (4.4), this one implies the formation of an inert intermediate (intermediate-"spectator") K_2 as a complex of the free form of the active center K and inhibitor I, where K_2 is reacting with neither R nor P. As before, K_1 is a catalytic intermediate, and K is the free form of the active center.

In the example under consideration, the balance of available forms of the active center is described as

$$\tilde{\mathrm{K}}_\mathrm{o} \cdot \exp\left(\quad \frac{\mu_\mathrm{K}^\mathrm{o}}{RT}\right) = \tilde{\mathrm{K}} \exp\left(\quad \frac{\mu_\mathrm{K}^\mathrm{o}}{RT}\right) + \tilde{\mathrm{K}}_1 \exp\left(\quad \frac{\mu_{\mathrm{K}_1}^\mathrm{o}}{RT}\right) + \tilde{\mathrm{K}}_2 \exp\left(\quad \frac{\mu_{\mathrm{K}_2}^\mathrm{o}}{RT}\right).$$

When assuming the partial equilibrium at step 3,

$$\tilde{\mathrm{K}}_2 = \tilde{\mathrm{K}} \cdot \tilde{\mathrm{I}}.$$

The condition of the system stationarity in respect to intermediate K_1 gives

$$\tilde{\mathrm{K}}_1 = \tilde{\mathrm{K}} \frac{\tilde{\mathrm{R}}\varepsilon_1 + \tilde{\mathrm{P}}\varepsilon_2}{\varepsilon_1 + \varepsilon_2}.$$

Hence, in conventional terms,

$$\begin{aligned} \frac{\theta_{\mathrm{K}_1}}{\theta_\mathrm{K}} &= \frac{\varepsilon_1 \tilde{\mathrm{R}} + \varepsilon_2 \tilde{\mathrm{P}}}{\varepsilon_1 + \varepsilon_2} \exp\left(\frac{\mu_\mathrm{K}^\mathrm{o} \quad \mu_{\mathrm{K}_1}^\mathrm{o}}{RT}\right), \\ \frac{\theta_{\mathrm{K}_2}}{\theta_\mathrm{K}} &= \frac{\tilde{\mathrm{K}}_2}{\tilde{\mathrm{K}}} \exp\left(\frac{\mu_\mathrm{K}^\mathrm{o} \quad \mu_{\mathrm{K}_2}^\mathrm{o}}{RT}\right) = \tilde{\mathrm{I}} \exp\left(\frac{\mu_\mathrm{K}^\mathrm{o} \quad \mu_{\mathrm{K}_2}^\mathrm{o}}{RT}\right). \end{aligned}$$

It is evident that the stationary rate of the catalyzed reaction is

$$v_\Sigma = \varepsilon_\Sigma \frac{\tilde{K}_o}{1+\dfrac{\theta_{K_1}}{\theta_K}+\dfrac{\theta_{K_2}}{\theta_K}}\left(\tilde{R}\quad\tilde{P}\right) = \varepsilon_\Sigma \frac{\tilde{K}_o\left(\tilde{R}\quad\tilde{P}\right)}{1+\lambda_{K_1}\dfrac{\tilde{R}\varepsilon_1+\tilde{P}\varepsilon_2}{\varepsilon_1+\varepsilon_2}+\lambda_{K_2}\tilde{I}} \tag{4.28}$$

where symbolization is identical to Example 1 that is, $\varepsilon_\Sigma = \dfrac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}$, $\lambda_{K_1} = \exp\left(\dfrac{\mu_K^o\quad\mu_{K_1}^o}{RT}\right)$, and $\lambda_{K_2} = \exp\left(\dfrac{\mu_K^o\quad\mu_{K_2}^o}{RT}\right)$.

This is only in the case of the high occupation of the active centers by the complex with inhibitor I as the preferable state of the active center that makes the obtained results different from the results of Example 1. The latter happens when inequalities $\dfrac{\theta_{K_2}}{\theta_K} \gg 1$ and $\dfrac{\theta_{K_2}}{\theta_K} \gg \dfrac{\theta_{K_1}}{\theta_K}$ are satisfied.

At this situation

$$v_\Sigma = \varepsilon_\Sigma \frac{\tilde{K}_o\left(\tilde{R}\quad\tilde{P}\right)}{\lambda_{K_2}\tilde{I}}.$$

Let us determine the apparent activation energy of the stepwise process in this case under additional conditions of the kinetic irreversibility of the catalyzed process: at $\tilde{R} \gg \tilde{P}$. Here,

$$v_\Sigma = \frac{\varepsilon_\Sigma\tilde{K}_o\tilde{R}}{\lambda_{K_2}\tilde{I}} = \varepsilon_\Sigma\frac{[K]_o[R]}{[I]}\exp\left(\frac{\mu_R^o+\mu_{K_2}^o\quad\mu_I^o}{RT}\right).$$

In the case under consideration,

$$\begin{aligned} E_{a\Sigma} &= \Delta_f H_{\lim}^{/o}\quad\Delta_f H_K^o\quad\Delta_f H_R^o+\Delta_f H_{K_2}^o\quad\Delta_f H_I^o+\Delta_f H_K^o+RT \\ &= E_{a\,\lim}\quad\Delta_r H_3^o = E_{a\,\lim}+Q_{ads\,I}, \end{aligned}$$

where $E_{a\,\lim}$ is the activation energy of the rate-limiting step (the step with the minimal $_i$), and $Q_{ads\,I} \equiv \quad \Delta_r H_3^o$ is the heat of formation of the complex between the inhibitor and free state of the active center by reaction 3 of scheme (4.27). Notice also that in this and the following examples, the initial reactant R or final product P may behave as the inhibitor I, too. All of the deduced expressions remain valid.

Example 5 Catalytic reaction with an inhibitor that forms an inactive complex with the catalytic intermediate

As before, we shall consider a simple catalytic stepwise reaction

$$R \rightleftarrows P,$$

which follows the scheme

$$\begin{aligned} R + K &\overset{\varepsilon_1}{\rightleftarrows} K_1, \\ K_1 &\overset{\varepsilon_2}{\rightleftarrows} P + K, \\ K_1 + I &\overset{\varepsilon_3}{\rightleftarrows} K_2, \end{aligned} \tag{4.29}$$

where I is the inhibitor, K is the free form of the active center, and K_1 and K_2 are the catalytic intermediate and the complex of this intermediate with the inhibitor, respectively.

The balance of various forms of the active center species is written as

$$\tilde{K}_o \cdot \exp\left(\frac{\mu_K^o}{RT}\right) = \tilde{K} \cdot \exp\left(\frac{\mu_K^o}{RT}\right) + \tilde{K}_1 \cdot \exp\left(\frac{\mu_{K_1}^o}{RT}\right) + \tilde{K}_2 \cdot \exp\left(\frac{\mu_{K_2}^o}{RT}\right).$$

In the stationary state in respect to the intermediates and in the case of partial equilibrium of step 3,

$$\begin{aligned} \tilde{K}_1 &= \tilde{K}\frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}}{\varepsilon_1 + \varepsilon_2} \\ \tilde{K}_2 &= \tilde{K}_1 \cdot \tilde{I} = \tilde{K}\frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}}{\varepsilon_1 + \varepsilon_2}\tilde{I}. \end{aligned}$$

Therefore,

$$\tilde{K}_o = \tilde{K}\left\{1 + \frac{\tilde{R}\varepsilon_1 + \tilde{P}\varepsilon_2}{\varepsilon_1 + \varepsilon_2}\left(\lambda_{K_1} + \lambda_{K_2}\tilde{I}\right)\right\}^{-1}.$$

where $\lambda_{K_1} = \exp\left(\frac{\mu_K^o \quad \mu_{K_1}^o}{RT}\right)$, $\lambda_{K_2} = \exp\left(\frac{\mu_K^o \quad \mu_{K_2}^o}{RT}\right)$.

When the complex of the catalytic intermediate with the inhibitor is the predominant form of the active center that is, $\frac{\theta_{K_2}}{\theta_K} \gg \frac{\theta_{K_1}}{\theta_K}$ and $\frac{\theta_{K_2}}{\theta_K} \gg 1$ the resulting rate of the catalyzed stepwise reaction is

$$
\begin{aligned}
v_{\Sigma} &= \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\tilde{K}(\tilde{R}-\tilde{P}) = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\tilde{K}_o\frac{\left(\tilde{R}-\tilde{P}\right)}{\exp\left(\dfrac{\mu_K^o-\mu_{K_2}^o}{RT}\right)\left(\dfrac{\varepsilon_1\tilde{R}+\varepsilon_2\tilde{P}}{\varepsilon_1+\varepsilon_2}\right)\tilde{I}} \\
&= \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1\tilde{R}+\varepsilon_2\tilde{P}}\frac{\tilde{K}_o\left(\tilde{R}-\tilde{P}\right)}{\exp\left(\dfrac{\mu_K^o-\mu_{K_2}^o}{RT}\right)\tilde{I}}.
\end{aligned}
\tag{4.30}
$$

We can find the apparent activation energy, $E_{a\Sigma}$, of the process by considering separately the limiting cases of controlling the concentration of complex K_2 by the "external" reactants either R or P and, as usual, under the condition of the kinetic irreversibility of the stepwise process: at $\tilde{R} \gg \tilde{P}$.

Case 1: The concentration of complex K_2 is controlled by the initial reactant R: $\varepsilon_1\tilde{R} \gg \varepsilon_2\tilde{P}$. Here,

$$
v_{\Sigma} \approx \varepsilon_2\frac{\tilde{K}_o}{\tilde{I}}\exp\left(\frac{\mu_{K_2}^o-\mu_K^o}{RT}\right) = \varepsilon_2\frac{[K]_o}{[I]}\exp\left(\frac{\mu_{K_2}^o-\mu_I^o}{RT}\right),
$$

which gives

$$
\begin{aligned}
E_{a\Sigma} &= \Delta_f H_2^{/o} - \Delta_f H_{K_2}^o + \Delta_f H_I^o + RT \\
&= E_{a2} + \Delta_f H_I^o + \Delta_f H_{K_1}^o - \Delta_f H_{K_2}^o = E_{a2} - \Delta_r H_3^o = E_{a2} + Q_{ads\,I}.
\end{aligned}
$$

Here, E_{a2} is the activation energy of elementary step 2, and $Q_{ads\,I} \equiv -\Delta_r H_3^o$ is the heat of the inhibitor adsorption on intermediate K_1 by reaction 3 of scheme (4.29).

Case 2: The concentration of complex K_2 is controlled by final product P: $\varepsilon_1\tilde{R} \ll \varepsilon_2\tilde{P}$. Here,

$$
v_{\Sigma} \approx \varepsilon_1\frac{\tilde{K}_o\tilde{R}}{\tilde{P}\cdot\tilde{I}}\exp\left(\frac{\mu_{K_2}^o-\mu_K^o}{RT}\right) = \varepsilon_1\frac{[K]_o[R]}{[P][I]}\exp\left(\frac{\mu_{K_2}^o+\mu_R^o-\mu_P^o-\mu_I^o}{RT}\right),
$$

which gives

$$
\begin{aligned}
E_{a\Sigma} &= \Delta_f H_1^{/o} - \Delta_f H_{K_2}^o - \Delta_f H_R^o + \Delta_f H_P^o + \Delta_f H_I^o + RT\left(\pm\Delta_f H_{K_1}^o\right) \\
&= E_{a1} + \Delta_r H_2^o - \Delta_r H_3^o = E_{a1} + \Delta_r H_2^o + Q_{ads\,I}.
\end{aligned}
$$

As before, E_{a1} is the activation energy of elementary step 1, $\Delta_r H_2^o$ is the standard enthalpy of reaction 2 of scheme (4.29), and $Q_{ads\,I}$ is the heat of complexing of intermediate K_1 with inhibitor I.

Several examples of analysis of simple kinetic schemes that are linear in respect to catalytic intermediates but whose initial or final reaction groups include several “external” reactants are considered following. Obviously, according to such schemes, some of the catalytic intermediates are interacting directly with the external reactants. In this situation, the catalytic heterogeneous reaction is usually said to follow the Eley-Rideal mechanism.

Example 6 Catalytic reaction with two initial reactants, one of which interacts with the catalytic intermediate by the Eley Rideal mechanism

Consider a catalytic reaction

$$R_1 + R_2 \rightleftarrows P \tag{4.31}$$

with two initial reactants, R_1 and R_2, that follow the scheme with two catalytic intermediates K_1 and K_2:

$$\begin{aligned} &R_1 + K \overset{\varepsilon_1}{\rightleftarrows} K_1, \\ &K_1 + R_2 \overset{\varepsilon_2}{\rightleftarrows} P + K. \end{aligned} \tag{4.32}$$

The second step is the interaction of the external reactant R_2 with intermediate K_1 by the Eley-Rideal mechanism. The stationary rate of this catalytic stepwise process is

$$v_{\boldsymbol{\Sigma}} = \frac{d[P]}{dt} = \varepsilon_2\left(\tilde{K}_1 \cdot \tilde{R}_2 \quad \tilde{P} \cdot \tilde{K}\right) = \varepsilon_1\left(\tilde{R}_1 \cdot \tilde{K} \quad \tilde{K}_1\right).$$

In the intermediate-stationary state,

$$\frac{d[K_1]}{dt} = \varepsilon_1(\tilde{R}_1 \cdot \tilde{K} \quad \tilde{K}_1) \quad \varepsilon_2(\tilde{K}_1 \cdot \tilde{R}_2 \quad \tilde{P} \cdot \tilde{K}) = 0,$$

hence,

$$\tilde{K}_1 = \tilde{K}\frac{\varepsilon_1\tilde{R}_1 + \varepsilon_2\tilde{P}}{\varepsilon_1 + \varepsilon_2\tilde{R}_2}$$

and

$$v_{\boldsymbol{\Sigma}} = \frac{\varepsilon_1\varepsilon_2\tilde{K}\left(\tilde{R}_1\tilde{R}_2 \quad \tilde{P}\right)}{\varepsilon_1 + \varepsilon_2\tilde{R}_2}. \tag{4.33}$$

The balance equation for all forms of the active center gives

$$\tilde{K}_o \exp\left(\quad \frac{\mu_K^o}{RT}\right) = \tilde{K} \exp\left(\quad \frac{\mu_K^o}{RT}\right) + \tilde{K}_1 \exp\left(\quad \frac{\mu_{K_1}^o}{RT}\right).$$

Therefore,

$$\tilde{K} = \frac{\tilde{K}_o}{1 + \dfrac{\theta_{K_1}}{\theta_K}} = \frac{\tilde{K}_o}{1 + \dfrac{\varepsilon_1 \tilde{R}_1 + \varepsilon_2 \tilde{P}}{\varepsilon_1 + \varepsilon_2 \tilde{R}_2} \cdot \lambda_{K_1}}.$$

Here, as before, $\lambda_{K_1} = \exp\left(\dfrac{\mu_K^o \quad \mu_{K_1}^o}{RT}\right)$. Thus, in general cases, the rate of the catalytic reaction (4.31) is written as

$$v_\Sigma = \frac{\varepsilon_1 \varepsilon_2 \tilde{K}_o}{\left(\varepsilon_1 + \varepsilon_2 \tilde{R}_2\right)\left(1 + \lambda_{K_1} \dfrac{\varepsilon_1 \tilde{R}_1 + \varepsilon_2 \tilde{P}}{\varepsilon_1 + \varepsilon_2 \tilde{R}_2}\right)} \left(\tilde{R}_1 \cdot \tilde{R}_2 \quad \tilde{P}\right) \tilde{K}_o. \tag{4.34}$$

Further analysis is easy to do by considering probable limiting situations in the same way used in the previous examples and in Section 1.4. For example, at the low coverage of the active center by the catalytic intermediate $\dfrac{\theta_{K_1}}{\theta_K} \ll 1$ and, therefore,

$$v_\Sigma = \varepsilon_\Sigma \left(\tilde{R}_1 \cdot \tilde{R}_2 \quad \tilde{P}\right) \tilde{K}_o,$$

where

$$\varepsilon_\Sigma = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2 \tilde{R}_2},$$

and so on.

Example 7 Catalytic reaction with two initial reactants and two catalytic intermediates

Let the catalyzed stepwise process

$$R_1 + R_2 \rightleftarrows P, \tag{4.35}$$

follow the scheme

$$\begin{aligned} R_1 + K &\overset{\varepsilon_1}{\rightleftarrows} K_1, \\ K_1 + R_2 &\overset{\varepsilon_2}{\rightleftarrows} K_2, \\ K_2 &\overset{\varepsilon_3}{\rightleftarrows} P + K \end{aligned} \tag{4.36}$$

with two catalytic intermediates K_1 and K_2.

It is obvious that the intermediate-stationary rate of the process (4.35) is expressed as

$$v_\Sigma = \frac{\varepsilon_\Sigma \tilde{K}\left(\tilde{R}_1 \cdot \tilde{R}_2 - \tilde{P}\right)}{1 + \dfrac{\theta_{K_1}}{\theta_K} + \dfrac{\theta_{K_2}}{\theta_K}}.$$

Indeed,

$$v_\Sigma = \frac{d[P]}{dt} = \varepsilon_3\left(\tilde{K}_2 - \tilde{P} \cdot \tilde{K}\right) = \varepsilon_1\left(\tilde{R}_1 \cdot \tilde{K} - \tilde{K}_1\right).$$

In the stationary state in respect to the intermediated

$$\begin{aligned} \frac{d[K_1]}{dt} &= \varepsilon_1(\tilde{R}_1 \cdot \tilde{K} - \tilde{K}_1) - \varepsilon_2(\tilde{K}_1 \cdot \tilde{R}_2 - \tilde{K}_2) = 0, \\ \frac{d[K_2]}{dt} &= \varepsilon_2(\tilde{K}_1 \cdot \tilde{R}_2 - \tilde{K}_2) - \varepsilon_3(\tilde{K}_2 - \tilde{P} \cdot \tilde{K}) = 0. \end{aligned}$$

Hence,

$$\tilde{K}_1 = \tilde{K} \cdot \frac{\varepsilon_1 \tilde{R}_1 + \dfrac{\varepsilon_2 \cdot \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\tilde{P}}{\varepsilon_1 + \dfrac{\varepsilon_2 \cdot \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\tilde{R}_2} \equiv \tilde{K} \cdot \alpha, \tag{4.37}$$

$$\tilde{K}_2 = \frac{\varepsilon_2 \tilde{K}_1 \tilde{R}_2 + \varepsilon_3 \tilde{P} \cdot \tilde{K}}{\varepsilon_2 + \varepsilon_3} = \tilde{K}\frac{\varepsilon_2 \alpha \tilde{R}_2 + \varepsilon_3 \tilde{P}}{\varepsilon_2 + \varepsilon_3}.$$

As a result, the stationary rate of stepwise process (4.35)

$$v_\Sigma = \frac{\varepsilon_1 \cdot \dfrac{\varepsilon_2 \cdot \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\tilde{K}(\tilde{R}_1 \cdot \tilde{R}_2 - \tilde{P})}{\varepsilon_1 + \dfrac{\varepsilon_2 \cdot \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\tilde{R}_2} \equiv \varepsilon_\Sigma \tilde{K}(\tilde{R}_1 \cdot \tilde{R}_2 - \tilde{P}),$$

where

$$\varepsilon_\Sigma = \frac{\varepsilon_1 \cdot \dfrac{\varepsilon_2 \cdot \varepsilon_3}{\varepsilon_1 + \varepsilon_3}}{\varepsilon_1 + \dfrac{\varepsilon_2 \cdot \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\tilde{R}_2} = \frac{\varepsilon_1 \cdot \varepsilon_2 \cdot \varepsilon_3}{\varepsilon_1(\varepsilon_2 + \varepsilon_3) + \varepsilon_2\varepsilon_3\tilde{R}_2}.$$

With the balance equation

$$\tilde{K}_o \exp\left(\quad \frac{\mu_K^o}{RT}\right) = \tilde{K} \exp\left(\quad \frac{\mu_K^o}{RT}\right) + \tilde{K}_1 \exp\left(\quad \frac{\mu_{K_1}^o}{RT}\right) + \tilde{K}_2 \exp\left(\quad \frac{\mu_{K_2}^o}{RT}\right),$$

we find eventually that

$$\frac{\theta_{K_1}}{\theta_K} = \alpha \cdot \lambda_{K_1},$$

$$\frac{\theta_{K_2}}{\theta_K} = \frac{\varepsilon_2 \alpha \tilde{R}_2 + \varepsilon_3 \tilde{P}}{\varepsilon_2 + \varepsilon_3}\lambda_{K_1}.$$

Here, α is defined by equality (4.37), $\lambda_{K_1} = \exp\left(\frac{\mu_K^o \quad \mu_{K_1}^o}{RT}\right)$, and $\lambda_{K_2} = \exp\left(\frac{\mu_K^o \quad \mu_{K_2}^o}{RT}\right)$. The further analysis should be performed by considering particular limit situations (see also Example 9).

Example 8 The process with two parallel routes of consecutive transformations of intermediates

Consider an intermediate-stationary catalyzed stepwise reaction

$$R_1 + R_2 \rightleftarrows P, \tag{4.38}$$

which proceeds through two independent routes (channels) of catalytic transformations over the same active center K:

$$\begin{gathered} K + R_1 \overset{\varepsilon_1}{\rightleftarrows} K_1 \\ K + R_2 \overset{\varepsilon_2}{\rightleftarrows} K_2 \\ K_1 + R_2 \overset{\varepsilon_3}{\rightleftarrows} P + K \\ K_2 + R_1 \overset{\varepsilon_4}{\rightleftarrows} P + K. \end{gathered} \tag{4.39}$$

This scheme is be used, for example, for describing synthesis of vinyl chloride from ethylene

$$C_2H_2 + HCl \rightleftarrows C_2H_3Cl$$

over mercury chloride supported on carbon.

In the stationary state for intermediates K_1 and K_2,

$$\frac{d[K_1]}{dt} = \varepsilon_1(\tilde{K}\cdot\tilde{R}_1 - \tilde{K}_1) - \varepsilon_3(\tilde{K}_1\cdot\tilde{R}_2 - \tilde{P}\cdot\tilde{K}) = 0$$

$$\frac{d[K_2]}{dt} = \varepsilon_2(\tilde{K}\cdot\tilde{R}_2 - \tilde{K}_2) - \varepsilon_4(\tilde{K}_2\cdot\tilde{R}_1 - \tilde{P}\cdot\tilde{K}) = 0.$$

Hence,

$$\tilde{K}_1 = \frac{\varepsilon_1\tilde{R}_1 + \varepsilon_3\tilde{P}}{\varepsilon_1 + \varepsilon_3\tilde{R}_2}\tilde{K}$$

$$\tilde{K}_2 = \frac{\varepsilon_2\tilde{R}_2 + \varepsilon_4\tilde{P}}{\varepsilon_2 + \varepsilon_4\tilde{R}_1}\tilde{K}.$$

As a result, we have

$$\begin{aligned} v_\Sigma &= \varepsilon_3\left(\tilde{K}_1\cdot\tilde{R}_2 - \tilde{P}\cdot\tilde{K}\right) + \varepsilon_4\left(\tilde{K}_2\cdot\tilde{R}_1 - \tilde{P}\cdot\tilde{K}\right) \\ &= \left[\frac{\varepsilon_3\varepsilon_1}{\varepsilon_1 + \varepsilon_3\tilde{R}_2} + \frac{\varepsilon_2\varepsilon_4}{\varepsilon_2 + \varepsilon_4\tilde{R}_1}\right]\tilde{K}\left(\tilde{R}_1\cdot\tilde{R}_2 - \tilde{P}\right) \equiv \varepsilon_\Sigma\tilde{K}\left(\tilde{R}_1\cdot\tilde{R}_2 - \tilde{P}\right). \end{aligned}$$

The stationary rate of the two-route stepwise reaction under consideration is proportional, as before, to the difference between rushes of the initial and final reaction groups.

With the balance equation

$$\tilde{K}_1\exp\left(-\frac{\mu^o_{K_1}}{RT}\right) + \tilde{K}_2\exp\left(-\frac{\mu^o_{K_2}}{RT}\right) + \tilde{K}\exp\left(-\frac{\mu^o_{K}}{RT}\right) = \tilde{K}_o\exp\left(-\frac{\mu^o_{K}}{RT}\right),$$

we have

$$v_\Sigma = \frac{\varepsilon_\Sigma\tilde{K}_o\left(\tilde{R}_1\cdot\tilde{R}_2 - \tilde{P}\right)}{1 + \lambda_{K_1}\dfrac{\varepsilon_1\tilde{R}_1 + \varepsilon_3\tilde{P}}{\varepsilon_1 + \varepsilon_3\tilde{R}_2} + \lambda_{K_2}\dfrac{\varepsilon_2\tilde{R}_2 + \varepsilon_4\tilde{P}}{\varepsilon_2 + \varepsilon_4\tilde{R}_1}}, \tag{4.40}$$

where $\lambda_{K_1} = \exp\left(\frac{\mu^o_K - \mu^o_{K_1}}{RT}\right)$, $\lambda_{K_2} = \exp\left(\frac{\mu^o_K - \mu^o_{K_2}}{RT}\right)$, and so on.

Example 9 Catalytic reaction with the successive formation of two final products

The catalytic stepwise reaction

$$R \rightleftarrows P_1 + P_2, \tag{4.41}$$

proceeds by mechanism

$$\begin{aligned} R + K &\overset{\varepsilon_1}{\rightleftarrows} K_1, \\ K_1 &\overset{\varepsilon_2}{\rightleftarrows} K_2 + P_1, \\ K_2 &\overset{\varepsilon_3}{\rightleftarrows} P_2 + K, \end{aligned} \tag{4.42}$$

where R is the initial reactant, P_1 and P_2 are final products of the stoichiometric catalytic stepwise process, K is the free active center, and K_1 and K_2 are catalytic intermediates formed on this center. This scheme is evidently identical to the preceding schemes (4.35) (4.36), provided that the stepwise reaction (4.35) goes right to left.

The stepwise process (4.41) with the transformation scheme (4.42) may be considered, for example, as a model of the alkane dehydrogenation into an olefin (product P_2) with releasing the molecular hydrogen (product P_1):

$$\text{alkane} \rightleftarrows \text{olefin} + H_2.$$

The stationary rate of stepwise process (4.41) is expressed as

$$v_{\Sigma} = \frac{d[P_2]}{dt} = \varepsilon_3(\tilde{K}_2 \quad \tilde{P}_2 \cdot \tilde{K}).$$

With the stationary concentrations of intermediates K_1 and K_2, the following relationships are valid:

$$\tilde{K}_1 = \frac{\varepsilon_1 \tilde{R} \cdot \tilde{K} + \varepsilon_2 \tilde{K}_2 \cdot \tilde{P}_1}{\varepsilon_1 + \varepsilon_2},$$

$$\tilde{K}_2 = \frac{\varepsilon_e \tilde{R} + \varepsilon_3 \tilde{P}_2}{\varepsilon_e \tilde{P}_1 + \varepsilon_3} \cdot \tilde{K},$$

where $\varepsilon_e \equiv \dfrac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}$.

Hence,

$$v_{\Sigma} = \frac{\varepsilon_3 \varepsilon_e \tilde{K}\left(\tilde{R} \quad \tilde{P}_1 \cdot \tilde{P}_2\right)}{\varepsilon_e \tilde{P}_1 + \varepsilon_3}.$$

The preceding expressions indicate that the rate-limiting stage is step 3 of the scheme at $\varepsilon_e \tilde{P}_1 \gg \varepsilon_3$ and either step 1 or step 2 (with the minimal $\boldsymbol{\varepsilon}_i$) (4.4.2) at $\varepsilon_e \tilde{P}_1 \ll \varepsilon_3$.

Express the stationary rushes and concentrations of the intermediates as functions of the stationary rush of intermediate $\tilde{K}$.

$$\begin{aligned} \tilde{K}_1 &= \frac{\varepsilon_1 \tilde{R} \cdot \tilde{K} + \varepsilon_2 \tilde{P}_1 \cdot \dfrac{\varepsilon_e \tilde{R} \cdot \tilde{K} + \varepsilon_3 \tilde{P}_2 \cdot \tilde{K}}{\varepsilon_e \tilde{P}_1 + \varepsilon_3}}{\varepsilon_1 + \varepsilon_2} \\ &= \tilde{K}\left\{\left(\varepsilon_e \tilde{P}_1 + \frac{\varepsilon_1 \varepsilon_3}{\varepsilon_1 + \varepsilon_2}\right)\tilde{R} + \frac{\varepsilon_2 \varepsilon_3}{\varepsilon_1 + \varepsilon_2}\tilde{P}_1 \cdot \tilde{P}_2\right\} \Big/ \left(\varepsilon_e \tilde{P}_1 + \varepsilon_3\right) \equiv \tilde{K} \cdot \alpha. \end{aligned} \tag{4.43}$$

The balance for all of the active species in the given stepwise reaction is written as

$$\begin{aligned} \tilde{K}_o = \tilde{K} + \lambda_{K_1}\tilde{K}_1 + \lambda_{K_2}\tilde{K}_2 = \tilde{K}\left\{1 + \lambda_K \cdot \alpha + \lambda_{K_2}\left(\frac{\varepsilon_e \tilde{R} + \varepsilon_3 \tilde{P}_2}{\varepsilon_e \tilde{P}_1 + \varepsilon_3}\right)\right\} \\ \equiv \tilde{K}\left(1 + \frac{\theta_{K_1}}{\theta_K} + \frac{\theta_{K_2}}{\theta_K}\right), \end{aligned}$$

where, as before, θ_K is the fraction of free forms of the active centers and θ_{K_i} is the occupation of the active center by intermediate K_i, $\lambda_{K_1} = \exp\left(\dfrac{\mu_K^o \quad \mu_{K_1}^o}{RT}\right)$, $\lambda_{K_2} = \exp\left(\dfrac{\mu_K^o \quad \mu_{K_2}^o}{RT}\right)$.

Then the final solution is

$$v_{\Sigma} = \frac{\varepsilon_1 \varepsilon_e \tilde{K}_o\left(\tilde{R} \quad \tilde{P}_1 \cdot \tilde{P}_2\right)}{\left(\varepsilon_e \tilde{P}_1 + \varepsilon_3\right)\left(1 + \frac{\theta_{K_1}}{\theta_K} + \frac{\theta_{K_2}}{\theta_K}\right)}. \tag{4.44}$$

Expression (4.44) is easy to analyze by considering, as before, different cases of the active center coverage by intermediates. Some specific cases are considered following.

Case *a*: Let K_2 be the predominant form of the active center: $\theta_{K_2}/\theta_K \gg 1$ and $\theta_{K_2}/\theta_K \gg \theta_{K_1}/\theta_K$. When so, then

$$\frac{\theta_{K_2}}{\theta_K} = \lambda_{K_2}\left(\frac{\varepsilon_e\tilde{R} + \varepsilon_3\tilde{P}_2}{\varepsilon_e\tilde{P}_1 + \varepsilon_3}\right)$$

and

$$v_\Sigma \approx \frac{\varepsilon_3\varepsilon_e\tilde{K}_o\left(\tilde{R} - \tilde{P}_1\cdot\tilde{P}_2\right)\left(\varepsilon_e\tilde{P}_1 + \varepsilon_3\right)}{\left(\varepsilon_e\tilde{P}_1 + \varepsilon_3\right)\lambda_{K_2}\left(\varepsilon_e\tilde{R} + \varepsilon_3\tilde{P}_2\right)} = \frac{\varepsilon_3\varepsilon_e\tilde{K}_o\left(\tilde{R} - \tilde{P}_1\cdot\tilde{P}_2\right)}{\lambda_{K_2}\left(\varepsilon_e\tilde{R} + \varepsilon_3\tilde{P}_2\right)}.$$

When product P_2 of the stepwise reaction controls the occupation of the active center with the intermediate K_2 (i.e., $\varepsilon_e\tilde{R} \ll \varepsilon_3\tilde{P}_2$), then

$$v_\Sigma \approx \frac{\varepsilon_3\varepsilon_e\tilde{K}_o\left(\tilde{R} - \tilde{P}_1\cdot\tilde{P}_2\right)}{\lambda_{K_2}\varepsilon_3\tilde{P}_2} = \frac{\varepsilon_e\tilde{K}_o}{\lambda_{K_2}}\frac{\left(\tilde{R} - \tilde{P}_1\cdot\tilde{P}_2\right)}{\tilde{P}_2}.$$

In the case of the kinetically irreversible "left-to-right" catalytic stepwise reaction, $\tilde{R} \gg \tilde{P}_1\cdot\tilde{P}_2$ and

$$v_\Sigma \approx \frac{\varepsilon_e\tilde{K}_o}{\lambda_{K_2}}\frac{\tilde{R}}{\tilde{P}_2} = \varepsilon_e\frac{[K]_o[R]}{[P_2]}\exp\left(\frac{\mu^o_{K_2} + \mu^o_R - \mu^o_{P_2}}{RT}\right).$$

One can easily find the apparent activation energy from this expression:

$$E_{a\Sigma} = E_{a\ \min 1,2} - \Delta_r H^o_3 = E_{a\ \min 1,2} + Q_{ads\ P_2}.$$

Here, $E_{a\ \min 1,2}$ stands for the activation energy at the step defining ε_e (E_{a1} is used at $\varepsilon_1 \ll \varepsilon_2$ and E_{a2} at $\varepsilon_1 \gg \varepsilon_2$), and $\Delta_r H^o_3 = -Q_{ads\ P_2}$ means the standard enthalpy of step 3.

Case *b*: Let intermediate K_1 be the dominating form of the active center — that is, $\theta_{K_1}/\theta_K \gg 1$ and $\theta_{K_1}/\theta_K \gg \theta_{K_2}/\theta_K$ — and the control of the active center coverage also be accounted for by product P of the stepwise reaction — that is,

$$\left(\varepsilon_e\tilde{P}_1 + \frac{\varepsilon_1\varepsilon_3}{\varepsilon_1 + \varepsilon_2}\right)\tilde{R} \ll \frac{\varepsilon_2\varepsilon_3}{\varepsilon_1 + \varepsilon_2}\tilde{P}_2\cdot\tilde{P}_1$$

(see expression (4.43)). Then,

$$v_\Sigma \approx \frac{\varepsilon_3\varepsilon_e\tilde{K}_o\left(\tilde{R} - \tilde{P}_2\cdot\tilde{P}_1\right)}{\lambda_{K_1}\left(\frac{\varepsilon_2\varepsilon_3}{\varepsilon_1 + \varepsilon_2}\tilde{P}_2\cdot\tilde{P}_1\right)} = \varepsilon_1\frac{\tilde{K}_o\left(\tilde{R} - \tilde{P}_2\cdot\tilde{P}_1\right)}{\lambda_{K_1}\tilde{P}_1\cdot\tilde{P}_2}.$$

Obviously, step 1 is the rate-determining stage here irrespective of the rate-limiting step.

When $\tilde{R} \gg \tilde{P}_1 \cdot \tilde{P}_2$ here, then

$$E_{a\Sigma} = E_{a1} - \Delta_r H_2^o - \Delta_r H_3^o = E_{a1} + Q_{ads\,P_1} + Q_{ads\,P_2}.$$

Here, $\Delta_r H_2^o = -Q_{ads\,P_1}$ and $\Delta_r H_3^o = -Q_{ads\,P_2}$ are, as before, the standard enthalpies of steps 2 and 3 of scheme (4.42).

Example 10 Catalytic dismutation of an initial reactant

Consider an even more complex catalytic stepwise reaction

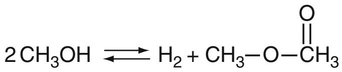
$$2R \rightleftarrows P_1 + P_2, \tag{4.45}$$

which proceeds by mechanism

$$\begin{aligned} R + K &\overset{\varepsilon_1}{\rightleftarrows} K_1, \\ K_1 &\overset{\varepsilon_2}{\rightleftarrows} K_2 + P_1, \\ K_2 + R &\overset{\varepsilon_3}{\rightleftarrows} K_3, \\ K_3 &\overset{\varepsilon_4}{\rightleftarrows} P_2 + K, \end{aligned} \tag{4.46}$$

where R is the initial reactant; P_1 and P_2 are the final products; and K_1, K_2, and K_3 are catalytic intermediates.

In principle, this scheme can describe dehydrogenation of methanol to form methylformate:



$$2\,CH_3OH \rightleftarrows H_2 + CH_3{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}H_3$$

The stationary rate of the catalytic stepwise process is

$$v_\Sigma = \frac{d[P_2]}{dt} = \varepsilon_4(\tilde{K}_3 - \tilde{P}_2 \cdot \tilde{K}).$$

If the process is stationary in respect to the intermediate concentrations, then

$$\frac{d[K_1]}{dt} = \varepsilon_1(\tilde{R} \cdot \tilde{K} - \tilde{K}_1) - \varepsilon_2(\tilde{K}_1 - \tilde{K}_2 \cdot \tilde{P}_1) = 0,$$

$$\frac{d[K_2]}{dt} = \varepsilon_2(\tilde{K}_1 - \tilde{K}_2 \cdot \tilde{P}_1) - \varepsilon_3(\tilde{K}_2 \cdot \tilde{R} - \tilde{K}_3) = 0,$$

$$\frac{d[K_3]}{dt} = \varepsilon_3(\tilde{K}_2 \cdot \tilde{R} - \tilde{K}_3) - \varepsilon_4(\tilde{K}_3 - \tilde{P}_2 \cdot \tilde{K}) = 0.$$

It follows from the first equality that

$$\tilde{K}_1 = \frac{\varepsilon_1 \tilde{R} \cdot \tilde{K} + \varepsilon_2 \tilde{K}_2 \cdot \tilde{P}_1}{\varepsilon_1 + \varepsilon_2}.$$

The second equality, into which we substitute $\tilde{K}_1$ and $\varepsilon_e = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}$, gives us the stationary value of $\tilde{K}_2$:

$$\tilde{K}_2 = \frac{\varepsilon_e \tilde{R} \cdot \tilde{K} + \varepsilon_3 \tilde{K}_3}{\varepsilon_e \tilde{P}_1 + \varepsilon_3 \tilde{R}}.$$

By substituting $\tilde{K}_2$ into the third equality, we find

$$\tilde{K}_3 = \frac{\varepsilon_e \varepsilon_4 \tilde{P}_1 \cdot \tilde{P}_2 + \varepsilon_3 \varepsilon_4 \tilde{R} \cdot \tilde{P}_2 + \varepsilon_e \varepsilon_3 \tilde{R}^2}{\varepsilon_e \varepsilon_4 \tilde{P}_1 + \varepsilon_3 \varepsilon_4 \tilde{R} + \varepsilon_3 \varepsilon_e \tilde{P}_1} \tilde{K}.$$

Hence, in general, the stationary rate of the catalytic stepwise process under consideration is written as

$$v_\Sigma = \varepsilon_4 \frac{\varepsilon_3 \varepsilon_e (\tilde{R}^2 \quad \tilde{P}_1 \cdot \tilde{P}_2) \cdot \tilde{K}}{\varepsilon_e (\varepsilon_4 + \varepsilon_3) \tilde{P}_1 + \varepsilon_3 \varepsilon_4 \tilde{R}}.$$

The balance relationship here is

$$\tilde{K}_o = \tilde{K} + \lambda_{K_1} \tilde{K}_1 + \lambda_{K_2} \tilde{K}_2 + \lambda_{K_3} \tilde{K}_3 = \tilde{K} \left(1 + \frac{\theta_{K_1}}{\theta_K} + \frac{\theta_{K_2}}{\theta_K} + \frac{\theta_{K_3}}{\theta_K} \right),$$

where $\lambda_{K_1} = \exp\left(\frac{\mu_K^o \quad \mu_{K_1}^o}{RT} \right)$, $\lambda_{K_2} = \exp\left(\frac{\mu_K^o \quad \mu_{K_2}^o}{RT} \right)$, and $\lambda_{K_3} = \exp\left(\frac{\mu_K^o \quad \mu_{K_3}^o}{RT} \right)$.
The stationary occupation of the active center by the intermediates can be easily determined using the found stationary values of $\tilde{K}_1$, $\tilde{K}_2$, and $\tilde{K}_3$.

For example, if K_3 species predominates in the active center, then $\theta_{K_3}/\theta_K \gg 1$, $\theta_{K_3}/\theta_K \gg \theta_{K_2}/\theta_K$, and the stationary rate of the overall catalytic stepwise process is described by the expression

$$v_\Sigma = \varepsilon_4 \frac{\varepsilon_3 \varepsilon_e \tilde{K}_o \left(\tilde{R}^2 \quad \tilde{P}_1 \cdot \tilde{P}_2 \right)}{\lambda_{K_3} \left\{ \varepsilon_e \varepsilon_4 \tilde{P}_1 \cdot \tilde{P}_2 + \varepsilon_3 \varepsilon_4 \tilde{R} \cdot \tilde{P}_2 + \varepsilon_3 \varepsilon_e \tilde{R}^2 \right\}}. \tag{4.47}$$

If product P_2 controls the stationary coverage of the active center by intermediate K_3, then

$$\begin{aligned} v_\Sigma &= \varepsilon_4 \frac{\varepsilon_3\varepsilon_e}{\lambda_{K_3}\left[\varepsilon_e\varepsilon_4\tilde{P}_1 \cdot \tilde{P}_2 + \varepsilon_3\varepsilon_4\tilde{R} \cdot \tilde{P}_2\right]}\tilde{K}_o\left(\tilde{R}^2 \quad \tilde{P}_1 \cdot \tilde{P}_2\right) \\ &= \frac{\varepsilon_3\varepsilon_e}{\lambda_{K_3}\left(\varepsilon_e\tilde{P}_1 + \varepsilon_e\tilde{R}\right)\tilde{P}_2}\tilde{K}_o\left(\tilde{R}^2 \quad \tilde{P}_1 \cdot \tilde{P}_2\right). \end{aligned} \tag{4.48}$$

The preceding procedures can be applied to find the apparent activation energies of the stationary stepwise process in any cases of interest.

4.2.3. Stationary Microkinetics of the Simplest Catalytic Reactions with Nonlinear Catalytic Intermediates

The preceding schemes of catalytic stepwise reactions were linear in respect to the catalytic intermediates. When several interacting external reactants are involved in the reaction groups of the heterogeneous catalytic stepwise process, this linearity condition relates to the Eley Rideal "collision" mechanism. Meanwhile, the thorough experimental studies on the mechanisms of real heterogeneous catalytic reactions concentrate more often on the Langmuir Hinshelwood rather than on the Eley Rideal mechanisms. The said mechanism implies a cross interaction of surface catalytic intermediates, so most of heterogeneous catalytic processes are intermediate nonlinear.

It is always much more difficult to analyze the intermediate nonlinear schemes than to analyze the linear schemes. Usually, there is no general analytic solution here, and only a narrow range of conditions can be considered via analyzing simple mathematical expressions without the help of computers. In some cases, one can use the mathematical solutions obtained for similar noncatalytic stepwise transformations, but these solutions must still be corrected via the balance for all possible forms of active centers that should be then taken into account.

Example 11 Catalytic dimerization of an initial reactant

Consider a simple stepwise catalytic reaction

$$2R \rightleftarrows P, \tag{4.49}$$

which occurs through the steps

$$\begin{aligned} R + K &\overset{\varepsilon_1}{\rightleftarrows} K_1 \\ 2K_1 &\overset{\varepsilon_2}{\rightleftarrows} P + 2K, \end{aligned} \tag{4.50}$$

and thus is nonlinear in respect of catalytic intermediate K_1. The noncatalytic version of this mechanism was considered in the respective Example of Section 1.3.2. From this example, near the thermodynamic equilibrium, for the stationary rate of the catalytic stepwise process,

$$v_\Sigma \equiv \frac{d[P]}{dt} = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + 4\varepsilon_2\tilde{K}\tilde{R}}\left(\tilde{K}^2\tilde{R}^2 \quad \tilde{K}^2 \cdot \tilde{P}\right) \tag{4.51}$$

(see (1.46)). The condition of neighboring to equilibrium is evidently $\tilde{R}^2 \approx \tilde{P}$ (or, more specifically, $\tilde{K}^2\left(\tilde{R}^2 \quad \tilde{P}\right) \ll \left(\tilde{K}\cdot\tilde{R} + \frac{\varepsilon_1}{2\varepsilon_2}\right)^2$).

The balance equation for all types of active centers of the catalyst is here

$$\tilde{K}_o = \tilde{K} + \lambda_{K_1}\tilde{K}_1 \approx \tilde{K}\left(1 + \lambda_{K_1}\tilde{R}\right), \tag{4.52}$$

in view of $\tilde{K}_1 \approx \tilde{K}\cdot\tilde{R}$ near the system equilibrium. As before, here, $\lambda_{K_1} = \exp\left(\frac{\mu_K^o \quad \mu_{K_1}^o}{RT}\right)$.

When the first reaction of the scheme (4.50) is the rate-limiting step of the overall process, the valid unequality is

$$\varepsilon_1 \ll 4\varepsilon_2\tilde{K}\cdot\tilde{R}.$$

Here,

$$v_\Sigma \approx \frac{\varepsilon_1\tilde{K}\left(\tilde{R}^2 \quad \tilde{P}\right)}{4\tilde{R}}.$$

With the balance equation (4.52), the target equation for the stationary rate can be written in an easily treatable form:

$$v_\Sigma \approx \frac{\varepsilon_1\tilde{K}_o}{\left(1 + \lambda_{K_1}\tilde{R}\right)\tilde{R}}\left(\tilde{R}^2 \quad \tilde{P}\right). \tag{4.53}$$

If step 2 is the rate-limiting one, then

$$\varepsilon_1 \gg 4\varepsilon_2\tilde{K}\cdot\tilde{R},$$

and

$$v_\Sigma \approx \frac{\varepsilon_2\tilde{K}_o^2}{\left(1 + \lambda_{K_1}\tilde{R}\right)^2}\left(\tilde{R}^2 \quad \tilde{P}\right). \tag{4.54}$$

It is easy enough to analyze expressions (4.53) and (4.54), for example, in order to find the apparent activation energy for the cases of both low ($\lambda_{K_1}\tilde{R} \ll 1$) and high ($\lambda_{K_1}\tilde{R} \gg 1$) occupation of the active center by the catalytic intermediate.

The limit cases are much more difficult to analyze when process (4.49) occurs far from equilibrium that is, $\tilde{R}^2 \gg \tilde{P}$ (the left-to-right process) or $\tilde{P} \gg \tilde{R}^2$ (the right-to-left process). The most difficult element here is finding the stationary value of $\tilde{K}_1$ as a function of $\tilde{K}$, which is necessary to calculate the stationary occupation of the active center by the catalytic intermediate.

Let us consider some of these situations:

The case of $\tilde{R}^2 \gg \tilde{P}$*:* If the rate-limiting step is step 1 ($\varepsilon_1 \ll 4\varepsilon_2\tilde{K}\cdot\tilde{R}$), then the consideration in the respective Example of Section 1.3.2 gives

$$v_{\Sigma} = \frac{d[P]}{dt} \approx \frac{\varepsilon_1\tilde{K}\cdot\tilde{R}}{2}, \tag{4.55}$$

and

$$\tilde{K}_1 \approx \tilde{K}\cdot\sqrt{\tilde{P}} \ll \tilde{K}\cdot\tilde{R}. \tag{4.56}$$

Here,

$$v_{\Sigma} \approx \frac{\varepsilon_1\tilde{K}_o\cdot\tilde{R}}{1+\lambda_{K_1}\sqrt{\tilde{P}}}. \tag{4.57}$$

Again, it is easy to analyze this expression and, for example, to find the apparent activation energy and so forth.

If the rate-limiting step is step 2 ($4\varepsilon_2\tilde{K}\cdot\tilde{R} \ll \varepsilon_1$), then

$$v_{\Sigma} \approx \varepsilon_2\tilde{K}^2\cdot\tilde{R}^2 = \frac{\varepsilon_2\tilde{K}_o^2\cdot\tilde{R}^2}{\left(1+\lambda_{K_1}\tilde{R}\right)^2} \tag{4.58}$$

because $\tilde{K}_1 \approx \tilde{R}\cdot\tilde{K}$ here.

Note that in this case the dominating form of the active site is the intermediate,

$$v_{\Sigma} \approx \frac{\varepsilon_2\tilde{K}_o^2}{\lambda_{K_1}^2} = \varepsilon_2[K]_o^2\exp\left(\frac{2\mu_{K_1}^o}{RT}\right); \tag{4.59}$$

that is, the rate is independent of the external reagents concentration, and the apparent activation energy is equal to the activation energy of step 2:

$$E_{a\Sigma} = E_{a2}.$$

The right-to-left reaction is considered in a similar way, provided that $\tilde{P} \gg \tilde{R}^2$ (the data of the respective Example in Section 1.3.2 can be used for the consideration). It is important that the stationary state for schemes (4.49) (4.50) is always stable.

Example 13 Catalytic oxidation of carbon monoxide by molecular oxygen

The catalytic stepwise reaction

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \tag{4.60}$$

is a classic example of the reaction with the thoroughly investigated mechanism for both homogeneous or heterogeneous catalysts, the mechanism being dependent on the nature of the catalyst.

For example, for many metal catalysts, the simplified mechanism is usually described via the following scheme:

$$\begin{aligned} &O_2 + 2K \overset{\varepsilon_1}{\rightleftarrows} 2K_1,\\ &K + CO \overset{\varepsilon_2}{\rightleftarrows} K_2,\\ &K_1 + K_2 \overset{\varepsilon_3}{\rightleftarrows} 2K + CO_2. \end{aligned} \tag{4.61}$$

Here, K is the free form of the active center, and K_1 and K_2 are catalytic intermediates (the chemisorbed forms of atomic oxygen and carbon monoxide).

Let us find the rate and apparent activation energy of the stationary process in a particular situation of the kinetically irreversible stepwise reaction of the CO oxidation, step 1 being the rate-limiting stage and intermediate K_2 being dominant on the surface. The stationary rate of the overall stepwise process (4.60) is

$$v_{\Sigma} = \frac{d[CO_2]}{dt} = \varepsilon_3\left(\tilde{K}_1 \cdot \tilde{K}_2 \quad \tilde{K}^2 \cdot \tilde{C}O_2\right) = \frac{1}{2}\varepsilon_1\left(\tilde{O}_2 \cdot \tilde{K}^2 \quad \tilde{K}_1^2\right).$$

When the process is stationary, then also

$$\begin{aligned} \frac{d[K_1]}{dt} &= 2\varepsilon_1\left(\tilde{O}_2 \cdot \tilde{K}^2 \quad \tilde{K}_1^2\right) \quad \varepsilon_3\left(\tilde{K}_1 \cdot \tilde{K}_2 \quad \tilde{K}^2 \cdot \tilde{C}O_2\right) = 0\\ \frac{d[K_2]}{dt} &= \varepsilon_2\left(\tilde{K} \cdot \tilde{C}O \quad \tilde{K}_2\right) \quad \varepsilon_3\left(\tilde{K}_1 \cdot \tilde{K}_2 \quad \tilde{K}^2 \cdot \tilde{C}O_2\right) = 0 \end{aligned} \tag{4.62}$$

If step 1 is rate-limiting, this is the kinetically irreversible step:

$$\tilde{O}_2 \cdot \tilde{K}^2 \gg \tilde{K}_1^2.$$

Therefore,

$$v_{\Sigma} = \frac{1}{2}\varepsilon_1 \tilde{O}_2 \cdot \tilde{K}^2. \tag{4.63}$$

The next step of the analysis is to express $\tilde{K}$ via the "external" parameters. By taking into consideration, as before, the balance for various type active centers, we get

$$\tilde{K} = \frac{\tilde{K}_o}{1 + \left(\frac{\theta_{K_1}}{\theta_K}\right) + \left(\frac{\theta_{K_2}}{\theta_K}\right)}.$$

By the condition, intermediate K_2 dominates on the surface that is, $\frac{\theta_{K_2}}{\theta_K} = \frac{\tilde{K}_2}{\tilde{K}}\lambda_{K_2} \gg 1$ and

$$\frac{\theta_{K_2}}{\theta_K} \gg \frac{\theta_{K_1}}{\theta_K},$$

where $\lambda_{K_2} = \exp\left(\frac{\mu_K^o \quad \mu_{K_2}^o}{RT}\right)$.

Hence,

$$v_\Sigma \approx \frac{\varepsilon_1 \tilde{O}_2 \cdot \tilde{K}_o^2}{2\lambda_{K_2}^2 \left(\tilde{K}_2 \tilde{K}\right)^2}.$$

The solution of the problem needs ratio $\tilde{K}_2/\tilde{K}$ to be expressed via external parameters and $\tilde{K}$. It follows from (4.62) and from the condition of kinetic irreversibility of step 1 that

$$\varepsilon_2\left(\tilde{K} \cdot \tilde{CO} \quad \tilde{K}_2\right) \approx 2\varepsilon_1 \tilde{O}_2 \cdot \tilde{K}^2$$

and, therefore,

$$\tilde{K}_2 = \frac{\varepsilon_2 \tilde{K} \cdot \tilde{CO} \quad 2\varepsilon_1 \tilde{O}_2 \cdot \tilde{K}^2}{\varepsilon_2} = \tilde{K} \cdot \tilde{C}O \quad \frac{2\varepsilon_1}{\varepsilon_2} \tilde{O}_2 \cdot \tilde{K}^2.$$

While the numerator expression is complex, it seems reasonable to inspect two limit situations.

Case *a*:

$$\varepsilon_2 \tilde{K} \cdot \tilde{CO} \gg 2\varepsilon_1 \tilde{O}_2 \cdot \tilde{K}^2.$$

This means partial equilibrium of the second step in scheme (4.61). When so, then

$$\tilde{K}_2 \approx \tilde{K} \cdot \tilde{CO}$$

and

$$\frac{\theta_{K_2}}{\theta_K} = \frac{\tilde{K}_2}{\tilde{K}} \exp\left(\frac{\mu^o_K \quad \mu^o_{K_2}}{RT}\right) = \tilde{CO} \cdot \exp\left(\frac{\mu^o_K \quad \mu^o_{K_2}}{RT}\right).$$

Hence, in the case under discussion,

$$v_\Sigma = \frac{\varepsilon_1 \tilde{O}_2 \cdot \tilde{K}^2_o}{2\tilde{CO}^2} \exp\left\{\frac{2\left(\mu^o_{K_2} \quad \mu^o_K\right)}{RT}\right\} = \frac{\varepsilon_1 [O_2][K]_o}{2[CO]^2} \exp\left(\frac{\mu^o_{O_2} + 2\mu^o_{K_2} \quad 2\mu^o_{CO})}{RT}\right)$$

and, in understandable terms, the activation energy of the stationary stepwise process is

$$\begin{aligned} E_{a\Sigma} &= \Delta_f H_1^{/o} \quad \Delta_f H^o_{O_2} \quad 2\Delta_f H^o_K + 2\Delta_f H^o_{CO} \quad 2\Delta_f H^o_{K_2} + 2\Delta_f H^o_K + RT \\ &= E_{a1} \quad 2\Delta_f H^o_{K_2} + 2\Delta_f H^o_K \quad 2\Delta_f H^o_{CO} = E_{a1} \quad 2\Delta_r H^o_2. \end{aligned} \tag{4.64}$$

Case *b*:

$$\varepsilon_2 \tilde{K} \cdot \tilde{CO} \ll 2\varepsilon_1 \tilde{O}_2 \cdot \tilde{K}^2.$$

Evidently, this is an unrealistic situation for the stationary occurrence of the reaction (4.60). Indeed, for such an occurrence, the necessary condition is $\tilde{K} \cdot \tilde{CO} > \tilde{K}_2$, which does not satisfy the preceding inequality.

As for the stability of the found stationary solutions, it needs an additional particular analysis, since some of steady states in the nonlinear catalytic reaction under discussion are known to be unstable.

Example 14 Catalytic synthesis of ammonia

Another classic example of nonlinear catalytic processes is synthesis of ammonia:

$$N_2 + 3H_2 \leftrightarrows 2NH_3. \tag{4.65}$$

The reaction is assumed to occur over iron catalysts as

$$\begin{aligned} &N_2 + K \overset{\varepsilon_1}{\rightleftarrows} K_1, \\ &K_1 + H_2 \overset{\varepsilon_2}{\rightleftarrows} K_2, \\ &K_2 + K \overset{\varepsilon_3}{\rightleftarrows} 2K_3, \\ &K_3 + H_2 \overset{\varepsilon_4}{\rightleftarrows} K + NH_3, \end{aligned} \tag{4.66}$$

where K is the free form of the active center, and K_1, K_2, and K_3 are catalytic intermediates.

Let us find the apparent activation energy of the stationary process provided that the overall process is kinetically irreversible, step 2 is rate-limiting, and the catalyst surface is covered predominantly by intermediate K_3 Under this statement of the problem, step 2 is kinetically irreversible, while the preceding step 1 being considered partially equilibrium that is, $\tilde{K}_1 = \tilde{N}_2 \cdot \tilde{K}$
Thus,

$$\begin{aligned} v_{\Sigma} = {} & \frac{d[N_2]}{dt} = \varepsilon_2 \tilde{K}_1 \cdot \tilde{H}_2 = \varepsilon_2 \tilde{N}_2 \cdot \tilde{K} \cdot \tilde{H}_2 \\ & = \frac{\varepsilon_2 \tilde{N}_2 \tilde{H}_2 \tilde{K}_o}{1 + \dfrac{\theta_{K_1}}{\theta_K} + \dfrac{\theta_{K_2}}{\theta_K} + \dfrac{\theta_{K_3}}{\theta_K}} \approx \frac{\varepsilon_2 \tilde{N}_2 \tilde{H}_2 \tilde{K}_o}{\dfrac{\theta_{K_3}}{\theta_K}}. \end{aligned} \tag{4.67}$$

As earlier,

$$\frac{\theta_{K_3}}{\theta_K} = \lambda_{K_3} \frac{\tilde{K}_3}{\tilde{K}},$$

where $\lambda_{K_3} = \exp\left(\dfrac{\mu_K^o \quad \mu_{K_3}^o}{RT}\right)$.

Find the ratio $\tilde{K}_3/\tilde{K}$ by solving the system of two equations:

$$\begin{aligned} \frac{d[K_3]}{dt} &= 2\varepsilon_3 \left(\tilde{K}_2 \cdot \tilde{K} \quad \tilde{K}_3^2\right) \quad \varepsilon_4 \left(\tilde{K}_3 \cdot \tilde{H}_2 \quad \tilde{K} \cdot \tilde{N}H_3\right) = 0, \\ \frac{d[K_2]}{dt} &= \varepsilon_2 \left(\tilde{K}_1 \cdot \tilde{H}_2 \quad \tilde{K}_2\right) \quad \varepsilon_3 \left(\tilde{K} \cdot \tilde{K}_2 \quad \tilde{K}_3^2\right) \\ &\approx \varepsilon_2 \cdot \tilde{K} \cdot \tilde{N}_2 \cdot \tilde{H}_2 \quad \varepsilon_3 \left(\tilde{K} \cdot \tilde{K}_2 \quad \tilde{K}_3^2\right) = 0. \end{aligned}$$

Hence,

$$\tilde{K}_3 \approx \tilde{K} \frac{2\varepsilon_2 \tilde{H}_2 \tilde{N}_2 + \varepsilon_4 \tilde{N}H_3}{\varepsilon_4 \tilde{H}_2}$$

and, therefore,

$$v_{\Sigma} = \frac{\varepsilon_2 \tilde{N}_2 \cdot \tilde{H}_2 \cdot \tilde{K}_o}{\lambda_3 \left(\dfrac{2\varepsilon_2 \tilde{H}_2 \cdot \tilde{N}_2 + \varepsilon_4 \tilde{N}H_3}{\varepsilon_4 \tilde{H}_2}\right)}.$$

There are two limit cases of this expression to be analyzed.

Case *a*:

At $2\varepsilon_2 \cdot \tilde{H}_2 \cdot \tilde{N}_2 \gg \varepsilon_4 \cdot \tilde{N}H_3$, the coverage of the surface with catalytic intermediates is controlled by starting reagents. At this condition,

$$v_\Sigma = \frac{\varepsilon_4 \tilde{H}_2 \cdot \tilde{K}_o}{2\lambda_{K_3}} = \varepsilon_4 \frac{[H_2][K]_o}{2} \exp\left(\frac{\mu^o_{H_2} + \mu^o_{K_3}}{RT}\right) \tag{4.68}$$

and the apparent activation energy in understandable notations equals

$$E_{a\Sigma} = E_{a4}.$$

Case *b*:

At $2\varepsilon_2 \cdot \tilde{H}_2 \cdot \tilde{N}_2 \ll \varepsilon_4 \cdot \tilde{N}H_3$, the coverage of the surface is controlled by the target product ammonia and thus,

$$\begin{aligned} v_\Sigma &= \varepsilon_2 \frac{\tilde{N}_2 \cdot \tilde{H}_2^2}{\lambda_{K_3} N\tilde{H}_3} \cdot \tilde{K}_o \\ &= \varepsilon_2 \frac{[N_2][H_2]^2[K]_o}{[NH_3]} \exp\left(\frac{\mu^o_{N_2} + 2\mu^o_{H_2} \quad \mu^o_{NH_3} + \mu^o_{K_3}}{RT}\right). \end{aligned} \tag{4.69}$$

The apparent activation energy in this situation equals

$$E_{a\Sigma} = E_{a2} + \Delta_r H^o_1 + \Delta_r H^o_4. \tag{4.70}$$

4.3. STABILITY OF THE STATIONARY STATE OF THE OPERATING CATALYST

The preceding examples demonstrate the possibility of the deduction of microkinetic expressions for the stationary rates of various stepwise catalytic processes followed by thermodynamic analysis of the obtained expressions. It is obvious, however, that the analysis is only meaningful when the said stationary states are stable in respect to the concentrations of the catalytic intermediates.

In a general case of catalytic stepwise reactions with a large number of catalytic intermediates, the kinetic methods are indeed preferable to analyze the stability of the stationary state of the system. This can be done by considering the evolution of minor fluctuations in the concentrations (rushes) of the catalytic intermediates or by finding the Lyapunov function of the given stepwise transformations. In the latter case, the possibility of constructing the Lyapunov function is unambiguous evidence of the stability of the stationary state of the system (see Section 3.4.1).

In general, the presence of a catalyst in the system with the catalytic intermediate linear transformations and, as a consequence, the necessarily existent balances of type (4.1) in respect to all forms of active centers does not affect the stability of the stationary state in the system. This is due to specific features of these systems where the said mass balance does not hinder writing the Lyapunov functions.

4.3.1. The Lyapunov Function for Catalytic Transformations with Linear Catalytic Intermediates

A specific feature of catalytic schemes that imply the type (4.1) balance is the potential involvement of independent internal variables like $\tilde{K}_i/\tilde{K}$ and θ_{K_i}/θ_K instead of, for example, thermodynamic rushes of intermediates $\tilde{K}_i$. This is due to the existent balance relations.

Let us demonstrate how this specific feature of the catalytic reactions appears with the Lyapunov function Φ for the catalytic stepwise reaction

$$R \rightleftarrows P,$$

which follows the simplest scheme of catalytic transformations (4.4):

$$\begin{aligned} &R + K \overset{\varepsilon_1}{\rightleftarrows} K_1,\\ &K_1 \overset{\varepsilon_2}{\rightleftarrows} P + K. \end{aligned}$$

It is easy to deduce the writing of the relevant Lyapunov function in the form

$$\Phi = \varepsilon_1\left(\tilde{R} - \frac{\tilde{K}_1}{\tilde{K}}\right)^2 + \varepsilon_2\left(\frac{\tilde{K}_1}{\tilde{K}} - \tilde{P}\right)^2. \tag{4.71}$$

The $\tilde{K}_1/\tilde{K}$ ratio (“reduced thermodynamic rush of catalytic intermediate K_1”) should be treated here as an independent internal variable that describes the spontaneous evolution of the system in tending to its stationary state. In fact,

$$\frac{\partial\Phi}{\partial\left(\tilde{K}_1/\tilde{K}\right)} = -2\varepsilon_1\left(\tilde{R} - \frac{\tilde{K}_1}{\tilde{K}}\right) + 2\varepsilon_2\left(\frac{\tilde{K}_1}{\tilde{K}} - \tilde{P}\right) \equiv -\frac{2}{\tilde{K}}\frac{d[K_1]}{dt} \sim \frac{d[K_1]}{dt} \equiv v_{K_1};$$

that is, the positively defined functional Φ is minimized (as a function of variable $\tilde{K}_1/\tilde{K}$) in the point of stationarity in respect of the intermediate K_1 concentration.

Function (4.71) is easier to obtain by modifying formally scheme (4.4) of catalytic transformations into scheme

$$\begin{gathered} R \overset{\varepsilon_1}{\rightleftarrows} (K_1 - K), \\ (K_1 - K) \overset{\varepsilon_2}{\rightleftarrows} P. \end{gathered}$$

Recall that the occurrence of the positively defined Lyapunov function is the necessary and sufficient condition of the uniqueness and stability of the stationary state (see Section 3.4).

The Lyapunov function Φ in the form of type (4.71) definite quadratic expression can be constructed for many other simple schemes of catalytic transformations, too, to allow the conclusion about stability of the catalyst in these systems. In particular, this conclusion is true in the case of any intermediate linear transformations—that is, one free of interactions between active centers of the catalyst. The conclusion also is valid for the cases of more complex schemes that imply possibilities of the formation and coexistence of intermediates of the stepwise transformations, which escape the catalyst surface for the gas (liquid) phase provided that the intermediate catalytic complexes do not interact with one another.

Functional Φ, expressed as (4.71), is easy to modify so it will describe an arbitrary set of monomolecular transformations of catalytic intermediates (i.e., intermediate "reactant–active center" complexes):

$$R + K \rightleftarrows \{K_i\} \rightleftarrows P + K, \tag{4.72}$$

where $\{K_i\}$ is an arbitrary array of monomolecular transformations of intermediates K_i (see also Section 3.4.1 and Example 3). The stationary catalytic reaction occurs here at the minimum of expression

$$\Phi \equiv \sum_{i=1}^{k}\sum_{j=1}^{k} \varepsilon_{ij}\left(\frac{\tilde{K}_i}{\tilde{K}} - \frac{\tilde{K}_j}{\tilde{K}}\right)^2 + 2\sum_{i} \varepsilon_{Ri}\left(\tilde{R} - \frac{\tilde{K}_j}{\tilde{K}}\right)^2 + 2\sum_{i} \varepsilon_{iP}\left(\tilde{P} - \frac{\tilde{K}_i}{\tilde{K}}\right)^2. \tag{4.73}$$

The $\tilde{K}_i/\tilde{K}$ ratio should be used here (like expression (4.71)), not individual thermodynamic rushes $\tilde{K}_i$, as an independent "internal" variable for minimizing the functional.

The $\tilde{K}_i/\tilde{K}$ ratios are independent internal variables that may be called reduced thermodynamic rushes of catalytic intermediates:

$$\tilde{K}_i/\tilde{K} \equiv \exp\left\{\left(\mu_{K_i} - \mu_K\right)/RT\right\}.$$

An illustrative result of applying the reduced thermodynamic rushes is the identical scale shifts by the same value μ_K in the diagrams of chemical potentials μ_{K_i} of the catalytic intermediates.

Expression (4.73) is a positively defined quantity, too, and it decreases monotonically in the course of the evolution of the spontaneous system. Therefore, the existence of Φ implies the existence of the intermediate stable stationary state of the system. The summation is over all the possible intermediates "i", "j" of the catalytic transformation. The sum is minimized by varying the Φ expression in respect of the independent "internal" variables $\left(\tilde{K}_i/\tilde{K}\right)$, $\left(\tilde{K}_j/\tilde{K}\right)$ at fixed $\tilde{R}$ and $\tilde{P}$.

As soon as the system approaches the stationary state, the Lyapunov function takes its minimal quantity:

$$\Phi = \varepsilon_\Sigma \tilde{K}^2\left(\tilde{R} - \tilde{P}\right)^2.$$

Thus, the approach to the stationary state of any "simple" (i.e., undergoing monomolecular or reduced to monomolecular transformations) reaction of the catalytic intermediates means the catalyst functioning at the minimal rate of energy dissipation in terms of the identical electric circuit.

An important consequence of this conclusion is that the reversible evolution of the system toward its stationary state, which is accompanied by reversible surface reconstruction, must tend in many cases to the minimal (under the given conditions) stationary rate of the catalyzed reaction. When fresh catalyst species are in the thermodynamic equilibrium and are at the same temperature as the environment that is incapable (because of an incomplete reactant set or thermodynamically equilibrium reactant composition) of entering the said conjugating reaction, this catalyst appears more catalytically active in the beginning of the reaction than in the end, when another stationary state is achieved under these conditions.

The assumption of the reversible "self inhibition" of the operating catalyst is based on the requirement on the minimal rate of entropy production (energy dissipation) at the real stationary mode. The applicability of this requirement for many catalytic systems is exemplified by particular simple schemes where the catalyst is capable of reversible phase transitions.

At the same time, phenomena of contrary natures are well known—for example, an increase in the concentration of high active catalyst centers during the reaction due to transforming the state of the catalyst precursor under the action of the reaction medium (reduction of inactive ionic species of the active metal to the active metal state, etc.).

The preceding algorithm allows the Lyapunov function to be deter mined for more complex schemes of catalytic transformations that are lin ear in respect to the involved catalytic intermediates. For example, in Example 6, the positively defined Lyapunov functional exists for the transformation scheme under consideration:

$$\Phi = \varepsilon_1\left(\tilde{R}_1 - \frac{\tilde{K}_1}{\tilde{K}}\right)^2 + \frac{\varepsilon_P}{\tilde{R}_2}\left(\frac{\tilde{K}_1 \cdot \tilde{R}_2}{\tilde{K}} - \tilde{P}\right)^2,$$

where another independent variable is the $\tilde{K}_1/\tilde{K}$ ratio (reduced thermo dynamic pressure of the catalytic intermediate).

In the two route transformation scheme (4.43) (see Example 8), there is also the stationary state due to the existence of the positively defined Lyapunov functional

$$\Phi = \varepsilon_1\left(\tilde{R}_1 - \frac{\tilde{K}_1}{\tilde{K}}\right)^2 + \frac{\varepsilon_3}{\tilde{R}_2}\left(\frac{\tilde{K}_1 \cdot \tilde{P}_2}{\tilde{K}} - \tilde{P}\right)^2 + \varepsilon_2\left(\tilde{R}_2 - \frac{\tilde{K}_2}{\tilde{K}}\right)^2 + \frac{\varepsilon_4}{\tilde{R}_1}\left(\frac{\tilde{K}_2 \cdot \tilde{R}_2}{\tilde{K}} - \tilde{P}\right)^2,$$

where $\tilde{K}_i/\tilde{K}$ ratios are independent variables.

It follows from considerations of the stability of stationary states in sim ple kinetic schemes (Section 3.4) that the positively defined Lyapunov functional can be found for any stepwise catalytic reaction provided that it proceeds through transformations that are linear in respect to catalysis intermediates. It is important to note that the catalyst stationary state remains stable in the stepwise reactions that are autocatalytic in respect to the "external" reactants.

4.3.2. Stability of the Catalyst Stationary State in Transformations with Nonlinear Catalytic Intermediates

In the general case of intermediate nonlinear catalytic reactions (i.e., the reactions with allowed interaction of the intermediates), the stationary state may be unstable. The conditions of stability that are far from thermo dynamic equilibrium in intermediate nonlinear stepwise catalytic processes need special consideration in each particular case. The stationary state may be stable (see Example 10) in some cases and unstable in others, and it may be ever evolving into dissipative structures in the system bulk or on the catalyst surface. It is rather difficult to have theoretical analysis of the “critical’ behavior of these systems. Examples of the analysis are available in special literature for more detailed studies on the problems under discussion. Some typical examples of the phenomena observed with the catalyst in unstable stationary state are given in Section 4.6.

4.4. ENERGY CORRELATIONS IN CATALYSIS

4.4.1. Energy Parameters of Intermediates and the Rate of the Catalytic Process

The catalytic theory developed rapidly during the 1950s and 1960s, when the dependence of the rates of some catalytic processes—for example, complete oxidation of metals—on the energy of oxygen to catalyst bonding was established. The dependence is based on the correlation of the observed (apparent) activation energy $E_{a\Sigma}$ of a stepwise catalytic process with some properties of the catalyst matter, such as with the bonding energy of the reactants to the surface.

In particular, attention was paid to the correlation of $E_{a\Sigma}$ with such a parameter as the compensation factor χ of energy in the course of the catalytic process:

$$E_{a\Sigma} = (1 - \chi) \sum_{i} D_i, \tag{4.74}$$

where D_i stands for energies of cleaved and created bonds.

In principle, the type (4.74) dependence is rather natural when the compensation means a total of enthalpies of steps preceding the rate limiting step: In Section 1.4 some simple cases were shown to have an apparent activation energy of the stationary stepwise process that was lower than the activation energy of the rate limiting step—the difference being equal to the enthalpy of the preceding steps.

While identifying the rate determining parameters of the catalytic transformation schemes under consideration, we understand better the reason for possible energy correlations in catalysis, the Broensted Polanyi relations for the transition state energies of surface transformations being typically applied. Such an approach was intensively used in 1960s–1970s to consider, for example, the correlations between specific catalytic activity and the adsorption heat of catalytic intermediates.

In general case, the linear Broensted Polanyi correlation ratio for the Gibbs energy of the formation of the transition state of process ij in a homological transformation group can be written as

$$\Delta_f G_{ij}^{\neq o} = \Delta_f G_{ij}^{\neq oo} + \Delta_{ij}^{\neq} \equiv \Delta_f G_{ij}^{\neq oo} + \Delta_i^{\neq} + \Delta_j^{\neq},$$

where $\Delta_f G_{ij}^{/ oo}$ is the Gibbs energy of the formation of the transition state of a reference pair of reaction groups i and j; increments $\Delta_i^{/}$ and $\Delta_j^{/}$ relate to variations in the standard chemical potentials against the reference compositions of participants of reaction groups i and j caused by changes in the nature of the participants of these reaction groups (within the homological series under consideration):

$$\begin{aligned} \Delta_i^{\neq} &= \chi_{ij}\left(\mu_i^o - \mu_i^{oo}\right) \equiv \chi_{ij}\Delta_i, \\ \Delta_j^{\neq} &= \chi_{ji}\left(\mu_j^o - \mu_j^{oo}\right) \equiv \chi_{ji}\Delta_j. \end{aligned} \tag{4.75}$$

Here, μ_i^{oo} and μ_j^{oo} are standard chemical potentials of reaction groups i and j of the reference composition; μ_i^o and μ_j^o the same of the groups of the inspected composition; and χ_{ij} and χ_{ji} are dimensionless correlation coefficients. Coefficients χ_{ij} usually fall in the range between 0.1 and 0.5.

Figure 4.4 presents a graphical interpretation of the correlation ratios under discussion. The type (4.75) correlation expressions are useful for semiquantitative analysis of variations in a large number of kinetic parameters of different processes on changing the nature of reactants within the given homological series.

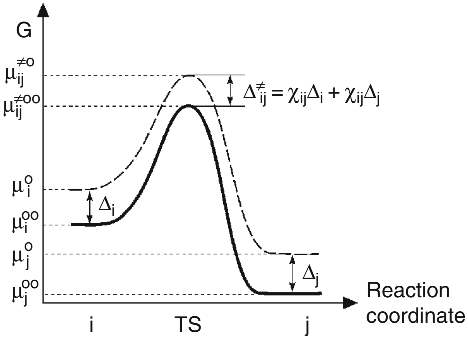


Figure 4.4 A graphical interpretation of the Broensted-Polanyi correlation in elementary reaction ij. TS symbolizes the transition state for the reaction.

Existence of type (4.75) correlations gives rise to evident correlations of kinetic parameters of the process—for example, due to correlations of truncated rate constants in values:

$$\begin{aligned}\varepsilon_{ij} &= \frac{k_B T}{h}\exp\left(-\frac{\Delta_f G_{ij}^{\neq o}}{RT}\right) = \frac{k_B T}{h}\exp\left(-\frac{\Delta_f G_{ij}^{\neq oo}}{RT}\right)\cdot\exp\left(-\frac{\Delta_{ij}^{\neq}}{RT}\right)\\ &\equiv \varepsilon_{ij}^{o}\exp\left(-\frac{\Delta_{ij}^{\neq}}{RT}\right).\end{aligned} \tag{4.76}$$

Here, ε_{ij}^{o} is the truncated rate constant for the chosen reference composition of reaction groups i.

4.4.2. Energy Correlations and the Conditions of Maximal Activity of the Catalyst Reaction Center

A typical problem resolved through correlation ratios is identifying the conditions of the maximal catalyst activity—that is, to optimize the catalyst properties at changes in energetic characteristics of catalytic intermediates due to, for example, variations in the energy of their bonding to the active center.

As a particular example, we shall consider in detail the simplest scheme of catalytic transformation with one catalytic intermediate K_1 (see Section 4.2.2). A system with several intermediate states is analyzed, in principle, in the same but a little more cumbersome way.

The routine approach to studying the effect of the thermodynamics of intermediate state K_1 (reaction complex "reactant–active center") on the overall reaction rate is to find the functional dependence of the reaction rate on standard chemical potential $\mu_{K_1}^{o}$ of this intermediate component (or increment Δ_K of this standard value with respect of the reference state: $\mu_{K_1}^{o} = \mu_{K_1}^{oo} + \Delta_{K_1}$) and to determine the maximum of this functional dependence. The influence of the intermediate state on the characteristics of transition complexes of both steps is expressed, in accordance with (4.76), as follows:

$$\varepsilon_1 = \varepsilon_1^{o}\cdot\exp\left(-\frac{\chi_1\cdot\Delta_{K_1}}{RT}\right),\ \varepsilon_2 = \varepsilon_2^{o}\cdot\exp\left(-\frac{\chi_2\cdot\Delta_{K_1}}{RT}\right), \tag{4.77}$$

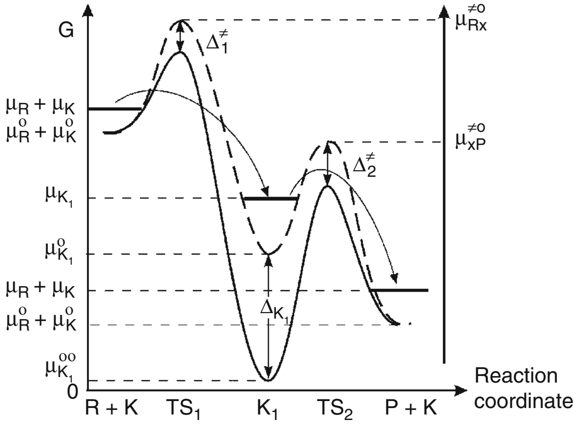


Figure 4.5 A graphical interpretation of the stationary occurrence of a catalytic reaction with one catalytic intermediate K_1 in coordinates of standard and current chemical potentials. The dashed lines show distortions of the potential curves upon changes in standard thermodynamic characteristics of catalytic intermediate K_1. TS_1 and TS_2 are the transition states.

where implication of ε_1 and ε_2 is explained in Figure 4.5, while $\varepsilon_1^o, \varepsilon_2^o$ are reference values that are independent of the characteristics of intermediate K_1; χ_1 and χ_2 are relevant correlation coefficients. The standard reaction rate in the one intermediate system can be written in accordance with (4.10) as

$$v_\Sigma = (\tilde{R} - \tilde{P}) \frac{\tilde{K}_o}{\dfrac{1}{\varepsilon_1} + \dfrac{1}{\varepsilon_2} + \lambda_{K_1} \cdot \left(\dfrac{\tilde{P}}{\varepsilon_1} + \dfrac{\tilde{R}}{\varepsilon_2} \right)},$$

or

$$\frac{1}{v_\Sigma} = \frac{1}{\tilde{K}_o \left(\tilde{R} - \tilde{P} \right)} \left\{ \frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} + \lambda_{K_1} \cdot \left(\frac{\tilde{P}}{\varepsilon_1} + \frac{\tilde{R}}{\varepsilon_2} \right) \right\}$$

where $\lambda_{K_1} = \exp\left\{ \left(\mu_K^o \quad \mu_{K_1}^o \right) / RT \right\}$.

Differentiating the latter expression for parameter $1/v_\Sigma$ (reciprocal to the reaction rate) with respect to independent increment Δ_{K_1} in view of expression (4.76) and setting the derivative to zero gives the equation on optimal Δ_{K_1}:

$$\frac{\partial(1/v_\Sigma)}{\partial\Delta_{K_1}} = -\frac{1}{RT}\tilde{K}_o(\tilde{R} - \tilde{P})\left\{\frac{\chi_1\exp(\chi_1\Delta_{K_1}/RT)}{\varepsilon_1^o} + \frac{\chi_2\exp(\chi_2\Delta_{K_1}/RT)}{\varepsilon_2^o}\right.$$
$$\left. + \left[\frac{(\chi_1 - 1)\tilde{P}\exp(\chi_1\Delta_{K_1}/RT)}{\varepsilon_1^o} + \frac{(\chi_2 - 1)\tilde{R}\exp(\chi_2\Delta_{K_1}/RT)}{\varepsilon_2^o}\right]\exp\left\{(\mu_K^o - \mu_{K_1}^o)/RT\right\}\right\} = 0. \tag{4.78}$$

Equation (4.78) has only an analytic solution in respect of Δ_{K_1} provided that $\chi_1 = \chi_2$. The traditional kinetic derivation of relationship (4.78) for the case of equal correlation coefficients χ_1 and χ_2 can be found in many textbooks on catalysis, including the ones at the end of this chapter. Otherwise, numerical methods should be used for determining the optimal quantity of Δ_{K_1} of the intermediate.

When $\chi_1 = \chi_2 = \chi$, expression (4.78) can be reduced to the form

$$\chi\left(\frac{1}{\varepsilon_1^o} + \frac{1}{\varepsilon_2^o}\right) + (\chi - 1)\left(\frac{\tilde{P}}{\varepsilon_1^o} + \frac{\tilde{R}}{\varepsilon_2^o}\right)\exp\left\{(\mu_K^o - \mu_{K_1}^o)/RT\right\} = 0. \tag{4.79}$$

Here, we can easily obtain the standard chemical potential of the optimal transition state:

$$\mu_{K_1}^o = \mu_K^o + RT\ln\left[\left(\frac{1-\chi}{\chi}\right)\left(\frac{\tilde{P}\varepsilon_2^o + \tilde{R}\varepsilon_1^o}{\varepsilon_2^o + \varepsilon_1^o}\right)\right]. \tag{4.80}$$

The given equality indicates unambiguously the relationship between optimal (for the stepwise process rate) thermodynamic characteristics of the transition state and the correlation coefficient in the Broensted–Polanyi equation.

We should keep in mind that equation (4.80) is identical to the relationship

$$\frac{\chi}{1-\chi} = \frac{\varepsilon_1^o\tilde{R} + \varepsilon_2^o\tilde{P}}{\varepsilon_2^o + \varepsilon_1^o}\exp\left(\frac{\mu_K^o - \mu_{K_1}^o}{RT}\right) = \frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}}{\varepsilon_2 + \varepsilon_1}\exp\left(\frac{\mu_K^o - \mu_{K_1}^o}{RT}\right) \equiv \frac{\theta_{K_1}}{\theta_K} \tag{4.81}$$

(see Section 4.2.2).

Hence, expression (4.79) relates to the condition of the optimal coverage of the active center by the catalytic intermediate

$$\frac{\theta_{K_1}}{\theta_K} = \frac{\chi}{1-\chi}. \tag{4.82}$$

The optimal coverage of the active center ensures the maximal rate of the catalytic transformation in the system under consideration:

$$v_{\Sigma\max} = \varepsilon_{\Sigma} \cdot \frac{\tilde{K}_o\left(\tilde{R} - \tilde{P}\right)}{1 + \dfrac{\chi}{1-\chi}} = \varepsilon_{\Sigma}(1-\chi) \cdot \tilde{K}_o\left(\tilde{R} - \tilde{P}\right),$$

where $\varepsilon_{\Sigma} = \dfrac{\varepsilon_1 \cdot \varepsilon_2}{\varepsilon_1 + \varepsilon_2} = \dfrac{\varepsilon_1^o \cdot \varepsilon_2^o}{\varepsilon_1^o + \varepsilon_2^o}$.

Hence, expression (4.79) indicates two possible ways to create the optimal coverage of the active center by the catalytic intermediate and, as a result, to optimize the rate of the catalytic process: (1) by varying the concentration (pressure) of the products and reactants (thus varying the active center coverage) and (2) by selecting the catalyst nature under preset external conditions (temperature, concentrations of the products and reactants) to achieve the optimal value of $\mu_{K_1}^o$ (or, that is the same, Δ_{K_1}). In the latter case, in the homological series of catalysts with similar geometric structures and chemical natures to the active centers, one can consider χ as keeping its magnitude at differing the standard chemical potentials of the surface species, $\mu_{K_1}^o$ μ_K^o. Naturally, it is possible to use a combination of both influence methods, too.

4.4.3. The Effect of the Active Component Size on the Rate of Catalytic Reactions

Applying the Broensted Polanyi correlations is sometimes useful for describing the dependence of the reaction rate on the size of the catalytically active component. A huge amount of experimental data have been compiled to date regarding the effect of the particle size of the catalyst active components on the specific catalytic activity, SCA, as well as on the turnover frequency, TOF, of the active center. Both parameters do not relate to the total surface area of the catalytically active phase or to the total number of active centers and, therefore, characterize directly the properties of the active center. There are also some experimental data on the size dependence of the adsorption properties of small metal particles, as well as on the selectivity of a few catalytic processes.

It is important that much the data relate to the case when the active component particles cannot be treated as clusters of atoms and that need strict consideration of the quantum size effects, but as a continuous phase with the properties described by standard methods of the continuous phase thermodynamics. Inspection of these experimental data reveals that a considerable change of SCA and TOF is usually observed at the active component particle size of no more than 10 nm.

In this section, we shall demonstrate the possibility of a successive understanding of the reasons for and the expected scale of the said phenomena by analyzing the changes in thermodynamic properties of the active component upon its dispersal. It is common knowledge that dispersing a condensed substance can considerably change its physicochemical properties. If the substance keeps its behavior as a condensed phase, its particles allow the quantum size effects to be disregarded. In this case, changes in properties that depend on particle size can be described in terms of classic thermodynamics. For example, changes in the active component size may lead to changes in the adsorption properties, as well as in the rate of elementary catalytic reactions that occur on the active phase surface.

When do thermodynamics of continuous phases become applicable for describing correctly the properties of nanosize objects? There is not yet a commonly accepted answer to this question. However, for the case of considering the chemical potential of a thermalized disperse matter (i.e., the one that is in the thermal Maxwell Boltzmann equilibrium with the surrounding), one can suppose that the necessary condition of applicability of the continuous phase thermodynamics is a small (less than k_BT) splitting between the energy levels of atomic or molecular orbitals of the species under consideration. Very roughly, the estimated minimal necessary number, N, of atoms in such a species seems to be given by the relationship $\Delta E/N < k_BT$, where ΔE is the characteristic splitting of energy levels of individual atoms comprised in the nanoparticles, k_B is the Boltzmann constant, and T is the temperature of the nanoobject under consideration. Typically, the scale of ΔE equals 1 eV $\approx$ 90 kJ/mol. Hence, the said inequality gives $N > \Delta E/k_BT \approx 40$ at temperature 300 K.

Therefore, the cluster that contains more than 100 atoms allows its properties, depending on the chemical potential, to be described correctly in terms of the continuous phase thermodynamics. It is important that the number of atoms in the cluster rather than its geometrical size (depending on the particle shape) is the critical parameter.

A decrease in size of a condensed phase particle results in an increase in the chemical potential of the substance due to excess surface energy and the elevation of the Laplace pressure inside the particle (see Section 1.1). With a spherical particles of radius r, one can estimate the increment Δ_i of the chemical potential of component i of the continuous phase by the expression

$$\Delta_i \approx \overline{V}_i \cdot \frac{2\sigma_i}{r}, \tag{4.83}$$

where $\overline{V}_i$ is the partial molar volume of substance i of the condensed phase under consideration, and σ_i is the surface tension coefficient (excess surface energy) of the disperse substance at the interphase boundary between substance i and the surrounding liquid or gas phase.

The increment relates predominantly to the enthalpy contribution to the Gibbs potential and, therefore, contributes to the standard chemical potential of the condensed phase components:

$$\mu_i^o(r) = \mu_{i\infty}^o + \Delta_i = \mu_{i\infty}^o + \overline{V}_i \frac{2\sigma}{r}, \tag{4.84}$$

where $\mu_i^o(r)$ and $\mu_{i\infty}^o$ are the standard chemical potentials of substance i in the disperse and bulky phases, respectively (see also expression (1.9)).

Thus, dispersing the particles of the active catalyst phase results in an increase of the standard chemical potentials of both the surface and the bulky species of this phase. In some cases, the same thing happens to the transition states of surface catalytic transformations and to the thermalized catalytic intermediates. Note that the particle size of the catalytically active phase has the most remarkable impact on the chemical potential of the components that constitute the particle phase, including the components that are dissolved inside the particle. At the same time, particle size must have far less influence on the chemical potential of the intermediate that is a surface molecular complex. Evidently, the influence of dispersing on the properties that are determined by the chemical potential must become considerable at $\Delta_i \geq RT$.

Let us estimate, for example, the size of spherical metal particles when the size effect appears considerable. With the nickel type metals, the molar metal volume is approximately $10\ ^{5}$ m^3/mol. While $\sigma \approx 1$–2 J/m^2 is a typical value for metals, then a considerable effect of the dispersion on the particle chemical potential and the related phenomena at, for example, $T \approx 300$ K should be expected at

$$r \leq \frac{\overline{V} \cdot 2\sigma}{RT} = \frac{10\ ^{5} \cdot 2 \cdot (1-2)}{8.31 \cdot 300}\,\mathrm{m} = (10-20)\ \mathrm{nm}.$$

This is close indeed to the previous size range when the change in the particle size of the catalytically active phase results in experimentally observed changes in the adsorptive properties and specific catalytic activity. When r is much larger than 10–20 nm, the thermodynamic properties of the particles are almost independent of their size but close to the properties of the bulky phase.

4.4.3.1. The Influence of Particle Size on the Adsorption Equilibrium in a System with the Langmuir Adsorption

Consider the influence of the nanoparticle size on the ideal Langmuir monolayer adsorption of some component R from an external (liquid or gas) phase by uniform adsorption centers K, which are the surface species of the bulky phase of the adsorbent substance:

$$R + K \rightleftarrows K_1. \tag{4.85}$$

Here, K_1 symbolizes the adsorbed molecular complex of substance R with the adsorbent substance.

In view of the balance relation for the surface concentrations of the K and K_1 species, the traditional relationship

$$\theta_K + \theta_{K_1} = 1 \tag{4.86}$$

is valid. Here, $\theta_K \equiv [K]/[K]_o$ is the fraction of the unoccupied adsorption centers, $\theta_{K_1} \equiv [K_1]/[K]_o$ is the coverage of the adsorption centers by the adsorbate, and $[K]_o$ is a total of the surface concentration of the adsorption centers.

In the Langmuir adsorption model, chemical potential μ_K of the unoccupied adsorption centers is described, like that of a component in an ideal solution, as $\mu_K = \mu_K^o + RT\ln\theta_K$, while chemical potential μ_{K_1} of the adsorbed molecular complex is described as $\mu_{K_1} = \mu_{K_1}^o + RT\ln\theta_{K_1}$ (see Section 1.1). The standard μ_K^o and $\mu_{K_1}^o$ relate to the cases of $\theta_K = 1$ (the "pure" adsorbent surface) and $\theta_{K_1} = 1$ (the surface fully covered by the adsorbate). For the sake of simplicity, we shall consider here and elsewhere that the adsorption has practically no effect on σ, this approximation being valid at least at relatively small ($\leq$60–80 kJ/mol) heat of adsorption of the adsorbate.

In the state of thermodynamic equilibrium, chemical potential of the unoccupied adsorption center K is evidently determined by chemical potential of the adsorbent substance, and, therefore, it depends on its particle size. At the same time, chemical potential of the "adsorbed molecule–adsorbent substance" complex is determined mainly by the particular structure of the complex and, therefore, depends only slightly on the adsorbent particle size.

In the thermodynamically equilibrium system (4.85),

$$\tilde{R} \cdot \tilde{K} = \tilde{K}_1$$

or, that is the same,

$$\mu_R + \mu_K = \mu_{K_1}.$$

While chemical potential μ_R of the adsorbate in the ideal gas phase is described as

$$\mu_R = \mu_R^o + RT\, \ln p_R,$$

where p_R is the partial pressure of R, then the following relationship is valid at the equilibrium state:

$$\mu_R^o + RT\, \ln_R + \mu_K^o + RT\, \ln\theta_K = \mu_{K_1}^o + RT\, \ln\theta_{K_1}. \tag{4.87}$$

From equation (4.87), the surface coverage with the adsorbate K_1 is expressed as

$$\frac{\theta_{K_1}}{\theta_K} = \frac{\theta_{K_1}}{1-\theta_{K_1}} = \frac{[K_1]}{[K]} = \exp\left(\frac{\mu_R^o + \mu_K^o - \mu_{K_1}^o}{RT}\right) \cdot p_R.$$

We discussed before that the decrease in r leads to an increase in μ_K^o in accordance with equation (4.84), whereas $\mu_{K_1}^o$ remains practically constant (see Figure 4.6A). Hence, in the case of the ideal Langmuir adsorption on a small particle, the adsorption center coverage with the adsorbate *must increase at a decrease in the particle size* as

$$\left(\frac{\theta_{K_1}}{\theta_K}\right)_r \approx \left(\frac{\theta_{K_1}}{\theta_K}\right)_\infty \cdot \exp\left(\frac{\Delta_K}{RT}\right) = \left(\frac{\theta_{K_1}}{\theta_K}\right)_\infty \cdot \exp\left(\frac{2\sigma\overline{V}_K}{rRT}\right), \tag{4.88}$$

where $\left(\frac{\theta_{K_1}}{\theta_K}\right)_r$ and $\left(\frac{\theta_{K_1}}{\theta_K}\right)_\infty$ are the values related with the adsorption center coverage by adsorbate for the particle of radius r and for the flat surface of

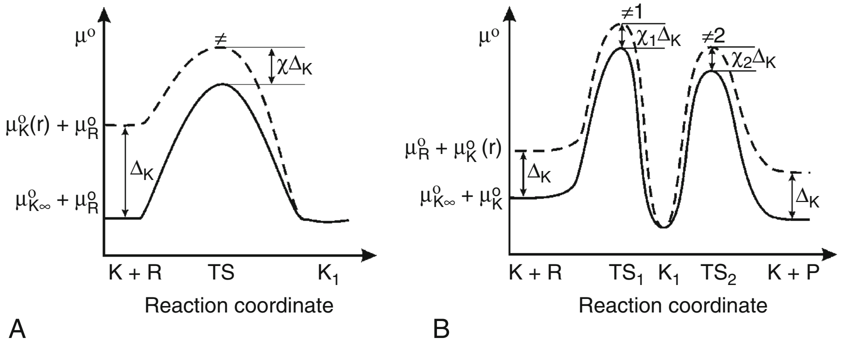


Figure 4.6 A graphical interpretation in terms of the Broensted-Polanyi correlations of variations in standard energy characteristics (the Gibbs potential) of participants of (A) reaction (4.85) and (B) catalytic process (4.3)–(4.4) with disperse active phase K and one thermalized molecular intermediate K_1. Sign ≠ indicates the transition state TS in elementary reaction (4.85); ≠1 and ≠2 relate to transition states TS_1 and TS_2 in elementary reactions 1 and 2 of scheme (4.4).

the same adsorbent, respectively, at the identical temperatures and adsorbate pressures.

It is interesting that equation (4.88) is completely identical to the Kelvin Thomson relation for the saturated vapor pressure over a spherical particle of the condense phase of the same substance. It is also important that expression (4.88) corresponds to an increase in the adsorption heat of the adsorbate on this particle by $\Delta Q_{ads} \approx \Delta_K = \dfrac{2\sigma \overline{V}_K}{r}$ in comparison to the adsorption heat of the same substance on the flat surface.

4.4.3.2. The Effects of the Active Phase Dispersion on the Rate of a Heterogeneous Reaction

Let us estimate variations in the rate of a heterogeneous homogeneous reaction on changes of the active phase (e.g., metal) particle size by considering the changes in the standard thermodynamic potential of the substance of the phase in terms of the correlation Broensted Polanyi relations. Consider the formation of adsorbate K_1 in the course, for example, of an elementary gas solid phase reaction (4.85). Rate v of the elementary reaction is written as

$$v = -\frac{d[R]}{dt} = \frac{d[K_i]}{dt} = \varepsilon\left(\tilde{R} \cdot \tilde{K} - \tilde{K}_1\right),$$

where the truncated rate constant ε depends on the standard Gibbs potential, $\Delta_f G^{/o}$, of the formation of the transition state only of reaction (4.85). Therefore,

$$\Delta_f G^{\neq o}(r) = \mu^{\neq o}(r) = \mu_{\infty}^{\neq o} + \Delta^{\neq},$$

where $\mu_{\infty}^{/o}$ is the "standard" potential of the transition state for the bulk phase of substance K, and $\Delta^{/}$ is increment of this potential due to the formation of the transition state on the surface of dispersed substance K with the particles radii r.

One may suppose that changes in the particle size should result in changes of $\Delta^{/}$ of the surface transition state, the changes being described correctly enough by the Broensted Polanyi relation with the increment Δ_K of substance K at its dispersing:

$$\Delta^{\neq} \approx \chi\Delta_K. \tag{4.89}$$

When relation (4.89) is satisfied, the decrease in the size of the phase K particles causes a decrease in ε due to an increase in $\mu^{/o}$:

$$\varepsilon(r) \approx \varepsilon_{\infty} \cdot \exp\left\{-\frac{\chi\Delta_K}{RT}\right\}, \tag{4.90}$$

where ε_{∞} is the truncated rate constant of reaction (4.85) on the flat surface. The phenomena described here are interpreted in Figure 4.6A.

The "traditional" rate constant $\vec{k}$ of the left to right reaction increases concurrently:

$$\vec{k}(r) \approx \vec{k}_{\infty} \cdot \exp\left\{\frac{(1-\chi)\Delta_K}{RT}\right\},$$

but the rate constant of the right to left reaction, $\overset{\leftarrow}{k}$, decreases:

$$\overset{\leftarrow}{k}(r) \approx \overset{\leftarrow}{k}_{\infty} \cdot \exp\left\{-\frac{\chi\Delta_K}{RT}\right\}.$$

Accordingly, the decrease of the particle size must lead to an increase in rate $\vec{v}$, while rate $\overset{\leftarrow}{v}$ will decrease.

The other examples of elementary surface reactions can be inspected the same way. Note that in the reaction between sorbates on the active phase surface, the magnitudes of ε, and, as a consequence, traditional rate constants $\vec{k}$ and $\overset{\leftarrow}{k}$ may be considered in the first approximation as independent of r.

4.4.3.3. The Active Phase Particle Size and the Stationary Rate of a Catalytic Reaction

Variations in parameter ε that are deduced for the "external bulky phase–surface" reactions must result in changes in the rate of the catalytic reactions. Consider a catalytic stepwise reaction when the transformation of initial reactant R to product P

$$\mathrm{R} \rightleftarrows \mathrm{P}$$

follows the simplest scheme of catalytic transformations (4.4), as was discussed in Example 1:

$$\mathrm{R} + \mathrm{K} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1,$$
$$\mathrm{K}_1 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{P} + \mathrm{K}.$$

In the stationary state of intermediate K_1, rate v_Σ of this catalytic process is described by equation (4.10):

$$v_\Sigma \equiv \varepsilon_\Sigma \tilde{K}_o \left(\tilde{R} - \tilde{P}\right) \Big/ \left(1 + \frac{\theta_{K_1}}{\theta_K}\right),$$

where

$$\frac{\theta_{K_1}}{\theta_K} = \lambda_{K_1} \frac{\varepsilon_2 \tilde{R} + \varepsilon_1 \tilde{P}}{\varepsilon_1 + \varepsilon_2}, \varepsilon_\Sigma = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}, \tilde{K}_o = \exp\left(\frac{\mu_{K_o}}{RT}\right) \equiv [K]_o \exp\left(\frac{\mu^o_K}{RT}\right),$$
$$\lambda_{K_1} \equiv \exp\left[\left(\mu^o_K - \mu^o_{K_1}\right)/RT\right].$$

Note that $\tilde{R}$ and $\tilde{P}$ are independent of r.

Let K_1 be an adsorbed intermediate and K be the active center arranged in the surface layer of the dispersed active phase. In such the case, the changes in the active component particle size will generate some changes in the profile of the standard energetic characteristics along the reaction coordinate that can be illustrated by the scheme in Figure 4.6B. Note that the value of $\mu^o_{K_1}$ is changed only slightly with changing r. The increments $\Delta_1^{/}$ and $\Delta_2^{/}$ of the "standard chemical potentials" of transition states 1 and 2 may be different (i.e., $\chi_1 \neq \chi_2$).

Like equation (4.90), the expressions for ε_1 and ε_2 are

$$\varepsilon_1(r) = \varepsilon_{1\infty} \exp\left\{\frac{-\chi_1 \Delta_K}{RT}\right\}, \varepsilon_2(r) = \varepsilon_{2\infty} \exp\left\{\frac{-\chi_2 \Delta_K}{RT}\right\},$$

where $\varepsilon_{1\infty}$ and $\varepsilon_{2\infty}$ are the relevant constants for the flat surface.

As r decreases, λ_{K_1} increases in value, and the stationary coverage by intermediate K_1 increases. For simplicity, let $\chi_1 = \chi_2 = \chi$. In this situation,

$$\varepsilon_\Sigma(r) = \frac{\varepsilon_1(r)\varepsilon_2(r)}{\varepsilon_1(r) + \varepsilon_2(r)} = \frac{\varepsilon_{1\infty} \cdot \varepsilon_{2\infty}}{\varepsilon_{1\infty} + \varepsilon_{2\infty}} \exp\left\{\frac{-\chi \Delta_K}{RT}\right\} = \varepsilon_{\Sigma\infty} \exp\left\{\frac{-\chi \Delta_K}{RT}\right\}.$$

Therefore, when the stationary coverage with intermediate K_1 is small—say, $\theta_{K_1}/\theta_K \ll 1$—then

$$\begin{aligned} v_\Sigma(r) \approx \varepsilon_\Sigma \tilde{K}_o(\tilde{R} - \tilde{P}) &= \varepsilon_{\Sigma\infty} \exp\left\{\frac{(1-\chi)\Delta_K}{RT}\right\} [K]_o(\tilde{R} - \tilde{P}) \\ &= v_{\Sigma\infty} \exp\left\{\frac{(1-\chi)\Delta_K}{RT}\right\}, \end{aligned} \tag{4.91}$$

where $v_{\Sigma\infty}$ is the rate of the catalytic reaction in the case of the bulky active phase. We see that in the given case, the decrease of the active particle size generates, via the correlation equations for ε_1 and ε_2, a *positive effect* on the catalytic reaction rate.

TOF varies in a similar way:

$$\mathrm{TOF}(r) = \mathrm{TOF}_\infty \cdot \exp\left\{\frac{(1-\chi)\Delta_K}{RT}\right\}.$$

However, as soon as the stationary coverage by intermediate K_1 becomes significant—say, at $(\theta_{K_1}/\theta_K) \gg 1$

$$v_\Sigma = \frac{\varepsilon_1(r)\varepsilon_2(r) \cdot [K]_o(\tilde{R} \quad \tilde{P})}{\varepsilon_1(r)\tilde{R} + \varepsilon_2(r)\tilde{P}} \exp\left(\mu^o_{K_1}/RT\right).$$

These are the only parameters ε_1 and ε_2 that make the rate dependent on the active particle size. These parameters decrease along with decreasing size r. Hence, as r decreases, v_Σ and TOF are expected to decrease as

$$\begin{aligned} v_{\Sigma}(r) &\approx \frac{\varepsilon_{1\infty}\varepsilon_{2\infty}}{\varepsilon_{1\infty}\tilde{R} + \varepsilon_{2\infty}\tilde{P}} \cdot \exp\left(-\frac{\chi\Delta_K}{RT}\right) \cdot [K]_o\left(\tilde{R} - \tilde{P}\right) \exp\left\{\frac{\mu^o_{K_1}}{RT}\right\} \\ &= v_{\Sigma\infty} \exp\left(-\frac{\chi\Delta_K}{RT}\right) \qquad (4.92) \\ \mathrm{TOF}(r) &= \mathrm{TOF}_{\infty} \cdot \exp\left(-\frac{\chi\Delta_K}{RT}\right). \end{aligned}$$

Under conditions that are typical of most practical catalytic processes, the surface coverage with catalytic intermediates is usually large enough that it allows a decrease in SCA and/or TOF determined by equation (4.92) to be experimentally observed.

Equations (4.91)–(4.92) assume that the variations in the catalytic reaction rate originate from the size dependent changes in the apparent activation energy, $E_{a\Sigma}$, of the stepwise catalytic process. If the stepwise process under consideration is kinetically irreversible, then $\tilde{R} \gg \tilde{P}$, and equation (4.91) gives at $\theta_{K_1}/\theta_K < 1$:

$$E_{a\Sigma}(r) \approx E_{a\Sigma\infty} + (1 - \chi)\Delta_K;$$

that is, the apparent activation energy of this stepwise process must increase with decreasing r. With $\theta_{K_1}/\theta_K > 1$ under identical conditions, it follows from equation (4.92) that

$$E_{a\Sigma}(r) \approx E_{a\Sigma\infty} - \chi\Delta_K;$$

that is, the apparent activation energy of this stepwise process must decrease with decreasing r.

A series of special experiments on model processes—for example, deep oxidation of methane and other substrates over supported Pt/Al_2O_3 catalysts—prove the assumption that the observed size effects are accounted for by variations in the apparent activation energy that are described satisfactorily even in terms of the given ideal models.

Figure 4.7 shows TOF as a function of the particle size of a monodisperse supported platinum catalyst Pt/Al_2O_3 in the reaction of deep methane oxidation. One can see that equation (4.91) is sufficient to describe the experimental data when the Pt particles are more than 2 nm in size. When they are smaller, TOF deviates from the monotonous dependence (4.91). The reason may be a considerable change in the chemical composition of the anchored active component due to the strong interaction of this component with the carrier surface.

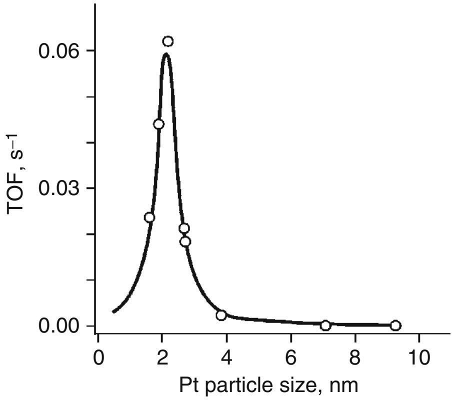


Figure 4.7 Experimental observations of the TOF variations for supported platinum catalysts Pt/Al_2O_3 as a function of the size of catalytically active metal nanoparticles during the stationary occurrence of the methane deep oxidation at 430°C [1].

A similar thermodynamic analysis was used to describe the changes in the Fischer Tropsch's process selectivity and $E_{a\Sigma}$ observed during experi mental studies of the process with a controllable change of the active com ponent size (see [5]). An important assumption here was the dramatic role of hydrogen atoms dissolved in nanoparticles of the active components like Fe and Co.

Thus, thermodynamic analysis of ideal models reveals that dispersing the active catalyst phase down to particles of no larger than 10 nm may affect considerably both the adsorption equilibrium as well as the rate (para meters SCA and TOF) and selectivity of the catalytic reaction. The neces sary condition here is the participation of either the matter of the dispersed active phase (active catalyst component) or an intermediate to be dissolved in the dispersed active phase (see [5]) in the catalytic transformations.

Equations (4.91) and (4.92) allow the optimal particle size of the active component to be determined, which provides the maximal stationary rate of the catalytic transformation for a given mass of the dispersed active component. In the case of the uniformly dispersed active component, rate V_Σ of catalytic transformations under kinetically controlled conditions equals

$$V_\Sigma \approx S(r) \cdot v_\Sigma(r),$$

where S(r) is a total of the surface area of spherical nanoparticles of radius r produced from unit mass of the catalytically active phase, while

$$S(r) = 4\pi r^2 \cdot \left[1 \Big/ \left(\frac{4}{3}\pi r^3 \cdot \rho\right)\right] \equiv \frac{3}{\rho \cdot r}$$

for the active phase with density ρ.

Therefore, for example, in the case of (4.92) with a high degree of the stationary surface coverage with the catalytic intermediate,

$$V_\Sigma \propto \frac{1}{r}\exp\left(-\frac{\chi\Delta_K}{RT}\right) \equiv \frac{1}{r}\exp\left(-\frac{2\chi\sigma\overline{V}_K}{rRT}\right). \tag{4.93}$$

Function (4.93) has the maximum at $r = \frac{2\chi\sigma\overline{V}_K}{RT}$. With the preceding typical parameters of active metal phases at, for example, $T \sim 600$ K, this corresponds to the maximum expected activity of the catalysts with active nanoparticles of a radius of approximately 5–10 nm.

4.5. CONJUGATION OF CATALYTIC PROCESSES

In practice, catalytic processes are never strictly selective in respect to the target product. Apart from target products, catalytic reactions generate also some side (nontarget) products in certain amounts. The target and side products often are formed through common catalytic intermediates, which make it possible to treat the target and side channels of catalytic transformations as thermodynamically conjugate processes. The existence of conjugation is most evident in the catalytic systems where the selective synthesis of the target product requires it's a more complete and often more thermodynamically favorable transformation—for example, deep oxidation or hydrogenation—to be prevented.

4.5.1. The Horiuti-Boreskov-Onsager Relations for Parallel Catalytic Reactions with Common Intermediates

When simple concurrent stepwise noncatalytic reactions proceed far from the equilibrium and are conjugated through common intermediates, their rates in the intermediate stationary state are in the Horiuti Boreskov Onsager relationship (2.17) with phenomenological reciprocity coefficients Λ_{ij} (see Section 2.3.4). Conjugation of catalytic processes is analyzed like that of the noncatalytic stepwise processes. It should be taken into account, however, that there are free catalyst active centers in the initial and final reaction groups. We shall illustrate this statement by considering the simplest example of two concurrent catalytic stepwise reactions Σ1 and Σ2,

$$\begin{aligned} R &\overset{\Sigma 1}{\rightleftarrows} P_1, \\ R &\overset{\Sigma 2}{\rightleftarrows} P_2, \end{aligned} \tag{4.94}$$

where the *main* product P_1 and *side* product P_2 are formed from their common initial reactant R, and the elementary steps have a common intermediate K_1:

$$\begin{aligned} &\mathrm{R} + \mathrm{K} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1, \\ &\mathrm{K}_1 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{P}_1 + \mathrm{K}, \\ &\mathrm{K}_1 \overset{\varepsilon 3}{\rightleftarrows} \mathrm{P}_2 + \mathrm{K}. \end{aligned} \tag{4.95}$$

In the catalytic intermediate K_1 stationary mode,

$$\frac{d[K_1]}{dt} = \varepsilon_1(\tilde{R} \cdot \tilde{K} - \tilde{K}_1) - \varepsilon_2(\tilde{K}_1 - \tilde{P}_1 \cdot \tilde{K}) - \varepsilon_3(\tilde{K}_1 - \tilde{P}_2 \cdot \tilde{K}) = 0.$$

Here, the rates of the products' formation via a given route are

$$\begin{aligned} v_{\Sigma 1} &= \frac{d[P_1]}{dt} = \varepsilon_2(\tilde{K}_1 - \tilde{P}_1 \cdot \tilde{K}) = \Lambda_{11}\tilde{K}(\tilde{R} - \tilde{P}_1) + \Lambda_{12}\tilde{K}(\tilde{R} - \tilde{P}_2) \\ v_{\Sigma 2} &= \frac{d[P_2]}{dt} = \varepsilon_3(\tilde{K}_1 - \tilde{P}_1 \cdot \tilde{K}) = \Lambda_{21}\tilde{K}(\tilde{R} - \tilde{P}_1) + \Lambda_{22}\tilde{K}(\tilde{R} - \tilde{P}_2). \end{aligned} \tag{4.96}$$

Like scheme (2.11), the calculations give modified Onsager reciprocity coefficients Λ_{ij} for the given scheme:[*]

$$\Lambda_{11} = \frac{\varepsilon_1\varepsilon_2 + \varepsilon_2\varepsilon_3}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3} > 0, \ \Lambda_{22} = \frac{\varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_3}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3} > 0, \ \Lambda_{12} = \Lambda_{21} = -\frac{\varepsilon_2\varepsilon_3}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3}.$$

The internal variable $\tilde{K}$ can be expressed here, like in Section 4.2, in terms of thermodynamic rushes of active centers $\tilde{K}_o$ and the active center coverage by intermediates. While

$$\begin{aligned} \tilde{K}_1 &= \tilde{K}(\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}_1 + \varepsilon_3\tilde{P}_2)/(\varepsilon_1 + \varepsilon_2 + \varepsilon_3), \\ \tilde{K} &= \frac{\tilde{K}_o}{1 + \dfrac{\theta_{K_1}}{\theta_K}}, \end{aligned}$$

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[*] In many cases, K may enter coefficients Λ_{ij} with no loss in generalities of the analytic results.

where

$$\frac{\theta_{K_1}}{\theta_K} = \lambda_{K_1}\frac{\varepsilon_1\tilde{R} + \varepsilon_2\tilde{P}_1 + \varepsilon_3\tilde{P}_2}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3},$$

$$\lambda_{K_1} = \exp\left(\frac{\mu^o_{K_1} - \mu^o_K}{RT}\right).$$

In general cases of several concurrent channels of catalytic stepwise transformations

$$\tilde{R}_{\Sigma i} \overset{\Sigma_i}{\rightleftarrows} \tilde{P}_{\Sigma i} \quad (i = 1, \ldots, N)$$

that follow the transformation *schemes linear in respect to catalytic intermediates,* stationary rates $v_{\Sigma i}$ for each channel are described by the Horiuti Boreskov Onsager equations

$$v_{\Sigma i} = \frac{d[P_{\Sigma i}]}{dt} = \sum_{j=1}^{N}\Lambda_{ij}\tilde{K}(\tilde{R}_{\Sigma j} - \tilde{P}_{\Sigma j}) \tag{4.97}$$

(see Section 2.3.4), where $\Lambda_{ii} \geq 0$, and the relationship between non diagonal elements Λ_{ij} and Λ_{ji} can be found by considering the near equilibrium situation when $\tilde{R}_{\Sigma j} \approx \tilde{P}_{\Sigma j}$. As shown in Section 2.3.4, at these conditions

$$\Lambda_{ij}\,\tilde{R}_{r\Sigma j}\,A_{r\Sigma j} \approx L_{ij}\,X_{\Sigma j},$$

where $X_{\Sigma j} = A_{r\Sigma j}$ is the actual thermodynamic driving force (affinity) of channel Σj of the catalytic stepwise process, and L_{ij} is the phenomenological coefficient of the traditional Onsager reciprocity equation for the near equilibrium system.

The expression that follows

$$\Lambda_{ij}\,\tilde{R}_{\Sigma j} \approx \Lambda_{ji}\,\tilde{R}_{\Sigma i}, \tag{4.98}$$

allows the functional relationship between Λ_{ij} and Λ_{ji} to be determined even though the particular schemes of elementary catalytic transformations are unknown for the concurrent catalytic stepwise processes under consideration.

Equations like (4.97) and (4.98) may be extremely useful, at least in the preliminary microkinetic analysis of the behavior of complex catalytic transformations with unknown elementary mechanisms: The kinetic scheme of the stationary stepwise transformation in such a system is only determined using empirical coefficients Λ_{ij}, while the sign or the absence of any thermodynamic forces X_j governs the system evolution along a given trajectory.

Two important conclusions follow from the analysis of the Horiuti Boreskov Onsager reciprocity relations (4.97) for the rates in different channels of catalytic transformations:

Conclusion 1: The validity of the commonly accepted statement that a catalyst is not shifting the achieved thermodynamic equilibrium between the initial reactants and the products of the catalytic transformation is limited either to the system in *full* thermodynamic equilibrium (i.e., $\tilde{R}_{\Sigma i} = \tilde{P}_{\Sigma j}$ for any i,j) or to the systems with "partial equilibrium" (i.e., $\tilde{R}_{\Sigma i} = \tilde{P}_{\Sigma j}$ for selected i and j) provided that the catalyst is 100% selective to the transformation at the supposed partial equilibrium. It is important that both cases are almost impracticable, since catalysts usually are not ideally selective, and not full but only "partial" thermodynamic equilibrium can be provided in the systems. The said shift of the established equilibrium happens due to the initiation of side transformation channels by a real catalyst.

This conclusion specifies applicability of the commonly accepted postulate about the absence of the catalyst influence on thermodynamic equilibrium in a reactive system; it is an evident consequence of plurality of thermodynamic forces that occur in a nonequilibrium nonselective systems and thus must be able to initiate concurrent reactions.

Conclusion 2: In some cases the selectivity of conjugate catalytic stepwise transformations can be controlled by varying chemical potentials of not only initial reactants but also of the transformation products. Moreover, stepwise side reactions may be sometimes reversed, while the side products can be even "utilized" to form the target products.

When the main and side reactions are conjugate through a common intermediate, the possibility of varying the selectivity, or even the direction, of the catalytic side process follows directly from the comparison of stationary chemical potentials of the catalytic intermediates, as well as of chemical potentials of the target and side products of the overall catalytic reaction. It is important that the phenomenon under consideration is of the "threshold" nature with respect to the side product concentration—that is, that it is observed when these product concentrations are above a certain value.

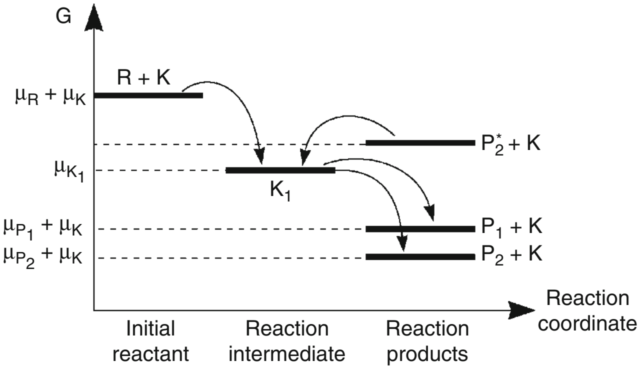


Figure 4.8 A graphical interpretation of the stationary occurrence of a catalytic process with two parallel channels of the conjugate catalytic transformations of initial reactant R to products P_1 and P_2. K_1 stands for a joint catalytic intermediate. Asterisks indicate points of the process reversion to involve the "side" product P_2 in synthesis of the "main" product P_1 (compare with Figure 2.4).

This phenomenon was interpreted in detail in Section 2.3.4 for the case of thermodynamically conjugated noncatalytic transformations. Figure 4.8 gives a graphical interpretation of the influence of the conjugation of catalytic transformations through a common catalytic intermediate. In the case of parallel reactions without common intermediate (Figure 2.4A), the transformation toward side product P_2 is reversed under much more severe conditions in respect of chemical potential μ_{P_2} (as in the case of reactions with common catalytic intermediate K_1—Figure 4.8). In fact, reversal of the side reaction $R \rightarrow P_2$ (Figure 2.4A) needs the inequality $\mu_{P_2} > \mu_R$ to be satisfied, whereas the case in Figure 4.8 requires the much milder condition $\mu_{P_2} > \mu_{K_1} - \mu_K$ for reversal of the reaction of the by product P_2 formation, since the necessary condition of R the transformation is $\mu_{K_1} - \mu_K < \mu_R$.

It is important that the kinetic thermodynamic analysis, unlike a simple equilibrium thermodynamic analysis, of conjugate processes allows more correct conditions of the reversal of some channels of the stepwise trans formations to be obtained and new practically significant catalytic systems to be created, even though the mechanism of the catalytic action is not fully understood. We shall consider now some simple examples of this analysis of the processes of catalyst coking, involvement of light molecules (CO_2, CH_4, etc.) into reactions with heavy paraffins, and so forth.

4.5.2. Application of the Horiuti-Boreskov-Onsager Equations for Identifying the Conditions of Reversal of a Catalytic Transformation

Example 15 Reactions of the coke formation

The coke deposition on a catalyst under operation of the latter is a typical reason for the catalyst deactivation. This process also can be considered as a manifestation of nonselectivity in the conversion of various organic compounds. Hence, the practically important problem is to find the conditions of the coking prevention. As an example, let us identify the conditions of no coke deposition on catalysts during the "dry" methane reforming described by a stepwise transformation as follows:

$$CH_4 + CO_2 \rightleftarrows 2H_2 + 2CO. \tag{4.99}$$

It is often possible to describe the mechanism of coke (elementary carbon) deposition during the process over metal catalysts using a system of linearly independent parallel reactions:

$$\begin{aligned} &CH_4 \rightleftarrows C + 2H_2,\\ &C + CO_2 \rightleftarrows 2CO. \end{aligned} \tag{4.100}$$

In the non-conjugated system, an evident condition of no coke deposition by scheme (4.100) is the simultaneous satisfaction of two inequalities:

$$\tilde{C} \cdot \tilde{H}_2^2 \geq \tilde{C}H_4, \quad \tilde{C} \cdot \tilde{C}O_2 \geq \left(\tilde{C}O\right)^2, \tag{4.101}$$

which is identical to inequalities

$$\mu_C + 2\mu_{H_2} > \mu_{CH_4}, \quad \mu_C + \mu_{CO_2} > 2\mu_{CO}. \tag{4.102}$$

Let us demonstrate that the conditions of no coke deposition during the main catalytic stepwise process (4.99) can differ from conditions (4.101) and (4.102). To start analyzing, we assume that the more detailed process scheme includes, for example, two common C_1-intermediates K_1 и K_2:

$$\begin{aligned} &CH_4 + K \overset{\varepsilon_1}{\rightleftarrows} K_1 + H_2,\\ &K_1 \overset{\varepsilon_2}{\rightleftarrows} K_2 + H_2,\\ &K_2 \overset{\varepsilon_3}{\rightleftarrows} K + C,\\ &K_2 + CO_2 \overset{\varepsilon_4}{\rightleftarrows} 2CO + K. \end{aligned} \tag{4.103}$$

Here, C symbolizes coke in its final condensed form, which is close to graphite in its thermodynamic properties. Therefore, assume $\mu_C \approx \mu_{graph} = \text{const}$ and, as a consequence, the quantity

$$\tilde{C} \approx \exp\left(-\mu^{o}_{graph}/RT\right)$$

also is a constant parameter.

An evident condition of no coke deposition is the potentially negative rate of its formation:

$$\frac{d[C]}{dt} < 0.$$

Let us find the conditions of satisfying this inequality by fulfilling combined kinetic and thermodynamic analysis of scheme (4.103) with the assumption of stationarity in respect to intermediates K_1 and K_2:

$$\frac{d[K_1]}{dt} = \varepsilon_1(\tilde{C}H_4 \cdot \tilde{K} - \tilde{K}_1 \cdot \tilde{H}_2) - \varepsilon_2(\tilde{K}_1 - \tilde{K}_2 \cdot \tilde{H}_2) = 0$$

$$\frac{d[K_2]}{dt} = \varepsilon_2(\tilde{K}_1 - \tilde{K}_2 \cdot \tilde{H}_2) - \varepsilon_3(\tilde{K}_2 - \tilde{K} \cdot \tilde{C}) - \varepsilon_4(\tilde{K}_2 \cdot \tilde{C}O_2 - \tilde{C}O^2 \cdot \tilde{K}) = 0.$$

Hence,

$$\tilde{K}_1 = \tilde{K}\frac{\varepsilon_1\varepsilon_2\tilde{C}H_4 \cdot \tilde{H}_2 + \varepsilon_2\varepsilon_4\tilde{H}_2 \cdot \tilde{C}O_2 + \varepsilon_2\varepsilon_3\tilde{H}_2 \cdot \tilde{C} + \varepsilon_1\varepsilon_3\tilde{C}H_4 + \varepsilon_1\varepsilon_4\tilde{C}H_4 \cdot \tilde{C}O_2}{\varepsilon_1\varepsilon_2\left(\tilde{H}_2\right)^2 + \left(\varepsilon_3 + \varepsilon_4\tilde{C}O_2\right)\left(\varepsilon_1\tilde{H}_2 + \varepsilon_2\right)},$$

$$\tilde{K}_2 = \tilde{K}\frac{\varepsilon_1\varepsilon_2\tilde{C}H_2 + \left(\varepsilon_3 + \varepsilon_4\left(\tilde{C}O\right)^2\right)\left(\varepsilon_1\tilde{H}_2 + \varepsilon_2\right)}{\varepsilon_1\varepsilon_2\left(\tilde{H}_2\right)^2 + \left(\varepsilon_3 + \varepsilon_4\tilde{C}O_2\right)\left(\varepsilon_1\tilde{H}_2 + \varepsilon_2\right)}.$$

From this we have

$$\begin{aligned} v_c = \frac{d[C]}{dt} = \varepsilon_3(\tilde{K}_2 - \tilde{K} \cdot \tilde{C}) = \frac{\varepsilon_3\tilde{K}}{\varepsilon_1\varepsilon_2(\tilde{H}_2)^2 + (\varepsilon_3 + \varepsilon_4\tilde{C}O_2)(\varepsilon_1\tilde{H}_2 + \varepsilon_2)} \cdot \\ \cdot\left\{\varepsilon_1\varepsilon_2(\tilde{C}H_4 - \tilde{C} \cdot \tilde{H}_2^2) + (\varepsilon_1\tilde{H}_2 + \varepsilon_2)\varepsilon_4\left[(\tilde{C}O)^2 - \tilde{C}O_2 \cdot \tilde{C}\right]\right\}. \end{aligned} \tag{4.104}$$

It follows from these considerations that coke is not formed when

$$\varepsilon_1\varepsilon_2(\tilde{C}\cdot\tilde{H}_2^2 \quad \tilde{C}H_4) + (\varepsilon_1\tilde{H}_2 + \varepsilon_2)\varepsilon_4\left[\tilde{C}\cdot\tilde{C}O_2 \quad \left(\tilde{C}O\right)^2\right] > 0.$$

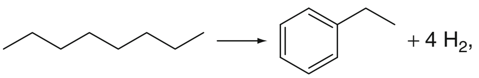
One can see that the derived condition of no coke formation during the main stepwise transformation (4.99) differs considerably from the necessary simultaneous satisfaction of a more rigid system of two inequalities (4.101).

Example 16 Catalytic reactions of direct insertion of methane and light alkanes into longer linear alkanes: the BIFORMING and BICYCLAR processes

In recent years, several catalytic processes based on potential thermodynamic conjugation of parallel channels of catalytic reactions have been developed and, in some cases, implemented in industry. The most spectacular processes like the direct insertion of the lightest and quite inert hydrocarbon, methane, into longer hydrocarbon chains were considered impossible not very long ago.

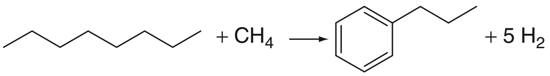
It is well known that many processes of oil or oil fraction refining produce methane as a by-product of the undesirable concurrent cracking of hydrocarbons. This results in common intermediates in the processes of methane formation and the target formation of oil-refining products. Hence, one can try to preserve the main (conjugating) channel of hydrocarbon transformation and, simultaneously, to reverse the channel of methane formation in order to provide the direct insertion of methane into longer hydrocarbon chains. Creating the appropriate conditions for the desired transformation does not require a thorough knowledge of the catalytic transformations. However, we need to identify the conditions when these thermodynamic forces arise, which favor the methane insertion.

For example, in the industrial process of reforming of gasoline fractions, one of the main target transformation channels is dehydrocyclization of linear C_{5+}-paraffin, such as



which is accompanied by undesirable cracking processes to form methane and light C_2-C_4 alkanes.

The dehydrocyclization of linear C_{5+}-paraffin may conjugate, for example, with methanation:



(in general form),

$$C_nH_{2n+2} + CH_4 \rightarrow C_{n+1}H_{2(n+1)+2} + 5H_2, \tag{4.105}$$

or with the insertion of another light alkane   for example, butane:

$$C_nH_{2n+2} + C_3H_8 \rightarrow C_{n+3}H_{2(n+1)+2} + 5H_2. \tag{4.106}$$

While $\Delta_r H^o > 0$ and $\Delta_r S^o > 0$ for all conjugate stepwise transformations (see Table 4.1), the temperature of the shift of their equilibrium is

$$T^* \approx \frac{\Delta_r H^o}{\Delta_r S^o} \approx 670 \quad 720K(400 \quad 450°C).$$

At the temperature above this point, $\Delta_r G^o < 0$ and, therefore, the equilibrium of processes (4.105) and (4.106) is shifted to the right.

Therefore, in the traditional complex process of gasoline fraction reforming (the process to enhance the octane number mainly due to dehydrocyclization of linear octanes), it is easy to excite driving forces at $T > T^*$ to provide the direct insertion of light hydrocarbons into heavier alkanes.

The BIFORMING process was recently developed by the Boreskov Institute of Catalysis (Russia) based on the preceding principle. The process is used in the production of "oil-refining" gases (light hydrocarbons) that are created during oil-refining processes (cracking, reforming, etc.). It has been industrially implemented using standard reforming platinum catalysts. The driving thermodynamic forces that are necessary for reversal of the side reaction of heavy hydrocarbon cracking into light alkanes and methane are generated by high-pressure recycling of the oil-refining gases through a standard reactor for reforming of gasoline fractions. The large-scale testing of the

Table 4.1 Thermodynamic parameters of gas-phase reactions of combined dehydrocyclization of light and long alkanes

	Reaction	$\Delta_r H^o_{298}$, kJ/mol	$\Delta_r S^o_{298}$, kJ/mol	T*, K
1	$CH_4 + n\ C_5H_{12} \rightarrow C_6H_6 + 5H_2$	304.6	386.0	790
2	$n\ C_6H_{14} + CH_4 \rightarrow C_6H_5CH_3 + 5H_2$	291.6	401.6	730
3	$n\ C_6H_{14} + C_3H_8 \rightarrow C_6H_5C_3H_7$(cumene) $+ 5H_2$	275.6	439.1	630

BIFORMING process has shown some potential for the insertion of light-to-heavy alkanes. The yield of high-octane gasoline increased by 3 4.5% without the need for additional oilfeed consumption (note that the capacity of individual gasoline fraction reforming reactors is approximately 70 100 tsnd t/y).

The ideas underlying the BIFORMING process can be applied to another process: the direct coaromatization of methane with light C_2 C_4 alkanes. In fact, the widely used processes of aromatization of C_2 C_4 alkanes over ZnZSM-5 zeolites for example, $2C_3H_8 \rightarrow C_6H_6 + 5H_2$ are often accompanied, as well as reforming of gasoline fractions, by side processes of partial cracking of light alkanes into methane.

Also, relevant thermodynamic data (Table 4.2) indicate that the rise of the methane pressure during standard aromatization of C_2 C_4 alkanes must result in the direct insertion of methane into aromatic hydrocarbons at 720 770 K (450 500°C) that is, by reaction $2C_3H_8 + CH_4 \rightarrow C_6H_5CH_3 + 6H_2$ (see Table 4.2).

Some direct experimental studies on coaromatization of methane and C_3 C_4 alkanes supported this conclusion and revealed, as expected, the "threshold" nature of the reversal of the methane formation absorption process (see Figure 4.9). In the

Table 4.2 Thermodynamic parameters of some reactions of light alkanes aromatization

	Reaction	$\Delta_r H^o_{298}$, kJ/mol	$\Delta_r S^o_{298}$, kJ/mol	T*, K
1	$6CH_4 \rightarrow C_6H_6 + 9H_2$	532.0	326.3	1630
2	$2C_3H_8 \rightarrow C_6H_6 + 5H_2$	290.6	382.0	760
3	$2n\ C_4H_{10} \rightarrow p\ C_6H_4(CH_3)_2 + 5H_2$	278.6	279.7	800
4	$C_3H_8 + n\ C_4H_{10} \rightarrow C_6H_5CH_3 + 5H_2$	278.6	393.4	710
5	$3C_2H_6 \rightarrow C_6H_6 + 6H_2$	336.9	363.9	930
6	$CH_4 + 2C_3H_8 \rightarrow C_6H_5CH_3 + 6H_2$	332.6	377.8	880
7	$CH_4 + C_3H_8 + n\ C_4H_{10} \rightarrow p\ C_6H_4(CH_3)_2 + 6H_2$	279.0	264.1	1060
8	$CH_4 + C_2H_6 + C_3H_8 \rightarrow C_6H_6 + 6H_2$	346.3	366.7	940
9	$CH_4 + 3C_3H_8 \rightarrow C_{10}H_8 + 10H_2$	537.4	644.9	830

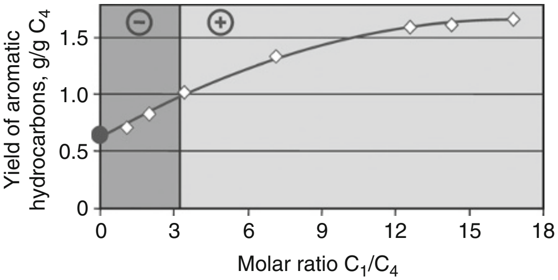


Figure 4.9 The rate of the uptake (sign "plus" zone) or formation (sign "minus" zone) of methane versus the concentration (pressure or C_1/C_4 ratio) of methane in the course of coaromatization of methane and butane over ZnZSM-5 zeolites at 400°C [2].

experiments, the share of the methane-originated carbon in the liquid coaromatization fraction was up to 70 wt %. The incorporation of methane into aromatic hydrocarbons in the said processes was approved by direct isotope methods using ^{13}C and ^{14}C labeled methane.

In comparison to direct aromatization of methane to benzene, the conjugate coaromatization of methane with heavier alkanes needs much milder conditions (about T^* for reaction 1 and reactions 6 9 in Table 4.2). This argues for the practical importance of the coaromatization processes that are called BICYCLAR.

4.5.3. Using the Horiuti-Boreskov-Onsager Equations for the Approximate Kinetic Description of Complex Catalytic Transformations

The phenomenological Horiuti Boreskov Onsager equations allow in some cases a first approximation to be made for the kinetic description of catalytic transformations in systems that involve numerous parallel transformation channels. Consider how these equations can be applied with the process of benzene alkylation with ethylene as an example.

The target process of benzene (B) alkylation with ethylene (E) to yield ethylbenzene (EB)

$$B + E \overset{\Sigma 1}{\rightleftarrows} EB$$

over zeolite catalysts is accompanied by the formation of a side product, diethylebenzene (DEB), due to overalkylation of the target product:

$$EB + E \overset{\Sigma 2}{\rightleftarrows} DEB.$$

In industry, the transalkylation process is used for removing undesired DEB and improving the process selectivity for the target product EB:

$$\mathrm{DEB + B \rightleftarrows 2EB.}$$

The transalkylation process is achieved in a separate reactor using the cat alyst and conditions that are almost identical to those of the target reaction.

Let us demonstrate that the presence of the thermodynamic conjugation with the undesired side transformation channels allows, in principle, the target process of the conversion of benzene to ethylbenzene to be achieved with the 100% selectivity provided that the undesired DEB product is added in a certain amount to the initial reaction mixture. Consider the first and second stepwise alkylation processes as thermodynamically conjugate (the third stepwise process is linearly dependent on these two processes). In doing so, the kinetic equations of the formation of ethylbenzene and diethylbenzene can be written in the Horiuti Boreskov Onsager form as

$$\mathrm{v}_{\Sigma 1} = \frac{\mathrm{d[EB]}}{\mathrm{dt}} = \Lambda_{11}\left(\tilde{\mathrm{B}} \cdot \tilde{\mathrm{E}} - \tilde{\mathrm{E}}\mathrm{B}\right) + \Lambda_{12}\left(\tilde{\mathrm{E}}\mathrm{B} - \mathrm{D}\tilde{\mathrm{E}}\mathrm{B}\right)$$

$$\mathrm{v}_{\Sigma 2} = \frac{\mathrm{d[DEB]}}{\mathrm{dt}} = \Lambda_{21}\left(\tilde{\mathrm{B}} \cdot \tilde{\mathrm{E}} - \tilde{\mathrm{E}}\mathrm{B}\right) + \Lambda_{33}\left(\tilde{\mathrm{E}}\mathrm{B} - \mathrm{D}\tilde{\mathrm{E}}\mathrm{B}\right),$$

where, in accordance to (4.98),

$$\Lambda_{12}\tilde{\mathrm{E}}\mathrm{B} \cdot \tilde{\mathrm{E}} = \Lambda_{21}\tilde{\mathrm{B}} \cdot \tilde{\mathrm{E}}.$$

These equations can be used as the first approximation for calculating, for example, the conversion of ethylene and ethylbenzene in a tubular plug flow reactor. The calculations can be based on the preceding kinetic equations using the concentrations of the "external" reactants B, E, EB, and DEB and equilibrium constants $\mathrm{K_{pi}}$ of the stepwise processes under consideration:

$$\frac{\mathrm{d[EB]}}{\mathrm{dt}} = \Lambda'_{11}\left(\mathrm{[B]} \cdot \mathrm{[E]} - \frac{\mathrm{[EB]}}{\mathrm{K_{p1}}}\right) - \Lambda'_{12} \cdot \left(\mathrm{[EB]} \cdot \mathrm{[E]} - \frac{\mathrm{[DEB]}}{\mathrm{K_{p2}}}\right),$$

$$\frac{\mathrm{d[DEB]}}{\mathrm{dt}} = -\Lambda'_{21}\frac{\mathrm{[EB]}}{\mathrm{[B]}} \cdot \left(\mathrm{[B]} \cdot \mathrm{[E]} - \frac{\mathrm{[EB]}}{\mathrm{K_{p1}}}\right) + \Lambda'_{22} \cdot \left(\mathrm{[EB]} \cdot \mathrm{[E]} - \frac{\mathrm{[DEB]}}{\mathrm{K_{p2}}}\right).$$

There are three phenomenological coefficients Λ'_{ij} in the derived equation system.

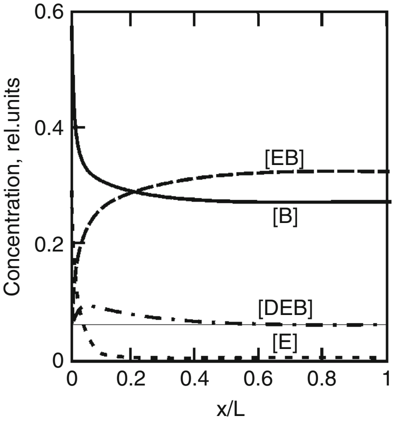


Figure 4.10 Typical results of the calculations of expected variations in the stationary concentrations of components at the benzene (B) alkylation with ethylene (E) along a plug-flow reactor of length L at 210°C; x is the distance from the inlet of the reactor. The calculations were performed in terms of the Horiuti-Boreskov-Onsager reciprocity relations to optimize the composition of the initial reaction mixture so the outlet and inlet diethylbenzene (DBE) concentrations would be identical, which means 100% selectivity of the process in respect to the target product ethylbenzene (EB).

Figure 4.10 illustrates the results of typical calculations of the reaction mixture composition evolution in the plug flow reactor; the calculations are made using the preceding relationships, the relevant mass balance equations, and literature data on K_{pi} at 210°C. The evolution in time of the initial product concentrations including DEB is seen to lead eventually to the situation when the inlet and outlet DEB concentrations become equal. This means that the proper choice of the composition of the initial reaction mixture makes the process 100% selective in respect to the conversion of the initial reactants, benzene and ethylene, to EB (see Figure 4.10) even though no transalkylation reactor is used.

4.5.4. Conclusions

When they occur over the same catalyst, stepwise catalytic transformations are usually conjugated through common catalytic intermediates, and, therefore, the methods of thermodynamics of nonequilibrium processes appear helpful in controlling the process selectivity even without any changes in the catalyst composition. It is important that these control methods are based on variations in the thermodynamic driving forces for the stepwise catalytic transformations and, therefore, do not need detailed knowledge of the mechanisms of these catalytic processes.

4.6. SPECIFIC PROPERTIES OF THE NONEQUILIBRIUM STATE OF OPERATING CATALYSTS

The phenomenon of catalysis is based on the formation of intermediate compounds of the active catalyst substance and the reactants of the catalyzed reaction. As a result, the state of the active component is inevitably controlled by its interactions with the reaction medium and undergoes certain changes during the catalyst operation. For heterogeneous catalysts, the results of such interactions are known as the surface reconstruction, which may be considerable. For example, the smooth surface of noble metals can be faceted under the action of high CO pressure to form a kind of regular surface roughness of supramolecular size. In the copper oxide catalysts, there was observed a reversible migration of copper ions from the bulk of the oxide phase to form epitaxial copper metal nanoparticles on the surface.

The consequence of the inevitable adaptation of a catalyst to the reaction medium was formulated by G. Boreskov in 1947 as a particular rule: In stationary conditions, the specific catalytic activity, SCA, of a heterogeneous catalyst (i.e., the rate of the catalytic reaction per unit of exposed surface of the catalytically active phase) is approximately constant at a given temperature and the reaction medium composition, thus SCA being dependent only on the chemical composition of the active catalyst phase. At present, turnover frequency (TOF) of the active center is normally used instead of SCA to characterize the activity of the center, TOF being in direct proportion to SCA. The Boreskov rule is evidently valid for the TOF value, too.

It is important from the point of view of thermodynamics of nonequilibrium processes that catalysts are operating usually at the condition of large affinities for the catalyzed stepwise process ($A_{r\Sigma} > RT$)—in other words, the process occurs far from thermodynamic equilibrium. Following we discuss the manifestation of only the phenomena of the nonequilibrium catalyst reconstruction under conjugation involving the catalyst transformations and the conjugating catalyzed reaction.

4.6.1. Specific Features of Nonequilibrium Stable States of the Operating Catalyst

The most spectacular nonequilibrium reconstruction of catalysts is observed in the case of unstable stationary states of the catalyst far from thermodynamic equilibrium. As mentioned in Chapter 3, this may result in the formation of easily detected dissipative structures and in the phenomena such as oscillation of the chemical reaction rate, generation of moving chemical waves in the system bulk or on the catalyst surface, and so on.

However, the stationary states of the catalyst may be stable far from thermodynamic equilibrium—for example, due to the existence of the positively defined Lyapunov function for the given catalytic process (see Section 3.4). In particular, there are always stable stationary states of catalytic systems with an arbitrary set of monomolecular transformations of catalytic intermediates ("the reactant–active center" complexes) or any other set of these transformations, when they are linear in respect to the intermediate concentration or its thermodynamic rush.

The experimentally observed manifestations of nonequilibricity of the stable catalyst state usually is less spectacular than those resulting in the formation of dissipative structures. The most frequently observed manifestations of the stable nonequilibrium state are those in homogeneous systems, when the stationary concentrations of catalytic intermediates are substantially different in the course of the catalytic process and in the equilibrium system.

In more general cases that include heterogeneous systems, the nonequilibricity of the stable stationary catalyst state is identified as follows:

1. Existence of a difference between the temperature of the active component of the operating catalyst and the temperature of the inert catalyst support and the surrounding medium
2. A decrease in the stationary chemical potential (concentration) of most reactive catalyst species (including intermediate "reactant–reaction center" complexes) and an increase in chemical potentials (concentrations) of less reactive species against their chemical potentials (concentrations) under conditions of thermodynamic equilibrium of the reaction medium
3. Existence of reversible nonequilibrium reconstruction of the active component surface or bulk
4. Changes in the phase transition temperature of the active component against relevant transition temperatures under thermodynamically equilibrium conditions—that is, shifting the curves of coexistence of active component phases against their positions in the equilibrium p T diagrams
5. Potential emergence of metastable states of the active component of the catalyst, including those in the form of spatial dissipative structures on the surface or in the bulk of the active component

We shall consider several examples of these phenomena.

Example 17 Temperature of the active component of an operating catalyst

The most characteristic example of nonequilibricity of a heterogeneous catalyst is a considerable difference between the actual temperature of the active component of an operating catalyst and the temperature of the surrounding medium or the catalyst granule bulk. In exothermic catalytic processes, the difference is accounted for by the finite rate of heat exchange between the active component, where a considerable quantity of heat of the catalyzed reaction is evolved, and the surrounding medium.

The heat fluxes J_Q evolved (in exothermic processes) by the catalyzing process and the fluxes J_c of the transformed substances (reactants) interact on the active component. With stationary J_c fluxes, the result is a nonzero J_Q quantity that is, the appearance of the thermodynamic force for heat abstraction from the active component to, for example, the catalyst granule bulk and then to the surrounding medium. This causes temperature gradients among the active component, the chemically inactive catalyst support, and the surrounding medium. In strongly exothermic processes, the difference can be experimentally detected, for example, as an "abnormally" large increase in the lattice constant of the active component during the reaction against the respective increase in the inert medium. Figure 4.11 illustrates experimental data on the highly exothermic ($\Delta_r H^o_{298} =$ 206 kJ/mol) reaction of the synthesis gas methanation

$$3H_2 + CO \rightarrow CH_4 + H_2O$$

over catalyst Ni/SiO_2.

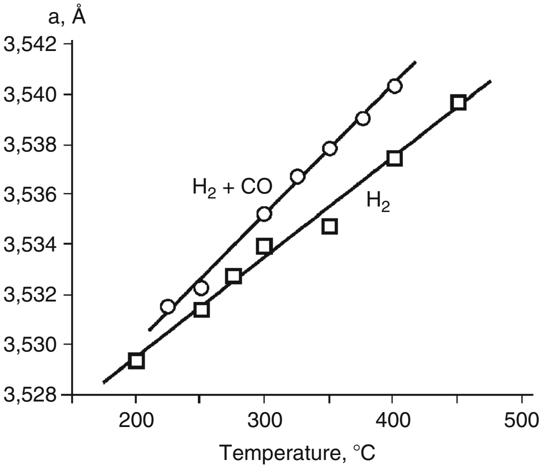


Figure 4.11 Temperature dependence of the lattice constant of Ni nanoparticles in the Ni/SiO_2 catalyst in the single gas medium (H_2) and in the reaction mixture $H_2 + CO$ at the stationary occurrence of the syngas methanation. The abscissa shows the temperature of the catalyst granules as measured with a thermocouple [3].

Example 18 Reduction of the melting temperature of an operating catalyst

Another example of the stable nonequilibricity of the catalytically active components is the subnormal melting temperature of metal nanoparticles in the course of amorphous carbon graphitization they catalyze (see Figure 4.12). The process follows the stepwise reaction

$$C_{\text{amorph}} \xrightarrow[\text{Fe, Ni, Co}]{} C_{\text{graphite}},$$

and is characterized by affinity $A_{r\Sigma} = \Delta_r G \approx 12$ kJ/mol that is much higher than RT at temperatures below 1000 K. The process is mediated by dissolving the carbon atoms in the metal catalyst nanoparticle (Figure 4.12B).

The process scheme is usually interpreted in terms of the "carbide cycle"

$$C_{\text{amorph}} \rightleftarrows C_{\text{Me}} \rightleftarrows C_{\text{graphite}},$$

where C_{Me} is carbon dissolved in the metal and behaving as the intermediate of the stepwise transformation.

In the course of graphitization, the standard chemical potential μ_C of carbon dissolved in the metal, $\mu_{C(\text{Me})}$, should necessarily obey the condition

$$\mu_{C(\text{amorph})} > \mu_{C(\text{Me})} > \mu_{C(\text{graphite})}$$

(see Figure 4.13). Therefore, the stationary concentration of carbon in the metal appears to be much higher than the carbon concentration in the eutectic solution, which is characteristic of the equilibrium

$$C_{\text{graphite}} = C_{\text{Me}}.$$

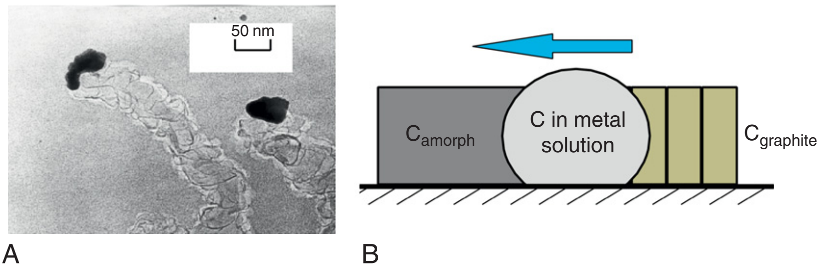


Figure 4.12 Micrograph (A) and a schematic (B) of catalytic graphitization of amorphous carbon in the presence of metal nanoparticles. The top arrow indicates the streamline of the fluidized particle [4]. (Courtesy of K. I. Zamaraev†)

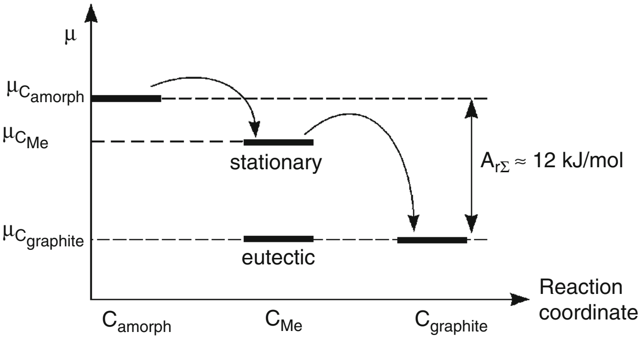


Figure 4.13 Variations in the chemical potential μ of carbon in the course of catalytic graphitization of amorphous carbon in the presence of metal nanoparticles (see Figure 4.12B). When the rate-limiting step is graphitization of the dissolved carbon, the stationary value is $\mu_{C_{Me}} \approx \mu_{C_{amorph}}$. In the equilibrium state, the chemical potential of the dissolved carbon is $\mu_{C_{Me}} \approx \mu_{C_{eutect}} = \mu_{C_{graph}}$.

Note that the said eutectic means establishing the thermodynamic equilibrium of the solution with bulk graphite but not with more energy-saturated carbon species for example, with the amorphous carbon.

When the formation of graphite particles from the metal-dissolved carbon is the rate-limiting step of the catalytic graphitization, then

$$\mu_{C(Me)} \approx \mu_{C(amorph)}.$$

While the carbon solution in the metal is close to the ideal solution, the chemical potential of the dissolved carbon is

$$\mu \approx \mu^{o} + RT\ \ln x,$$

where x is the molar fraction of the dissolved carbon in the metal.

In the equilibrium between the carbon solution and amorphous carbon, x is estimated as

$$x \approx x_{eut} \exp(\quad \Delta_r G/RT),$$

which is much more than x_{eut} for the equilibrium of the eutectic solution with graphite. In fact, at $T \leq 1000$ K $\frac{\Delta_r G}{RT} \approx \frac{12000}{8.3 \cdot 1000} \approx 1.4$. This corresponds to approximately fourfold stationary oversaturation of the metal with carbon in comparison to the solution-graphite equilibrium. The melting point of this oversaturated but dynamically stable solution may be calculated by the Schröder equation

$$R \ln x = \Delta_{melt} H^{o} \left(\frac{1}{T} \quad \frac{1}{T_o} \right),$$

where $\Delta_{melt}H^{o}$ and T_o are enthalpy and melting temperature, respectively, of pure metals (at $x = 0$), and T is the melting temperature of the solution under discussion. The calculation shows that the melting point of this oversaturated solution is 500 900 K (!) lower than the melting temperatures of the corresponding equilibrium eutectics of catalytically active metals (Figure 4.14).

The phenomenon of abnormally low temperature melting of catalytically active metals can be experimentally observed by using, for example, the in situ electron microscopy (Figure 4.15 and Table 4.3).

There are good reasons to suppose that a similar phenomenon of fluidization of nanoparticles of the same catalytically active metals may happen to some other catalytic processes when they are accompanied by the formation of graphitized carbon. Examples of such processes are catalytic pyrolysis of methane

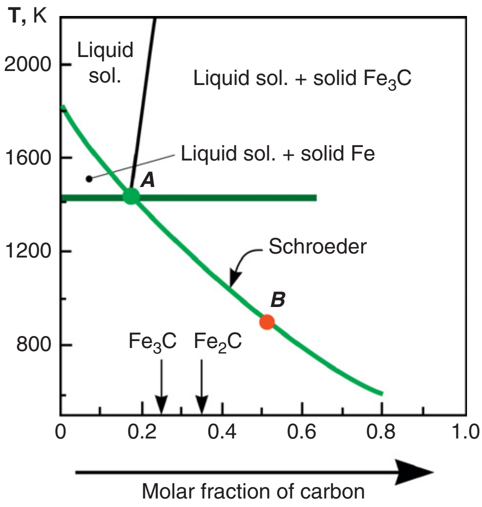


Figure 4.14 A very simplified melting diagram of the Fe–C system where a stationary metastable phase can form during the catalytic graphitization of amorphous carbon. Fe_3C (cementite) and Fe_2C are stoichiometric iron carbides. ***A*** is the equilibrium eutectic point ($T = 1420$ K, $x = 0.173$), and ***B*** is the stationary oversaturated state ($T = 920$ K).

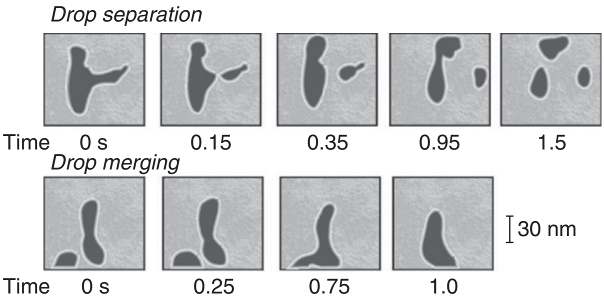


Figure 4.15 An in situ electron microscopic video of the migration of fluidized Fe-C particles in the amorphous carbon layer at temperature 650°C [4]. (Courtesy of K. I. Zamaraev†)

Table 4.3 Melting temperatures (°C) of pure metals and their eutectic and stationary mixtures with carbon

Metal	Pure metal	Eutectic mixture with carbon	Stationary state
Fe	1539	1147	640
Co	1493	1320	600
Ni	1453	1318	670

$$CH_4 \rightarrow C + 2H_2 \uparrow$$

at 800 850 K, as well as disproportionation of carbon monoxide

$$2CO \rightarrow C + CO_2$$

at temperatures below 800 K. The fluidization of the operating active component prevents it from "poisoning" through encapsulation by the graphite and can lead to the formation of long filamentous graphite-like structures and even graphite nanotubes (see Figure 4.16 and Chapter 5).

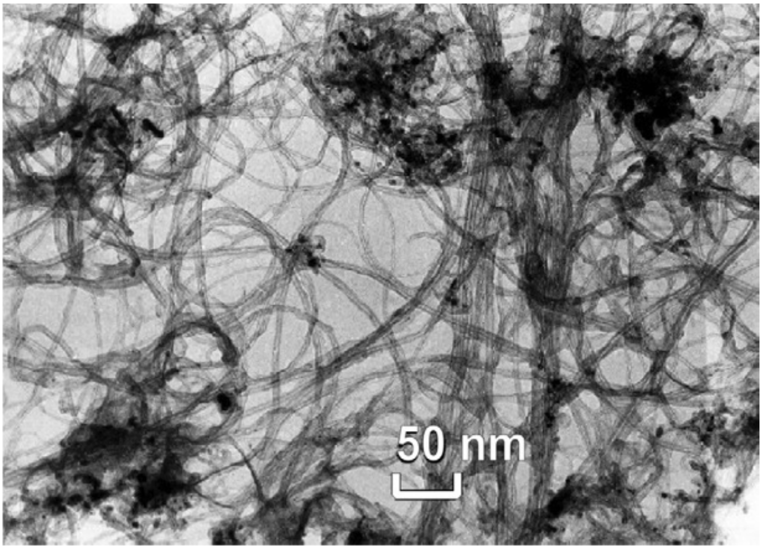


Figure 4.16 Micrographs of filamentous (nanotubular) carbon synthesized through disproportionation of CO over small (less than 25 nm in diameter) cobalt nanoparticles. The external diameter of the filaments equals the diameter of the initial Co^0 nanoparticle, the wall thickness of the graphite nanotube being 3–5 nm [6].

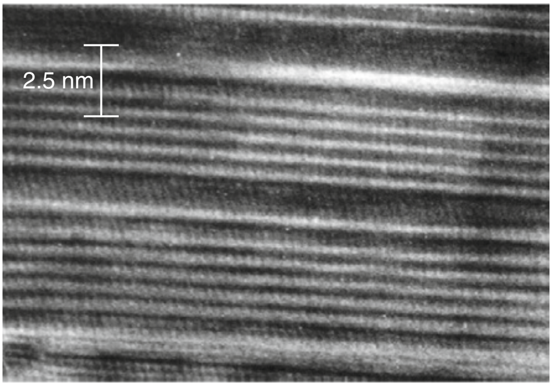


Figure 4.17 Regular layers inside a cobalt nanoparticle larger than 20 nm in diameter, which are observed after the particle has been exposed to CO at the pressure of 1 bar and temperature 700 K. The light regions are the fine (approximately five atoms in thickness) hexagonal cobalt layers, dark region are the cubic cobalt layers [6].

When the CO disproportionation is catalyzed by cobalt, some ordered metastable structures are detected inside the active metal nanoparticles after the reaction. These structures are regular thin (approximately 5 atoms in thickness) alternating cobalt layers of different crystallographic modifications (Figure 4.17). Note that the appearance of such structures at thermodynamically equilibrium states of the catalyst substance is contrary to the Gibbs phase rule for the phase equilibria in solids. Thus, the metastable layered structures may be considered an analogue of spatial dissipative structures.

4.6.2. Temporal and Spatio-Temporal Dissipative Structures in Catalytic Systems

The phenomenon of self organization occurs at nonstabilities of the stationary state and leads to the formation of temporal and spatio temporal dissipative structures. Remember that oscillating instabilities of stationary states of dynamic systems can be observed for the intermediate nonlinear stepwise reactions only, when no fewer than two intermediates are involved (see Section 3.5) and at least one of the elementary steps is kinetically irreversible. The minimal sufficient requirements for the scheme of a process with temporal instabilities are not yet strictly formulated. However, in all known examples of such reactions, the rate of the kinetically irreversible elementary reaction at one of the intermediate steps is at least in a quadratic dependence on the intermediate concentrations. Among these reactions are autocatalytic steps.

4.6.2.1. The Belousov-Zhabotinsky Reaction

The easily visualized Belousov Zhabotinsky (BZ) reaction is now a classic example of the emergence of temporal and spatio temporal dissipative structures in homogeneous chemical systems. The reaction was discovered by Soviet military chemist B. P. Belousov in 1951 when he was studying homogeneous oxidation of citric acid by potassium bromide, $KBrO_3$, in the presence of cerium sulfate $Ce(SO_4)_2$ as the catalyst for redox processes. In the dissolved mixture of these compounds under certain process conditions, Belousov discovered a *time-oscillating* synchronous reduction of cerium(4+) ions:

$$Ce^{4+} \longrightarrow Ce^{3+} + f\ Br\ , \tag{4.107}$$

followed by the also synchronous oxidation of thus formed cerium(3+) ions

$$Ce^{3+} \longrightarrow Ce^{4+}, \tag{4.108}$$

to close the transformation cycle of the ion catalyst (here, $f > 1$ is an effective stoichiometric coefficient). The oscillations of the chemical composition of the mixture were first visualized as periodical changes in the solution color due to the said time synchronized changes in the oxidation state of the homogeneous catalyst. The oscillations of the concentrations of different forms of the catalyst can be detected, apart from the color changes, via potentiometric measurements, NMR spectroscopy, and so on (Figures 4.18–4.21). As expected, the oscillations are observed in the process of the catalyst transformations, which is conjugated to the main catalyzed reaction—that is, to the oxidation of citric acid.

The results obtained by Belousov were not properly understood at that time because of their principal novelty. The leading Soviet scientific journals refused to publish Belousov's papers in both 1951 and 1957, citing the

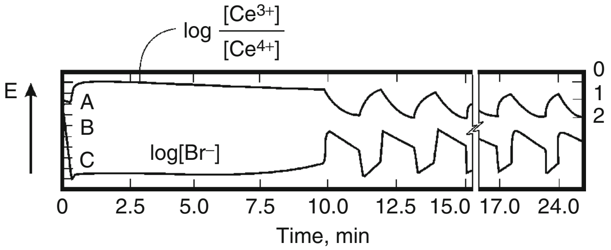


Figure 4.18 Results of one of the first potentiometric measurements of the Br^- concentrations and concentration ratios Ce^{4+}/Ce^{3+} at 25°C in the oscillating BZ reaction. The citric acid concentration is 0.032 M, $[KBrO_3] = 0.063$ M, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.01$ M, $[H_2SO_4] = 0.8$ M, $[KBr] = 1.5 \cdot 10^{-5}$ M.

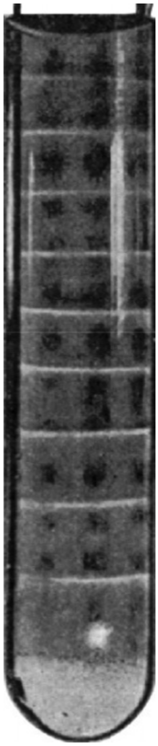


Figure 4.19 A photo of a cylindrical reaction tube with the occurring BZ reaction. The horizontal regions result from the formation of spatio-temporal dissipative structures in the tube. The light bands indicate the step of the formation of badly colored Ce^{4+} complexes.

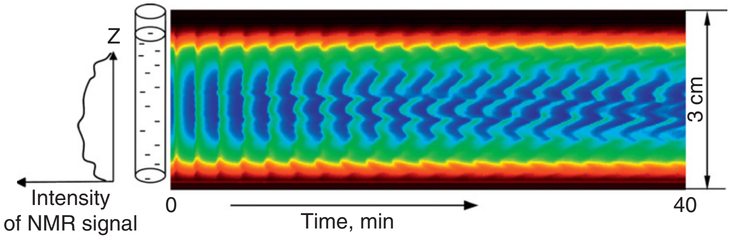


Figure 4.20 The moving concentration waves corresponding to variations in the oxidation state of the $Mn^{2+} \rightleftarrows Mn^{3+}$ cations during the BZ reaction in a cylindrical reactor. The pattern presents the time evolution of the concentration profiles along the reactor, which is observed using the NMR tomographic technique. The dark regions indicate a higher concentration of Mn^{2+}. A total of Mn concentration is 0.006 M [7].

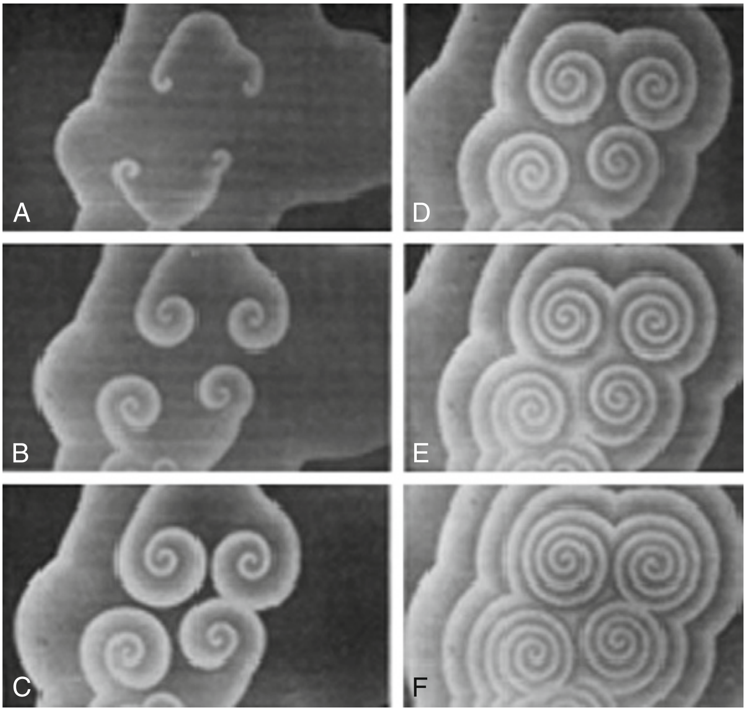


Figure 4.21 The moving spiral chemical waves generated during the BZ reaction occurrence in a flat Petri dish. Frames A–F are acquired in successive moments of time.

"theoretical impossibility" of the described oscillating reactions. However, Belousov's research was continued and developed by A. M. Zhabotinsky, and in 1980, Belousov (posthumously) and Zhabotinsky and his colleagues were awarded the Lenin Prize, the highest Soviet award, for the discovery of a new family of autowave and auto oscillating processes. In the world literature, the reaction type they studied was named the Belousov Zhabotinsky reactions (BZ reactions).

Formally, the BZ reactions are described by a simple stepwise reaction of the reduction of bromic acid to hypobromous acid under the action of an organic reductant D in the presence of homogeneous catalysts:

$$2HBrO_3 + D \xrightarrow[\text{catalyst}]{} D_{OX} + 2HBrO_2 + H_2O,$$

where D_{ox} is an oxidized form of D.

A variety of easily brominated organic compounds, such as citric ($(HOOCCH_2)_2C(OH)COOH$) and malonic ($HOOC–CH_2–COOH$)

acids, acetylacetone (CH_3–CO–CH_2–CO–CH_3), and so on, can behave as the organic reductant D. The general formula of these compounds comprises a brominable group –CH_2– in the molecule R_1–CH_2–R_2, where R_1 and R_2 can be organic moieties of rather different composition. In the final oxidized compound D_{ox}, group –CH_2– is oxidized to form R_1–CO–R_2. The homogeneous catalyst for the oscillating reactions may be not only $Ce^{3+/4+}$ ions but also $Mn^{2+/3+}$ ions, as well as phenanthroline and other complexes of iron, $Fe(phen)_3^{2+/3+}$, and compounds of other transition metals having several oxidation states.

Autocatalytic reaction (4.108), with its reaction products, accelerates the reaction per se (see following). A free Br ion generated by reaction (4.107) behaves as a strong inhibitor (decelerator) of the reaction (4.108). That is why only reaction (4.107) occurs first as long as all of the Ce^{4+} ions are transformed to Ce^{3+}. Then the self accelerating reaction (4.108) starts to convert all the Ce^{3+} ions to Ce^{4+}, and the process starts again from the very beginning. As a result, the system evolution is characterized by periodically changing its color from colorless (Ce^{3+} excess) to yellow (Ce^{4+} excess) and back to colorless. At the conditions of the first Belousov experiments, the color oscillated at approximately 4 minute intervals. The oscillations go on until the main reactants—the organic compound to be oxidized or bromate anion—are fully consumed—in other words, as long as the system is far from thermodynamic equilibrium and the driving force exists for the conjugate processes. A generally accepted scheme of elementary transformations in the course of the BZ reaction is presented in Table 4.4.

One reason for the instability of the stationary state of the overall BZ reaction is easy to identify when analyzing the following simplified diagram:

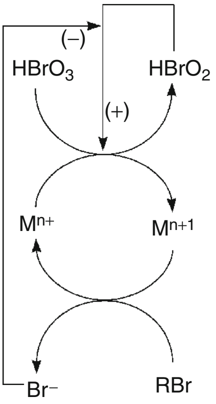


Table 4.4 Elementary transformations at the Belousov-Zhabotinsky reaction with malonic acid as the oxidized substrate

Process A
$3\ (Br\ + HOBr + H^{+} \rightleftarrows Br_2 + H_2O)$ $Br\ + HBrO_2 + H^{+} \rightleftarrows 2\ HOBr$ $Br\ + BrO_3\ + 2\ H^{+} \rightleftarrows HOBr + HBrO2$
$5\ Br\ + BrO_3\ + 6\ H^{+} \rightleftarrows 3\ Br_2 + 3\ H_2O$ *stepwise A*
Process B
$2\ HBrO_2 \rightleftarrows HOBr + BrO_3\ + H^{+}$ $2\ (HBrO_2 + BrO_3\ + H^{+} \rightleftarrows 2\ BrO_2^{\bullet} + H_2O)$ $4\ (BrO_2^{\bullet} + M^{n+} + H^{+} \rightleftarrows M^{n+1} + HBrO_2)$
$BrO_3\ + 4\ M^{n+} + 5\ H^{+} \rightleftarrows 4\ M^{n+1} + HOBr + 2\ H_2O$ *stepwise B*
Process C
$CH_2(COOH)_2 \rightleftarrows (HO)_2C{=}CHCOOH$ $(HO)_2C{=}CHCOOH + Br_2 \rightarrow BrCH(COOH)_2 + H^{+} + Br$ $2\ M^{n+1} + CH_2(COOH)_2 + BrCH(COOH)_2 \rightarrow 2\ M^{n+} + f\,Br\ +$ other products

This scheme has some dramatic steps:

1. An auto acceleration (indicated by (+)) conjugated to the oxidation of catalyst M^{n+} ions:

$$HBrO_3 + HBrO_2 \rightleftarrows 2Br\dot{O}_2 + H_2O,$$

$$Br\dot{O}_2 + M^{n+} + H^{+} \rightleftarrows M^{n+1} + HBrO_2.$$

Formally, this reaction sequence is identical to the autocatalytic formation of $HBrO_2$:

$$HBrO_2 + HBrO_3 \rightarrow 2HBrO_2.$$

With sufficiently high concentrations of initial reactants, the autocatalytic mode may cause instability of the stationary state of the system (see Section 3.3).

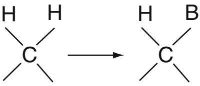
2. The inhibition (indicated by (–)) is

$$H^+ + Br\ \ + HBrO_2 \rightleftarrows 2HOBr.$$

   This reaction results in a decrease in the autocatalyst $HBrO_2$ concentration, thus avoiding the system instability.

3. The bromination of reducing agent RH:

$$RH + HOBr \longrightarrow RBr + H_2O$$

(this is the bromination of the $–CH_2–$ group: ).

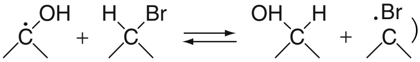
4. The reduction of deeply oxidized catalyst ions M^{n+1} to M^{n+} and the formation of inhibitor Br :

$$M^{n+1} + RBr \rightleftarrows \dot{R}Br + M^{n+} + H^+,$$

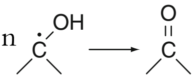
$$\dot{R}Br + H_2O \rightarrow \dot{R}OH + H^+ + Br\ \ ,$$

$$\dot{R}OH + RBr \rightleftarrows ROH + \dot{R}Br$$

(this reaction results in the transformation

)

$$M^{n+1} + \dot{R}OH \longrightarrow R{=}O + M^{n+} + H^+$$

(this is the transformation ).

Evidently, chemical transformations of catalytic intermediates—M^{n+}/M^{n+1} ions—are conjugated by the main reaction of the reduction of bromic acid. Due to the known instability of autoaccelerating step 1, the concentrations of catalyst species with different oxidation states may oscillate even in the initially homogeneous system at certain reactant concentration ratios. The oscillations are easy to detect visually or using special techniques (see Figures 4.18–4.21). Changes in the oxidation state of the catalyst ion may reach 90% of the catalyst content and even more.

The observed oscillations of concentrations of different catalyst species in the BZ reaction in homogeneous solutions are examples of the *temporal* dissipative structures. In an inhomogeneous system (for example, reactions conducted in a shallow plates or inside moist filter paper), the phenomenon of moving "*chemical" waves* may appear that indicates the appearance of spatial temporal dissipative structures (see Figures 4.19–4.21). Sometimes the structures may look like moving concentric or spiral waves (Figure 4.21). The emergence of such structures during nonlinear chemical reactions is accounted for by local fluctuations of the reactant concentrations and diffusion.

At present, many oscillating catalytic reactions are recognized in homogeneous media. One of them is the Bray Libafsky reaction discovered in 1921. The reaction is the decomposition of hydrogen peroxide

$$2H_2O_2 \xrightarrow[IO_3\ ,H^+]{} 2H_2O + O_2$$

in the presence of IO_3 anions as a homogeneous catalyst. The catalyst can participate in a number of intermediate transformations during the reaction to form various catalytic intermediates—for example, IO_3 , I_2O_2, HIO_2, I_2O, HIO, I_2, and I . A variety of such intermediates comprising iodine in different oxidation states favors the development of strong process nonlinearities, and, therefore, instability of the stationary state resulted in the concentration oscillations of these species. These are easy to detect using, for example, electrochemical techniques. The Bray Libafsky reaction is less well known than the Belousov Zhabotinsky and similar reactions because the oscillations are poorly visualized due to practical noncoloration of the intermediate catalyst species.

4.6.2.2. Oscillating Heterogeneous Catalytic Reactions and Chemical Waves on the Catalyst Surface

Isothermal oscillations of the reaction rate may be observed not only in homogeneous but also in a number of heterogeneous catalytic reactions. One of the first examples of an oscillating heterogeneous catalytic reaction was oxidation of CO by dioxygen over Ni in early 1970s. The most thoroughly studied examples are the oxidation of H_2 and CO by dioxygen over supported noble metals, as well as over individual crystallographic faces of single crystals of these metals (Figure 4.22). Note that in many real cases, the oscillations cannot be considered as purely isothermal ones; this introduces some additional nonlinearities into the process.

It is assumed that, for example, stepwise oxidation of dihydrogen over platinum metals

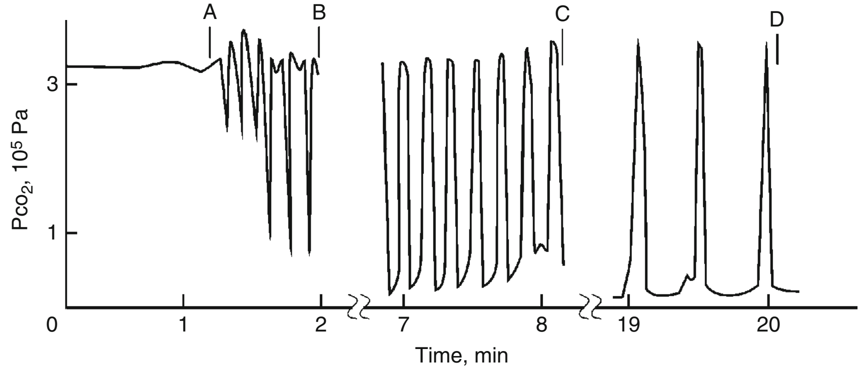


Figure 4.22 Isothermal autooscillations of the rate of heterogeneous catalytic reaction $CO + 1/2\ O_2 \rightarrow CO_2$ over monocrystal Pt(100) accompanied by a monocrystal surface reconstruction and, as a result, by changing the oscillation mode. Temperature 450 K, CO pressure $4.5 \cdot 10^{-3}$ Pa, the dioxygen pressure $1.7 \cdot 10^{-2}$ Pa [8]. (Courtesy of V. I. Savchenko†)

$$O_2 + 2H_2 \rightarrow 2H_2O$$

is mediated by the reactions of both atomic and molecular hydrogen. The simplified scheme of the respective surface reactions is nonlinear in respect to catalytic intermediates:

$$\begin{aligned} &O_2 + 2K \xrightarrow{1} 2K_1, \\ &H_2 + 2K \xrightarrow{2} 2K_2, \\ &K_1 + 2K_2 \xrightarrow{3} H_2O + 3K, \\ &H_2 + K_1 \xrightarrow{4} H_2O + K. \end{aligned} \tag{4.109}$$

Here, K_1 and K_2 stand for the surface catalytic intermediates, and K stands for the free active center of the catalyst.

A precise analysis of strongly nonlinear schemes similar to scheme (4.109) allows many critical events to be understood, including the observation of a multiplicity of stationary states, for example, during the reaction over nickel and platinum, as well as the emergence of the oscillating reaction modes at a certain composition of the reactions mixture. Note that scheme (4.109) per se seems to provide only an unambiguous and stable solution in the assumption of ideal adsorption on a uniform surface. To explain the critical phenomena and the emergence of the oscillation in the isothermal mode, a few important additional assumptions appear to be necessary. One was, for example, a dependence of the activation energies,

E_{ai}, and, correspondingly, the reaction rates of both elementary steps of the water formation on the catalyst surface coverage with the adsorbed oxygen atoms (the concentration of intermediate K_1):

$$E_{a3} = E^{o}_{a3} + \alpha_3[K_1]; \quad E_{a4} = E^{o}_{a4} + \alpha_4[K_1].$$

The latter assumption also relates to the strong nonlinearity of elementary steps in the scheme. The solution of the resulted kinetic equations for the overall scheme leads indeed to auto oscillating behavior of the system within the certain parameter range.

Another reason for the emergence of the oscillations in the scheme would be in preserving the assumption of the surface uniformity, the exis tence of a "buffer" step of dissociative adsorption of molecular oxygen

$$O_2 + 2K \rightleftarrows 2K_3,$$

where K_3 is an inert intermediate state of the adsorbed oxygen that does not participate in steps 3 and 4 of the water formation. We shall thus have a set of nonlinear equations that give, on their solving, auto oscillations of the intermediates' surface concentrations at certain parameter values and, therefore, auto oscillations of the overall rate of the heterogeneous cata lytic reaction of the water formation.

Similar speculations are applicable for explaining the oscillations observed during heterogeneous catalytic oxidation of CO by the stepwise reaction

$$CO + ½O_2 \rightarrow CO_2.$$

This oxidation is usually supposed to follow mainly the Langmuir Hinshelwood scheme—in other words, through interaction of the adsorbed intermediates:

$$\begin{gathered} CO + K \rightleftarrows K_1, \\ O_2 + 2K \rightleftarrows 2K_2, \\ K_1 + K_2 \rightarrow CO_2 + 2K. \end{gathered} \tag{4.110}$$

However, this scheme also needs a few additional assumptions on the pos sible existence of, for example, "buffer" steps to identify the conditions of the oscillation emergence; these steps should decelerate involving of some intermediate species to the CO_2 formation.

Numerous intent studies are focused on the mechanisms of oscillating reactions in model catalytic systems. For example, the mechanism of the CO oxidation over the surface of noble metal monocrystals are written now in much more detail than scheme (4.110), a dramatic reconstruction of the crystallographic surface state being supposed:

$$\begin{aligned}
&CO + K \rightarrow K_1,\\
&K_{1,hex} \rightarrow CO + K_{hex},\\
&(hex) \rightarrow (1 \times 1),\\
&4K_1 \rightarrow K_{1,1\times1}\\
&K_{1,1\times1} \rightarrow 4CO + K_{1\times1},\\
&(1 \times 1) \rightarrow (hex),\\
&K_{1\times1} \rightarrow K_{hex},\\
&O_2 + 2K_{1\times1} \rightarrow 2K_{3,1\times1},\\
&K_{3,1\times1} + K_1 \rightarrow CO_2 + K_{1\times1} + K,\\
&CO_2 + K \rightarrow K_3 + K_1.
\end{aligned}$$

Here, indices $(1\times1) \rightarrow (hex)$ relate to the said reconstruction of the surface and catalytic intermediate that reside on the pertinent faces.

Of primary importance is the synchronization of the reaction rate oscillations on various active microcenters on the crystal faces within the macroscopic oscillation of the overall process rate. This synchronization is supposedly accounted for by diffusion of the gas phase components along the surface, among other factors.

With many catalysts capable of initiating the rate oscillations in the reactions they catalyze, the phenomenon of the so called moving "chemical" waves—the "ordered" motion of fronts of the surface fragments covered by various adsorbate molecules—is observed (Figure 4.23). The spatially

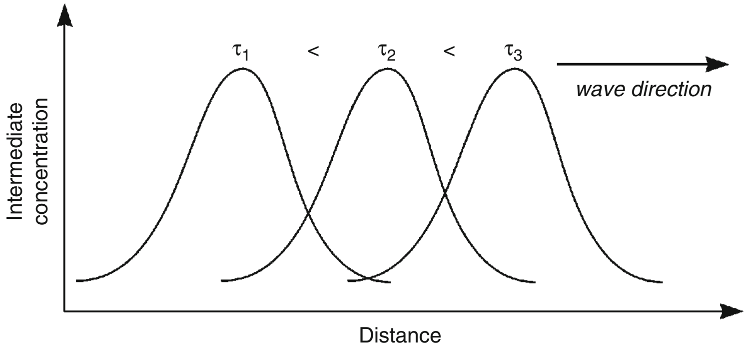


Figure 4.23 Schematic of the phenomenon of the isothermal "chemical" wave propagation. The profiles exhibit the concentrations of catalytic intermediates in the successive moments of time $\tau_1 < \tau_2 < \tau_3$.

oriented diffusion processes appear to be involved in the formation of such chemical waves. The moving chemical waves are examples of the emergence of spatio temporal dissipative structures on the catalyst surface; they can be observed on both mesoscopic (i.e., semimacroscopic, with the characteristic size of several microns; see Figures 4.24 and 4.25) as well as atomic and molecular (with the nanometer characteristic size; see Figure 4.26) levels. Monitoring and investigating the like isothermal

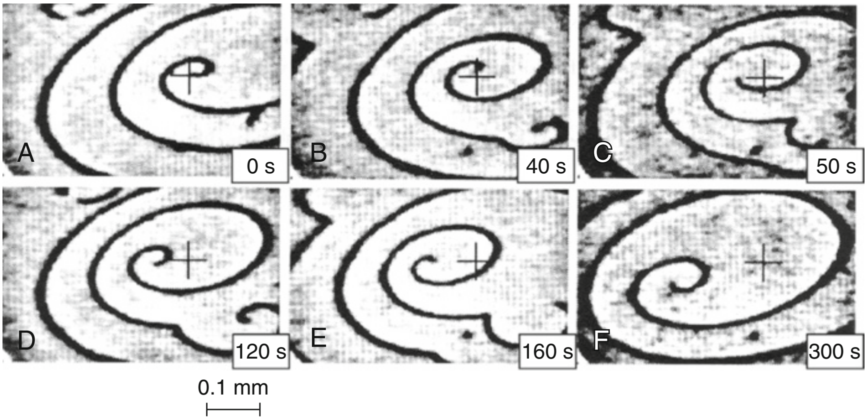


Figure 4.24 Successive photoemission electron micrographs of the propagation of moving spiral chemical waves during reaction $CO + 1/2\ O_2 \rightarrow CO_2$ on the surface of monocrystal Pt(110). The dark and light zones correspond to different coverage of the Pt surface with the adsorbed species. Temperature is 398 K, oxygen pressure is $4 \cdot 10^{-2}$ Pa, and CO pressure is $1.8 \cdot 10^{-3}$ Pa [9].

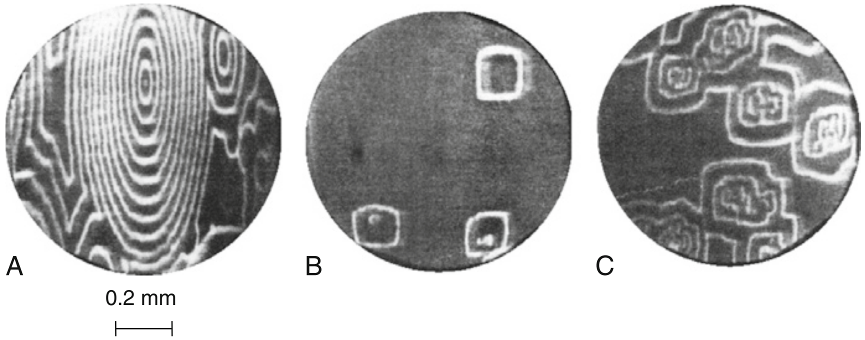


Figure 4.25 Photoemission electron micrograph patterns of different-shaped chemical waves observed during reaction $NO + H_2 \rightarrow ½\ N_2 + H_2O$ in particular surface regions of a Rh(110) monocrystal. Temperature is 540–600 K, NO pressure is $1.6 \cdot 10^{-4}$ Pa, and hydrogen pressure is $(2–5) \cdot 10^{-4}$ Pa [9].

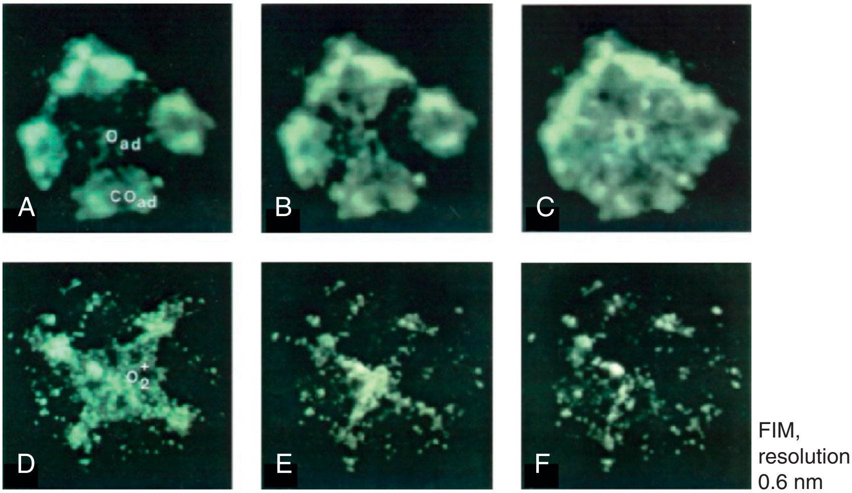


Figure 4.26 Motion of isothermal chemical waves at the oscillation mode of the CO oxidation over the top of a platinum needle. The pattern with the atomic resolution is made by field-ion microscopy (FIM), and the photo frames are acquired in the successive several-second intervals [10]. (Courtesy of V. V. Gorodetsky)

dissipative structures were recognized as important advances in modern physical chemistry, and G. Ertl, the author and initiator of the first studies in the field, was awarded the Nobel Prize in chemistry in 2007.

We should emphasize that the studies and descriptions of homogeneous and heterogeneous oscillating catalytic reactions are based so far on the direct analysis of relevant kinetic schemes. It has been discovered that traditional kinetic modeling of some phenomena can only be satisfactory when particular mathematical approaches, such as the Monte Carlo method, are used. Tools of thermodynamics of nonequilibrium processes are not properly applied as yet.

One can suppose that the methods of combined kinetic and thermodynamic analysis of nonequilibrium processes will be efficient also for describing another important physicochemical phenomenon related to the emergence of spatio temporal dissipative structures: the emergence of moving ordered "heat" waves in the fixed bed of catalyst or inert granules when a reactive chemical mixture is filtered through them. The propagation of the stationary heat wave through an isotropic chemically reactive medium is shown to obey, as expected, the principle of the minimal rate of energy dissipation.

4.7. CHAPTER EXERCISES

1. The stepwise catalytic process

$$\mathrm{R} \rightarrow \mathrm{P}$$

follows the scheme

$$\mathrm{R} + \mathrm{K} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{K}_2 \overset{\varepsilon_3}{\rightleftarrows} \mathrm{K}_3 \overset{\varepsilon_4}{\rightleftarrows} \ldots \overset{\varepsilon_\eta}{\rightleftarrows} \mathrm{K}_n \overset{\varepsilon_{n+1}}{\rightleftarrows} \mathrm{K} + \mathrm{P}.$$

Find the expression of the stationary rate of this process and the apparent activation energy provided that (a) step 3 is rate limiting and the active center is mainly covered by intermediate K_3; and (b) step 1 is rate limiting and the active center is mainly covered by intermediate K_n.

2. The stepwise catalytic process

$$\mathrm{R} \rightarrow \mathrm{P}$$

follows the scheme

$$\mathrm{R} + \mathrm{K} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1$$

$$\mathrm{K}_1 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{K} + \mathrm{P}$$

$$\mathrm{K}_2 \overset{\varepsilon_3}{\rightleftarrows} \mathrm{K} + \mathrm{P}.$$

Find the apparent activation energy of the stationary catalytic process when step 1 is rate limiting and the active center coverage by intermediate K_2 is high. What are the rate determining process parameters in this case?

3. The stepwise catalytic process

$$\mathrm{R}_1 + \mathrm{R}_2 \rightarrow \mathrm{P}_1 + \mathrm{P}_2,$$

follows the scheme

$$\mathrm{R}_1 + \mathrm{K} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1$$

$$\mathrm{K}_1 + \mathrm{R}_2 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{K}_2 + \mathrm{P}_1$$

$$\mathrm{K}_2 \overset{\varepsilon_3}{\rightleftarrows} \mathrm{K} + \mathrm{P}_2.$$

What are the parameter ratios that make the stationary process rate limited by step 2? By step 3? What are the apparent activation energies of this reaction under conditions of large and minor coverage of the active center by the catalytic intermediates?

4. The stepwise catalytic reaction

$$\mathrm{R} \rightleftarrows \mathrm{P}_1 + \mathrm{P}_2$$

follows the scheme

$$\mathrm{R} + \mathrm{K} \overset{\varepsilon_1}{\rightleftarrows} \mathrm{K}_1 + \mathrm{P}_1 \tag{1}$$

$$\mathrm{K}_1 \overset{\varepsilon_2}{\rightleftarrows} \mathrm{P}_2 + \mathrm{K}. \tag{2}$$

An inert substance A is added to the system and strongly sorbed on active center K:

$$\mathrm{K} + \mathrm{A} \rightleftarrows \mathrm{A}_{\mathrm{ads}}. \tag{3}$$

Find the dependence of the apparent activation energy of the catalyzed stepwise reaction on thermodynamic parameters of the processes under consideration when the active center is predominantly covered by the $\mathrm{A_a}$ sorbate. Consider the case when reaction 1 is rate limiting and, additionally, the active center coverage by intermediate K_1 is negligible in the absence of A.

5. Compound A_2 is dissociatively sorbed on a particle of substance K with radius r:

$$\mathrm{K} + \mathrm{A}_2 \rightleftarrows 2\mathrm{A}_{\mathrm{a}}.$$

What is the dependence of the surface coverage by adsorbate $\mathrm{A_a}$ on the particle size? What are the K particle sizes that allow this dependence to be expected?

6. The stepwise catalytic reaction

$$\mathrm{R} \rightleftarrows \mathrm{P}$$

follows the mechanism

$$R + K \overset{\varepsilon_1}{\rightleftarrows} K_1$$

$$K_1 \overset{\varepsilon_2}{\rightleftarrows} K + P,$$

intermediate K_1 being dissolved in the dispersed catalytically active phase.

How will the stationary rate of the catalytic process change when there is a decrease in the size of the active component nanoparticles? Is the surface coverage by intermediate K_1 minor? The rate limiting step is reaction 1. What if the rate limiting step is reaction 2?

7. Estimate the changes in the stationary rate of stepwise catalytic reaction

$$R \rightleftarrows P,$$

that occurs on nanoparticles of active component K when the nano particle size decreases from 100 to 5 nm.

The reaction scheme is

$$R + K \overset{\varepsilon_1}{\rightleftarrows} K_1 \qquad (1)$$

$$K_1 \overset{\varepsilon_2}{\rightleftarrows} P + K, \qquad (2)$$

where K_1 is a molecularly adsorbed intermediate.

Take the excess surface energy of compound K as equal to 1 J/m^2 and the correlation coefficients between enthalpy of the elementary step and the potential barrier height for the transition state of elementary reactions 1 and 2 as equal to $\chi = 0{,}5$.

Consider the case of the large (minor) surface coverage by intermediate K_1.

8. Can carbon deposits (coke as graphite) form in the course of the stationary stepwise catalytic reaction

$$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2,$$

with the mechanism

$$CH_4 \overset{\varepsilon_1}{\rightleftarrows} C_1 + 2H_2,$$

$$C_1 + 2H_2O \overset{\varepsilon_2}{\rightleftarrows} CO_2 + 2H_2,$$

where C_1 is a carbon containing intermediate capable of crystallizing to form graphite? Process conditions: 900 K, $p(CH_4) = 0.5$ bar, $p(CO_2) = 0$, $p(H_2O) = 10$ bar, $p(H_2) = 0.1$ bar.

The figures in the following table are from thermodynamic reference books.

Compound	$\Delta_f H^o_{298}$, ***kJ/mol***	S^o_{298}, ***J/mol***	ρ, ***g/cm³***
Graphite	0	5.740	2.265
CH_4	–74.85	186.19	—
H_2	0	130.52	—
CO_2	–393.51	213.68	—
H_2O (g)	–241.82	188.72	—

Consider individual situations of (a) reaction 1 and (b) reaction 2 as the rate limiting steps.

9. The mechanism of CO disproportionation over the iron catalyst is

$$2CO \rightarrow C_{Fe} + CO_2$$

$$C_{Fe} \rightarrow C_{gr}$$

where C_{Fe} is carbon solute in the iron particles, and C_{gr} is the graphite phase on the catalyst surface. Find the maximal and minimal concentrations of carbon dissolved in iron in the course of the reaction at temperature 800 K if $p_{CO} = p_{CO_2} = 1$ bar, $\mu^0{}_{CO,800} = -245$ kJ/mol, $\mu^o{}_{CO_2,800} = -512$ kJ/mol, $\mu^o{}_{C_{gr},800} = -5$ kJ/mol, and $\mu_{C_{Fe},800} = 25 + RT\ln(x)$ kJ/mol (here x is the molar fraction of the carbon solute in iron).

10. Estimate the maximal potential overheating of the active component (spherical nanoparticles of $2r = 5$ nm in size) in the catalyst 1%Pt/SiO$_2$ during the reaction

$$2CO + O_2 \rightarrow 2CO_2$$

that proceeds over disperse platinum at the reaction flow rate 10^5 h ^{1}.

Enthalpy of the stepwise reaction $\Delta_r H^o =$ 570kJ/mol. The catalyst granules are spherical and have size 2 R = 1 mm. Temperature in the reactor is 600°C. The platinum molecular weight and density are 195 and 21.45 g/cm^3, respectively.

11. Estimate the maximal potential overheating of the catalyst active component in the reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O,$$

which proceeds with the heat effect $\Delta_f H^\circ = \quad 206$kJ/mol over disperse nickel in the catalyst 5%Ni/Al_2O_3 at the reaction flow rate 10^3 h ^{1}.

The spherical particles of the active component are $2r = 10$ nm in size, and spherical granules of the catalyst are $2R = 2$ mm in size. Temperature in the reactor is 400°C. The nickel molecular weight and density are 59 and 8.9 g/cm^3, respectively.

12. Alkylation of benzene (B) with ethylene (E) into ethylbenzene (EB)

$$B + E \rightarrow EB$$

over zeolites follows the scheme

$$B + K \overset{\varepsilon_1}{\rightleftarrows} K_1$$

$$K_1 + E \overset{\varepsilon_2}{\rightleftarrows} EB + K,$$

and is accompanied by "realkylation" of ethylbenzene into diethylbenzene (DEB)

$$EB + E \rightarrow DEB$$

by scheme

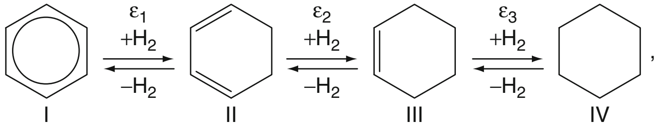
$$EB + K \overset{\varepsilon_3}{\rightleftarrows} K_2$$

$$K_2 + E \overset{\varepsilon_4}{\rightleftarrows} DEB + K.$$

Here, K, K_1, and K_2 are the free active center and catalytic intermediates, respectively.

Find the expressions for the reaction rates in each of the stepwise channels and the selectivity of the ethylbenzene formation for the process that is stationary with respect to catalytic intermediates K_1 and K_2. How will the selectivity change when DEB is fed to the reactor as an additional initial reactant?

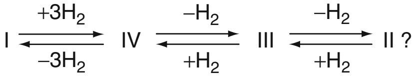
13. The supposed consecutive scheme of the hydrogenation of benzene to cyclohexane over a Ni containing catalyst is



,

where all compounds II–IV can be isolated as individual products.

Is it possible, without using nonstationary kinetic experiments, to prove or disprove the validity of this consecutive scheme but not, for example, the consecutive scheme

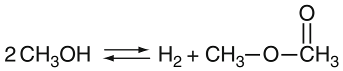


$$\mathrm{I} \underset{-3H_2}{\overset{+3H_2}{\rightleftarrows}} \mathrm{IV} \underset{+H_2}{\overset{-H_2}{\rightleftarrows}} \mathrm{III} \underset{+H_2}{\overset{-H_2}{\rightleftarrows}} \mathrm{II}\ ?$$

What are the relationships between ε_i and chemical potentials of the involved compounds that allow the maximal selectivity for cyclohexene (compound III) to be obtained in the intermediate stationary mode? What should be done to improve the selectivity?

14. Dehydrogenation of methanol over copper containing catalysts at the temperature range 200–400°C is achieved by two linearly independent stepwise channels

$$CH_3OH \rightleftarrows 2H_2 + CO$$



$$2\,CH_3OH \rightleftarrows H_2 + CH_3{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}H_3$$

Is it possible, without recourse to nonstationary kinetic experiments, to know which of the channels of the overall process should be considered as primary? What should be done to improve the selectivity of the methylformate formation?

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CHAPTER 5

Application of Non-equilibrium Thermodynamics to Material Science

Contents

5.1. FEATURES OF THERMODYNAMICS OF MATERIAL SYNTHESIS

Our world is full of a variety of substances and materials that are used in human practice for very different purposes. Note that terms *material* and *substance* are not identical. A substance (chemical compound) is an ensemble of a great number of atoms, molecules, ions, and/or radicals that define properties of the substance as an object for investigations, whereas materials are the phase separated forms of substances (chemical individuals) or their ensembles (for example, specialty mixtures and *composites*) that feature a set of properties necessary for practical applications of the material. To create the material that possesses the required properties for particular practical applications, a specialty substance must be prepared and stabilized. Of importance is that the required substance modifications are often in a *metastable* state that differs from the thermodynamically equilibrium state and is, nevertheless, appropriate for the material storage and operation.

For example, diamond is a metastable modification of carbon that is out of thermodynamic equilibrium under ordinary external conditions. The equilibrium forms of numerous materials referred generally to as glasses are crystalline phases, but the glass materials are interesting because they exist in a state that is not crystalline and is a thermodynamically nonequilibrium amorphous state. Polymorphism of solid phases is characteristic of the active substances of some drugs, the required or strongest biological effect being sometimes inherent in the phase that is nonequilibrium under the conditions of the drug storage and application by patients.

A very severe problem has arisen in South Russia and Kazakhstan as a result of stockpiling millions of tons of elemental sulfur over the past few decades. This sulfur has been extracted from high sulfuric oil and natural gas but has not been used because it is chemically unstable when it comes into contact with atmospheric gases and moisture and thus can become a serious ecological threat. The last problem might be resolved by transforming the orthorhombic sulfur modification (equilibrium under ambient conditions) into its polymeric modification; the latter is chemically more inert and can be used as a valuable component of large scale composite materials such as sulfur concrete, sulfur bitumen, and so on.

Thus, there are numerous tangency points between material science and the thermodynamics of nonequilibrium processes. This chapter deals with only a few aspects related to the application of nonequilibrium thermodynamics tools for the solution of some problems in the material synthesis.

Many materials are prepared via chemical synthesis in a mother liquor or mother gas mixture to have synthesis conditions that will ensure the "quantitative" yield of the desired substance—at least with respect to one of the initial reactants. The quantitative yield implies considerable shifting of the equilibrium of the stepwise reaction toward the formation of the required substance modification. This corresponds to the condition of kinetic irreversibility of the process and, as a consequence, to the system going far away from the initial state of the material precursors.

In terms of thermodynamics, materials are mostly solid phase states of the substance. Thus, their chemical potentials μ_M depend only slightly on the quantity of the synthesized substance but mainly on the temperature and pressure in the system. Therefore, initial concentrations, c_α, of the substances precursors, A_α, $\alpha = 1, 2, \ldots$, which determine chemical potential μ_R of the reaction groups R to synthesize the material in the mother liquor, must be no less than that required by inequality

$$\mu_R(p, T, c_\alpha) - \mu_M(p, T) > RT. \qquad (5.1)$$

These conditions correspond usually to the saturated or oversaturated mother liquors or gas mixtures.

Again, the primary phase particles of the required substance modification (material precursors) are usually very small. When seeds of the synthesized phase are used, these primary particles are identical in size to the seeds. In the homogeneous liquid solutions or gas mixtures, the size of primary particles is determined by the nucleation processes. The small size of the primary phase particles can influence considerably the chemical potential of the phase to be formed. For example, in the case of spherical particles, the chemical potential is determined by equation (1.5). Hence, the equilibrium partial pressure, p_r, of the saturated vapor or concentration, c_r, of the saturated solution of the substance—for example, of the synthesized one component phase—is determined by the Kelvin Thomson equation

$$p_r = p_\infty \exp\left(\frac{2\sigma\overline{V}}{RTr}\right) \tag{5.2}$$

or by the Gibbs Freundlich Ostwald equation

$$c_r = c_\infty \exp\left(\frac{2\sigma\overline{V}}{RTr}\right), \tag{5.3}$$

where p_∞ and c_∞ are partial pressure of the saturated vapor or concentration of the saturated solution of the substance over the surface of a bulky phase, r is the spherical particle radius, σ is the surface tension coefficient at the interphase boundary, and $\overline{V} = M/\rho$ is the molar volume of the condensed phase where M and ρ are molecular weight and density, respectively, of the phase substance. With the concentrated solutions, the molar ratio x of the solute rather than its concentration c is preferable for describing the thermodynamic properties. When so, equation (5.3) can be rewritten in a more understandable form

$$x_r = x_\infty \exp\left(\frac{2\sigma\overline{V}}{RTr}\right).$$

Thus, if the material seed is small, the initial phase should be even more oversaturated, which is determined by condition (5.1). For example, at the synthesis of a one component material, it is determined by inequalities

$$p_{init} > p_r = p_\infty \cdot \exp\left(\frac{2\sigma\overline{V}}{RTr}\right) \tag{5.4}$$

or

$$x_{init} > x_r = x_\infty \cdot \exp\left(\frac{2\sigma\overline{V}}{RTr}\right), \tag{5.5}$$

where r is the seed size.
The exponent values in expressions (5.2)–(5.5) depend on the particular parameters in the exponent index, but they are usually much larger than the unit at $r < 10–50$ nm (see Table 5.1). In a homogeneous mother sys tem (free of seeds for the solid phase condensation), the process rate depends on the rate of homogeneous nucleation of the new phase from nonequilibrium (oversaturated) systems. The high partial pressure of the equilibrium vapor or solute over small particles allows the first condensed particles (*nuclei* of the new phase) to form at a considerable oversaturation of the vapor in the initially homogeneous system.

Let us consider the thermodynamics of processes of the homogeneous nucleation of a new phase with the formation of fluid drops from the over saturated vapor as an example. While the chemical potential of the equilib rium substance vapor over spherical particles of its condensed phase is given by the Kelvin Thomson equation (5.2), only those drops that have the critical size r_{cr}

$$r_{cr} = 2\sigma\overline{V}/RT\ln(p/p_\infty) \tag{5.6}$$

can be in equilibrium with the oversaturated vapor at partial pressure p.

This is an unstable equilibrium: The smaller drops evaporate and dis appear, while larger drops grow due to the vapor condensation. Similar phenomena are characteristic of the synthesis of disperse solids as well: Larger crystals grow and overcome smaller crystals that are more soluble.

Table 5.1 Thermodynamic parameters of pure water droplets at 25°C

Vapor oversaturation, p/p_∞	8.1	2.84	1.42	1.11
Critical radius of the drop, nm	0.5	1	3	10
Laplace pressure inside the drop, bar	2880	1440	480	144
Number of molecules in one drop, n	18	140	3780	1.4×10^5
ΔG_{cr}, kJ/(mol of drops)	45.2	180	1620	18000

This phenomenon of the increased growth of larger crystals compared to smaller ones that have a higher solubility than the larger ones is known as the second Ostwald rule or the rule of *ripening* of a new phase.

Therefore, in the case under consideration, the overall rate of the condensation process is controlled by the rate of the formation of drops with radius r_{cr} in the oversaturated vapor and by the concentration of these drops.

Consider the drop formation in the homogeneous vapor phase as a chemical reaction

$$nA = A_n, \tag{5.7}$$

where $n = N_A(4/3)\pi r^3/\overline{V}$ is the number of molecules in the drop, N_A is the Avogadro number, and r is the drop radius.

The equilibrium constant of this reaction equals

$$K_p = p(A_n)/p^n = \exp(-\Delta_r G_n^o/RT), \tag{5.8}$$

where $p(A_n)$ is the partial pressure of the drops treated as a thermalized ensemble of large molecules, p is the actual partial pressure of the oversaturated vapor, and $\Delta_r G_n^o$ is the standard change in the Gibbs energy for the formation of one mole of drops with given size r from the standard state of the vapor. In the ideal case, the latter value is described by the expression

$$\Delta_r G_n^o = n(\mu_l^o - \mu_v^o) + N_A\, 4\pi r^2\sigma = N_A\left[\left(\frac{4}{3}\pi r^3 \Big/ \overline{V}\right)(\mu_l^o - \mu_v^o) + 4\pi r^2\sigma\right], \tag{5.9}$$

where μ_l^o and μ_v^o are standard chemical potentials of the bulk phase of the condensed liquid and of its oversaturated vapor, respectively. Evidently, at the not very large pressure

$$\mu_l^o - \mu_v^o = RT\ \ln p_\infty.$$

Hence, expression (5.9) of the standard change in the Gibbs potential during the "reaction" of the formation of one mole of drops with size r may be substituted for by the expression

$$\Delta_r G_n^o = N_A\left[\left(\frac{4}{3}\pi r^3 \Big/ \overline{V}\right)RT\ \ln p_\infty + 4\pi r^2\sigma\right]. \tag{5.10}$$

In view of the preceding circumstances, we may suppose that all of the nuclei that are smaller than or the same size as the critical drops are in the partial equilibrium with the oversaturated vapor that makes the growth of the nucleus of the critical size a kinetically irreversible process. In other words, the formation of the nuclei of the critical size is the rate limiting step of the process of the homogeneous vapor condensation.

Now let us apply expression (5.10) to formula (5.8) for the equilibrium constant and find the equilibrium pressure of drops of size r:

$$\begin{aligned} p(A_n) &= p^n \exp(-\Delta_r G_n^o/RT) \\ &= \exp\{N_A[(4/3\pi r^3/\overline{V})RT \ln(p/p_\infty) - 4\pi r^2\sigma]/(RT)\}. \end{aligned} \tag{5.11}$$

The index of the latter exponent is the change in the Gibbs energy during the formation of one mole of drops (nuclei) of radius r from the vapor at partial pressure p:

$$\begin{aligned} \Delta G(\text{nucl}, r) &= -N_A\left[\left(\frac{4}{3}\pi r^3 \Big/ \overline{V}\right)RT \ln\left(\frac{p}{p_\infty}\right) - 4\pi r^2\sigma\right] \\ &= 4\pi r^2\sigma N_A\left[1 - \frac{rRT}{3\overline{V}}\ln\left(\frac{p}{p_\delta}\right)\right]. \end{aligned} \tag{5.12}$$

Evidently $\Delta G(\text{nucl}, r)$ can be considered as the affinity $A_{r\ \text{nucl}}(r)$ of this nucleation reaction:

$$A_{r\ \text{nucl}}(r) = -\Delta G(\text{nucl}, r).$$

$\Delta G(\text{nucl}, r)$, as a function of r, at $p > p_\infty$ has its maximum at r_{cr}, when the drop is in equilibrium with the vapor of the given pressure (see Figure 5.1).

By applying radius r_{cr} from equation (5.6) to the expression for $\Delta G(\text{nucl}, r)$ in (5.12), we get

$$\Delta G_{cr} = 4\pi r_{cr}^2\sigma N_A\left[1 - \frac{r_{cr}RT}{3\overline{V}}\ln\left(\frac{p}{p_\infty}\right)\right] = 1/3N_A\ 4\pi r_{cr}^2\sigma = 1/3N_A\ \sigma S_{cr} \tag{5.13}$$

where $S_{cr} = 4\pi r_{cr}^2$ is the surface area of one drop of the critical size.

While the formation of the critical size drop is the rate limiting step in the reaction sequence (5.7) of the homogeneous gas to liquid condensation, the quantity ΔG_{cr} may be identified as the activation energy of the

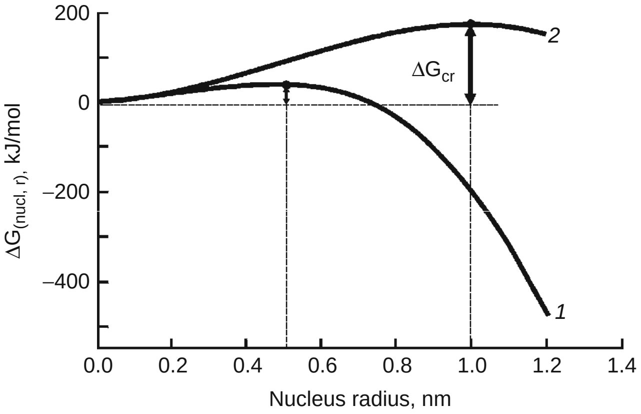

Figure 5.1 Gibbs energy of nucleation of water drops at different water vapor oversaturations of at 25°C. Curve 1 is plotted for oversaturation $p/p_{\infty} = 8.1$ ($r_{cr} = 0.5$ nm), and curve 2 for $p/p_{\infty} = 2.84$ ($r_{cr} = 1$ nm); see Table 5.1.

nucleation process. Thus, the rate v_{Σ} of the droplet mass growing per se is strictly dependent (in the first approximation) on the surface area of the critical size nuclei:

$$v_{\Sigma} \sim S_{cr} \cdot p(A_{n\ cr}) = S_{cr} \cdot \exp\left(-\frac{N_A \sigma S_{cr}}{3RT}\right). \tag{5.14}$$

As a particular example, one can consider the homogeneous nucleation in the pure water vapor at 25°C. The surface tension coefficient of water is $\sigma = 71.96$ N/m at this temperature. Table 5.1 shows some characteristics of the new phase. When the oversaturation is $p/p_{\infty} = 8.1$, the critical nucleus of 0.5 nm radius is seen to comprise 18 water molecules. The equilibrium pressure of such nuclei is not high (approximately 10 ^{8} bar). Since the water vapor pressure in real clouds is usually no more than 0.1% over that of the saturated vapor, it is unrealistic to expect in the reasonable time scale the homogeneous formation of water drops in Earth's atmosphere.

The curves plotted in Figure 5.1 illustrate the dependencies $\Delta G(\text{nucl}, r)$ on the water drop radius at 25°C at various oversaturation ratios. Supposedly, expression (5.13) may be used for the crude estimation of the apparent activation energy of the synthesis of solids in an initially homogeneous gas or liquid phase system.

5.2. SYNTHESIS OF THERMODYNAMICALLY UNSTABLE COMPOUNDS AND MATERIALS

Obviously, under given conditions, only one form of a substance—the one with the lowest chemical potential (i.e., the Gibbs potential)—is thermodynamically stable. Nevertheless, it often appears necessary in practice to synthesize a material in the form that is *metastable* under conditions of storage and/or application of the material.

There are many ways to synthesize metastable forms of substances (usually, as isolated solid phases or crystals). For example, a thermodynamically unstable solid can be produced in some cases from its thermodynamically stable form by changing temperature and/or pressure and by creating conditions when the target material form becomes the most stable. If the phase transformation is kinetically favored under these conditions, the target substance phase is formed in the system. A classic example is the synthesis of diamond from graphite under extremely high temperature and high pressure falling into the range of the diamond phase stability.

Nevertheless, metastable forms of substances often can be synthesized under much milder conditions. In these cases the thermodynamically unstable phase is (co)precipitated or (co)deposited from a solution or gas phase under conditions when the formation of the target phase results from chemical transformations of deliberately chosen reactants. Usually, at least two conditions must exist: (1) the initial chemical potential of the initial reaction group (the precursor of the phase to be synthesized) must meet conditions (5.1)–(5.5), and (2) the seeds in the target phase must be in the system to favor, on the (co)precipitation or (co)deposition step, the formation of the phases replicating the seed phase structure. In epitaxial growth of films, the substrate with the deliberately chosen structure may be the seeding agent.

Let us illustrate this with the diamond synthesis as an example. It is common knowledge that the graphite to diamond phase transformation is only possible at ultrahigh pressures and temperatures. However, it has become habitual in recent years to synthesize diamond "whiskers" and fine diamond films under far from extreme conditions.

The feasibility of such synthesis is easy to demonstrate with pyrolysis of a hydrocarbon as an example, such as the pyrolysis of methane by stepwise reaction

$$CH_4 \rightarrow C_{\text{diamond}} + 2H_2.$$

At the conditions when the rate limiting step is crystallization of the target carbon phase (diamond) from the energy saturated primary carbon atoms C^* generated by the methane pyrolysis, the stepwise process can be written as a series of steps:

$$\begin{gathered}CH_4 \rightleftarrows C^* + 2H_2,\\ C^* \rightarrow C_{\text{diamond}}.\end{gathered}$$

Here, the estimated chemical potential μ_{C^*} of the active atomic carbon C^* is

$$\mu_{C^*} \approx \mu_{CH_4} - 2\mu_{H_2}.$$

Obviously, when this condition is met, the diamond phase can be synthesized at

$$\mu_{\text{diamond}} < \mu_{C^*} + RT. \tag{5.15}$$

Let us estimate the required partial pressure of methane under particular external conditions, such as at 900 K. From reference books on thermodynamic parameters,

$$\begin{gathered}\mu^{o}_{CH_4,900} \approx \Delta_f H^{o}_{CH_4,298} - 900 \cdot S^{o}_{CH_4,298} = -242,4 \text{ kJ/mol},\\ \mu^{o}_{H_2,900} \approx \Delta_f H^{o}_{H_2,298} - 900 \cdot S^{o}_{H_2,298} = -117,5 \text{ kJ/mol},\\ \mu^{o}_{\text{diamond},900} \approx \Delta_f H^{o}_{\text{diamond},298} - 900 \cdot S^{o}_{\text{diamond},298} = -0,72 \text{ kJ/mol}\end{gathered}$$

(correction for heat capacities of the involved substances may be skipped in crude estimating calculations). Therefore, expression (5.15) is rewritten in the quantitative form as

$$\ln p_{CH_4} - 2\ln p_{H_2} \geq (\mu^{o}_{\text{anm},900} + 2\mu^{o}_{H_2,900} - \mu^{o}_{CH_4,900} + RT)/RT \approx 1,9.$$

With the assumption that, for example, the hydrogen partial pressure is low, such as $p_{H_2} \leq 1$ bar, we get the estimation

$$\ln p_{CH_4} \geq 1.9$$

or

$$p_{CH_4} \geq 7 \text{ bar}.$$

One can see that diamond may be synthesized indeed through pyrolysis of methane under rather mild conditions.

While method for stabilization of the synthesized diamond modification is available yet, the method under discussion does not allow large diamonds to be produced. However, diamond "whiskers" or fine epitaxial diamond layers are easy to synthesize.

5.3. THE OSTWALD STEP RULE FOR THE PHASE TRANSFORMATIONS

In 1897, W. Ostwald formulated a general rule that remains important to this day for synthesizing materials: If a chemical reaction produces several modifications of a compound, it is not the most stable but the most labile modification that forms first, while more stable modifications are produced via further transformations of the labile one [1, 2, 3]. Hence, the Ostwald step rule indicates the possibility of the formation of metastable (labile) intermediate phases on phase transitions due to the kinetically preferential formation of metastable phases rather than a thermodynamically stable phase immediately.

The Ostwald step rule is, evidently, a particular case of the general requirement (see Section 1.3.3) for a sequential decrease in chemical potentials of the transformation intermediates in the course of a stepwise transformation. In the transformation of the constant composition solid phases, the said requirement refers to chemical potentials of the solid phases. If the state diagram of a particular matter comprises several allowed phases (the ones differing, for example, by their crystal structures, etc.), the initial phase transformation into the thermodynamically stable state at a constant temperature will be successively mediated by all of the phases along the reaction pathway from the initial point to the stable phase.

A spectacular example is the experimental observation of decomposition of solid light alkane hydrates at ambient pressure and temperature −1°C—that is, under conditions of their thermodynamic instability. The final products are ice (solid) and a hydrocarbon gas. However, the decomposition of, for example, propane hydrate follows the sequence

$$\begin{aligned} \mathrm{C_3H_8 \cdot 17H_2O(solid\ hydrate)} &\longrightarrow \mathrm{C_3H_8(gas) + H_2O(liquid)}, \\ \mathrm{H_2O(liquid)} &\longrightarrow \mathrm{H_2O(ice)}; \end{aligned}$$

that is, it is mediated by the formation of supercooled liquid water that is then replaced with thermodynamically stable water ice [4].

5.4. SYNTHESIS OF CARBON NANOFILAMENTS, NANOFIBERS, AND NANOTUBES

In recent years, we have seen an explosive interest in nanomaterials, in particular in nanofibers, nanofilaments, and nanotubes of the very different chemical composition. The interest arises from the specific mechanical and physicochemical properties of these nano objects, which allow them to be used, for example, as specific adsorbents, catalyst supports, reinforcing components of composite materials, and so on. The most cited generic types of nanomaterials are carbon nanofilaments and nanotubes. Numerous methods for preparing these carbon materials are known. However, the simplest method seems to be thermal pyrolysis of various carbon containing precursors (e.g., carbon monoxide, saturated and unsaturated hydrocarbons, etc.) in the presence of special catalysts that are typically nanosized particles of nickel, cobalt, iron metals, or their alloys with different metals.

The underlying concept of this method for the synthesis of filamentous carbonaceous nanomaterials is fairly simple. As the temperature rises above a certain limit, which depends on the thermodynamic and kinetic parameters of carbon containing compounds, such as hydrocarbons, such compounds tend to pyrolyze in the air free conditions to form free carbon. For example, the noncatalytic pyrolysis of methane can be achieved at ambient pressure and at temperatures above 900–1000 K to produce soot (near spherical nanosized carbon particles) and hydrogen:

$$CH_4 \longrightarrow C + 2H_2. \tag{5.16}$$

The presence of deliberately chosen catalysts allows the pyrolysis to occur at lower temperatures, such as 700–800 K.

In the elementary reactions of the pyrolysis, the atomic carbon is formed first. Then it transforms into the final product, whether it be soot, graphite, carbon nanofibers, or so forth. Why does the presence of catalysts make it possible to grow carbon nanofibers or nanotubes instead of soot? In many cases, this is the so called carbide cycle that is characteristic of the catalytic process of hydrocarbon pyrolysis that is responsible for the growth of the elongated structures but not soot particles. The primary carbon atoms produced by pyrolytic decomposition of the hydrocarbon molecules are dissolved in the metal particle of the active catalyst component to form a nonstoichiometric carbide (the carbon solution in the metal) and then condensed from the solution as an individual carbon phase similar to graphite in properties.

As shown in Section 4.6.1, when the formation of the solid carbon phase is the rate limiting step of the overall catalytic pyrolysis process, a considerable oversaturation of the metal phase with carbon (against the temperature of the standard eutectic mixture) may happen to the operating catalyst. As the result, under certain conditions, the active component particle may become (pseudo)liquid at temperatures that are much lower than the melting temperature of the eutectics. While the active component is labile enough in the operating catalyst, it is prevented from deactivation through covering the active surface with the carbon deposition, and the active metal particle appears mounted in the tip of the growing carbon nanofibers because the solid carbon phase is only formed at the available seeds of this phase (see Figure 5.2).

A large variety of very different crystal structures and morphologies may be characteristic of the growing nanofiber depending on the nature of the catalyst active component and pyrolyzed hydrocarbon, as well as on the pyrolysis temperature (Figure 5.3).

Apart from a considerable cryoscopic effect, which is caused by the said oversaturation of the carbon solution in metal and described by the

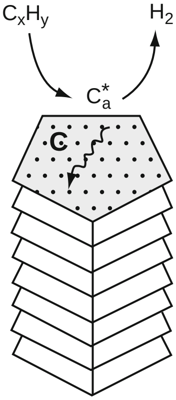

Figure 5.2 A schematic of the mechanism of the nanofilaments growth at catalytic pyrolysis of hydrocarbons. Hydrocarbon decomposition on the metal nanoparticle (the dark area) surface produces chemisorbed atomic carbon C_a^* species with a high chemical potential. In the (pseudo)fluidized catalyst particle, the atomic carbon is capable of diffusing through the metal nanoparticles toward the interphase boundary between the active component and the growing face of the carbon nanofiber (the light areas).

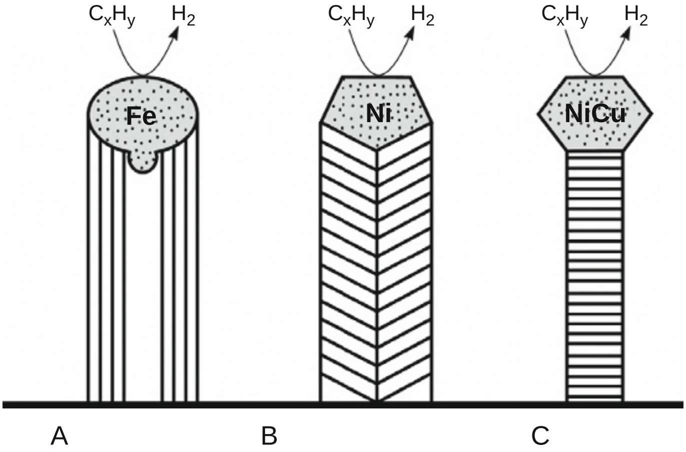

Figure 5.3 Main types of the crystalline structure of the carbon nanofilaments produced by pyrolysis of hydrocarbons over transition metal nanoparticles: coaxial cylindrical (multilayer nanotube) (A), coaxial conical (fishbone) (B), and pile (C). The nanofilaments are 10 nm in characteristic diameter. The catalyst nanoparticle behaves as a nanofilament seed.

equation in Section 4.6.1, there are at least two additional factors that affect the melting point of the catalytically active component. The first one is the well known reduction of the melting temperature T_r on the decrease in the metal catalyst particle size r:

$$T_r = T_\infty \exp\left(\frac{-2\sigma\overline{V}}{r\Delta_{melt}H}\right), \tag{5.17}$$

where T_∞ and $\Delta_{melt}H$ are the melting temperature and enthalpy of the pure bulky component (solvent—in our case, metal). The second factor is the influence of the size of the graphite crystallization seeds on the solution oversaturation with the depositing matter (carbon) in the quantity needed to initiate the crystallization (see equation (5.5)).

Disproportionation of CO by reaction

$$2CO \rightarrow C + CO_2 \tag{5.18}$$

over the catalyst bearing 5 to 500 nm nanoparticles of cobalt metal was used as an example for the experimental studies of the role of the active particle size in the formation of carbon nanofibers. The studies of the process in a wide range of conditions revealed that the disproportionation gives rise to the formation of two morphological types of the structures, depending on the diameter of the cobalt metal particles.

On elevating the temperature of the sample comprising cobalt metal and blowing by CO, the disproportionation of CO is observed to start at 560 K to form CO_2 and elemental carbon. Three temperature ranges were identified where the elemental carbon formed undergoes different ways of the transformations:

1. At 570–620 K, the adsorbed carbon atoms are dissolved in cobalt metal to form high defect particles of Co^0. Such a structure comprises some features of both the cubic (β) and hexagonal (α) modifications of cobalt and thus seems to be intermediate between the mentioned cobalt modifications.
2. At 570–720 K (with the maximal rate at 690 K), a thick graphite layer (the so called crust of more than 10 nm in thickness) is formed to cover the metal nanoparticles.
3. At 720–1020 K (with the maximal rate at 850–890 K), the disproportionation reaction gives rise to the formation of thin carbon nanotubes with an external diameter of 10 nm and an internal diameter of 3 nm.

The formation of either of two morphologically different types of graphite crystallites depends on the diameter of the Co^0 particles. The graphite crust that forms over the coarse cobalt particles causes a rapid catalyst deactivation due to hindered mass exchange between the catalyst surface and gas phase. At the same time, fine cobalt particles behave as centers of nanotube growth at higher temperatures (see Figure 5.4).

A thermodynamic analysis (when performed as discussed in Section 4.6.1) reveals that the CO disproportionation is also mediated by the formation of the oversaturated solution of carbon in the operating cobalt metal. This resembles graphitization of amorphous carbon that is accompanied by fluidization of the metal particles at the temperature below the traditional eutectic point. In the disproportionation of CO, it is important that the limit concentration of carbon in the metal is determined by the maximal size of graphite crystallites allowed under the given conditions. The coarse (over 25 nm in diameter) cobalt particles behave as large seeds of the graphite crystallization, and, therefore, they can only provide a low excess concentration of the carbon solute. Graphite starts forming on these particles at low temperatures and deactivates the active component due to its covering with the graphite crust. When the particles are small, the stationary concentration of the dissolved carbon is so high that it causes

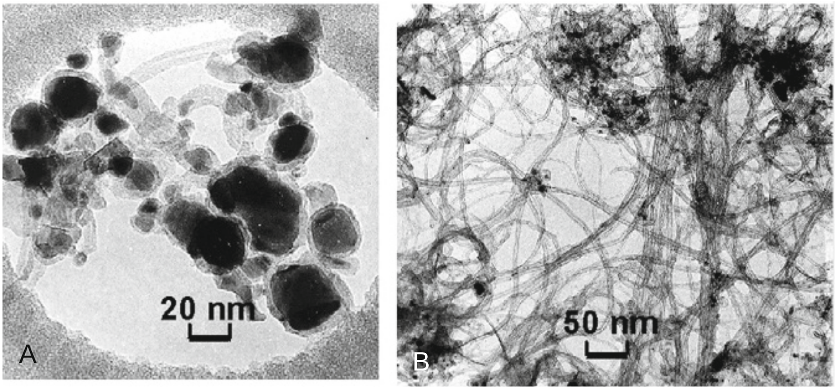

Figure 5.4 Micrographs of carbon structures generated over large (A) and small (B) cobalt nanoparticles. The large nanoparticles (more than 25 nm in diameter) give rise to the graphite shell over their surface, while the small particles (less than 25 nm in diameter; approximately 10 nm in the sample under study) to fine carbon nanotubes with the external diameter equal approximately to the diameter of the Co^0 particle and wall thickness of approximately 3–5 nm [5].

fluidization of the metal nanoparticle due to the oversaturation with carbon (see Section 4.6.1). The concurrent abrupt increase in the mechanical mobility of the metal nanoparticles prevents the catalyst from deactivation and results in the growth of long carbon nanotubes.

One can estimate the diameter of the growing nanofibers through the calculation of the molar fraction of dissolved carbon when the catalytically active phase responsible for stepwise process (5.18) is in the stationary state. If the metal oversaturation with carbon is $\alpha \equiv x/x_\infty$, it follows from equations (5.3) and (5.5) that the size of a spherical seed required for the formation of carbon phase is

$$r = \frac{2\sigma\overline{V}}{RT\ln\alpha}. \tag{5.19}$$

For cobalt, $\sigma \approx 2\ \mathrm{J/m^2}$ and $\overline{V} \approx 6.7 \cdot 10^{\ 5}\ \mathrm{m^3}$.

In the stepwise process (5.18) at 900 K, the carbon phase formation is supposed to be the rate limiting step. The estimated stationary oversaturation of an active species during the reaction in the latter condition is $\alpha \approx 5$. Hence, $\ln\alpha \approx 1.6$ and, therefore,

$$r \approx \frac{2 \cdot 2 \cdot 6.7 \cdot 10^{\ 5}}{8.31 \cdot 900 \cdot 1.6}\,\mathrm{m} = 2.2 \cdot 10^{\ 9}\,\mathrm{m} = 2.2\ \mathrm{nm}.$$

Thus, the growing graphite nanofiber (or nanotube wall) should be close in thickness to

$$2\,r = 4.4\ \mathrm{nm},$$

which is close enough to the experimental observations.

The similar thermodynamic analysis along with the modern experimental data argue for the possibility of fluidization of small metal nanoparticles due to the formation of the oversaturated carbon solution not only during the graphitization of amorphous carbon or CO disproportionation but also during pyrolysis of low hydrocarbons by stepwise reaction

$$C_nH_m \xrightarrow[720\quad 920K]{\text{catalyst}} nC + \frac{m}{2}H_2. \tag{5.20}$$

The reaction often is accompanied by the growth of carbon nanofibers of different textures (see Figure 5.3). Notice that the supported metal catalysts are normally used for the purpose and that processes like (5.20) can lead to the increase of the catalyst granules' weight by a factor of 300 and more compared to their initial weight to allow extremely pure carbonaceous filamentous materials to be produced.

The experimental rate of the growth and formation of carbon nanofilaments and nanotubes are in conformity with the carbon diffusion through the catalyst active component with the diffusion coefficient $D \gg 10^{\ 10}\ \mathrm{cm}^2/\mathrm{s}$ that indicates a high enough mobility of the carbon atoms. Again, the high diffusion rate of carbon atoms through the catalyst metal particles is an argument for the fluidized state of the metal in the course of the catalytic reaction.

The recent use of the transmission electron microscopy of high resolution at the in situ condition at large enough pressure of methane resulted in the direct observation of the metal nanoparticle liquefaction at the catalytic methane pyrolysis. Thus, the formation of carbon fibers and nanotubes often results from fluidization of the catalytically active phase via its oversaturation with carbon at the catalyst operation. This may happen to a variety of processes when the deposition of graphitized carbon is preceded by the primary atomic or another energy saturated carbon species formed on the surface of the catalytically active metals (see Figure 5.2). Supposedly, the formation of the very specific structures of the carbon filament, like the so called fishbone structure (see Figure 5.3B), may be easily accounted for by the oscillating mode of the mentioned graphite crystallization.

The discussed models of the carbon nanofilaments and nanotubes formation allow many other thermodynamic factors to be taken into consideration, all of which affect the shape, texture, and growth rate of the nanoobjects under discussion (see, e.g., Refs. [6, 7]). It is assumed that the formation of the fluidized active component of the catalyst nanoparticles due to its stationary oversaturation with the crystallizing component gives rise to the possibility to synthesize nanofilaments and nanotubes from not only carbon but also from different substances, such as silicon carbide (over catalysts capable of dissolving carbon and silicon simultaneously), germanium metal (over gold metal catalysts [8]), and so on.

5.5. CHAPTER EXERCISES

1. Which temperatures are required for the synthesis of diamond species through the decomposition of CO by reaction $2CO \rightleftarrows C + CO_2$ at the partial pressures of CO and CO_2 equal to 0.1 bar?
   Reference books tell us the following:

Substance	***$\Delta_f H^o_{298}$, kJ/mol***	***S^o_{298}, J/mol·K***	***ρ, g/cm^3***
Graphite	0	5.740	2.265
Diamond	1.828	2.833	3.515
CO	–110.52	197.54	—
CO2	–393.51	213.68	—

2. The standard electrode potential of the electrode semireaction $Pd^{2+} + 2\ e\ = Pd^o$ is $E^o_{Pd^{2+}/Pd} = 0.987$ V in respect to NHE. This indicates the principal possibility of dissolving palladium metal in a strong acid under the action of air oxygen because the potential of the electrode semireaction $O_2 + 4H^+ + 4e\ = 2H_2O$ equals $E^o = 1.228$ V in respect of NHE. Will the palladium metal dissolve in an acidic solution where the catalytic oxidation of Fe^{2+} cations

$$O_2 + 4Fe^{2+} + 2H^+ \rightarrow 4Fe^{3+} + 2OH$$

takes place, the reaction being the palladium catalyzed by mechanism

$$O_2 + 2Pd^o + 2H^+ \rightleftarrows 2Pd^{2+} + 2OH^-,$$

$$Pd^{2+} + 2Fe^{2+} \rightleftarrows Pd^o + 2Fe^{3+}?$$

The standard electrode potential of semireaction

$$Fe^{3+} + e^- = Fe^{2+}$$

equals $E^o_{Fe^{3+}/Fe^{2+}} = 0.771$ V in respect of NHE, and the concentrations of Fe^{2+} and Fe^{3+} are 0.1 M and 10^{-3} M, respectively.

3. Is it possible to obtain the solid AgBr precipitate by reaction

$$Ag^+ + Br^- \rightleftarrows AgBr \downarrow$$

if the Ag^+ cations participate simultaneously in the stepwise reaction

$$Ag^+ + 1/2H_2 \rightleftarrows \{Y_i\} \rightleftarrows Ag^o + H^+,$$

where $\{Y_i\}$ are some intermediates of the Ag^+ reduction?
The reactant concentrations: $[Ag^+] = 10^{-3}$ M, $[Br^-] = 10^{-4}$ M, $p(H_2) =$ 1 bar, pH 3. The solubility product for AgBr at the reaction temperature is $\Pi = 10^{-9}$ M^2.

4. Is it possible to obtain the solid AgBr precipitate by reaction

$$Ag^+ + Br^- \rightleftarrows AgBr \downarrow$$

if the Ag^+ cations participate simultaneously in the stepwise reaction

$$Ag^+ + O_2 \rightleftarrows \{Y_i\} \rightleftarrows Ag_2O + H^+,$$

where $\{Y_i\}$ are intermediates of the Ag^+ oxidation?
The reactant concentrations: $[Ag^+] = 10^{-3}$ M, $[Br^-] = 10^{-4}$ M, $p(O_2) =$ 1 bar, pH 3. The solubility product for AgBr at the reaction temperature is $\Pi = 10^{-9}$ M^2.

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CHAPTER 6

Entropy and Information

Contents

6.1. TIMING HIERARCHY OF PROCESSES IN COMPLEX DYNAMIC SYSTEMS

The word *information* is extremely popular in the modern world. It is used to indicate that a particular event has happened or will happen to a system, the event being one of several or even numerous probable events in the expected evolution of the system under consideration. The said statistical basis of *information* allows the identification of many common features for information and entropy, the latter function of the system state being also closely related to statistics.

Let us try to consider the relationship of these important terms in more detail. In the previous chapters we considered the background of thermodynamics of irreversible processes in those open systems, for which one can use the concepts of elementary reaction rates and of chemical potentials of the reactive components. This allows both the kinetic and thermodynamic analysis of the dynamic evolution of a reactive system to be performed via calculating the rates and driving forces of the involved processes on the basis of traditional chemical kinetics. At the same time, all existing mathematical models of numerous complex catalytic, techno logical, and, in particular, biological systems are capable of reflecting only a few individual features of the processes in these systems but not of describing the behavior of the complex systems in all details.

The most efficient methods for mathematical analysis of complex evolving systems usually take into consideration that the potential transformations may strongly differ in their time scales. The scales refer to different process categories from the short characteristic times of the molecule relaxation to the Maxwell Boltzmann equilibrium, as well as fast interactions of the most reactive aggregate elements up to long times of evolutionary transformations of the whole system. The possibility of subdividing the entropy of a partly equilibrium open system into two independent parts attributed to *external* and *internal* variables ($dS = d_eS + d_iS$) is postulated, namely due to the assumption of very differing time scales for the different process categories within one large system. The slow processes are attributed to mass or energy exchange with the environment, while fast processes are considered as irreversible, spontaneous internal transformations of the reaction intermediates.

A hierarchical classification of processes in respect to their characteristic times underlies, in fact, the theorem on the minimum of the rate of entropy production as well. Let us consider two conjugate processes described by the Onsager equations:

$$J_1 = L_{11}X_1 + L_{12}X_2,$$
$$J_2 = L_{21}X_1 + L_{22}X_2.$$

Evidently, the (quasi)stationary mode of one of these two processes—$\bar{J}_1 = 0$ at $\bar{J}_2 \neq 0$—can only be established when the stationary process is met by a differential equation related to fast changes in one of two internal variables. The second process at $\bar{J}_2 \neq 0$ proceeds with a slowly changing variable, which is practically constant within the time period of establishing the stationary state in respect to the fast variable. This is the same as the assumption of system stratification into two subsystems with fast and slow variables—that is, to the assumption of two time scales of the processes under consideration.

Classifying variables into fast or slow is a typical approach in chemical kinetics to apply the method of (quasi)stationary concentrations, which allows the initial set of differential equations to be largely reduced. In the chemically reactive systems near thermodynamic equilibrium, this means that the subsystem of the intermediates reaches (owing to quickly changing variables) the stationary state with the minimal rate of entropy production (the Rayleigh Onsager functional). In other words, the subsystem of the intermediates becomes here a subsystem of internal variables, with the subsystem with the slowly changing variables being a subsystem of external variables.

In the systems that are far from equilibrium, the stratification into subsystems with fast and slow is also possible, with the subsystem with fast internal variables being characterized by the minimum of the relevant Lyapunov function (provided that such a function exists for the particular process scheme). The ways to describe systems that can be stratified in accordance with the timing hierarchy of the processes involved are under intensive study in modern chemical engineering and biophysics. The methods are based on models that take into account mechanistic (deterministic) and statistical degrees of freedom and their contribution to processes of energy transfer and chemical conversions in the systems with a very complicated process hierarchy (for example, catalytic and biological processes).

6.2. THE RELATIONSHIP BETWEEN ENTROPY AND DYNAMIC STABILITY OF A SYSTEM

The potentiality of hierarchical stratification of complex reactive systems, according to the characteristic times of the involved processes, makes it difficult to use directly thermodynamic tools as well as to apply the concept of stability to very complicated (in particular, biological) systems. The statistical approach to describe the behavior of a system that contains a large number of particles takes into account the instability of mechanical trajectories of individual particles. Indeed, any infinitesimally small disturbances in the particles' motion can make it impossible to determine from the starting conditions the trajectory of even one particle's motion. As a result, a global instability of mechanical states of individual particles is observed, the system becomes statistical as a whole, and the trajectories of individual particles are no longer predictable. At the same time, the states that correspond to stable solutions of any dynamic (kinetic) problem can only be observed in real systems. In terms of a statistical approach, the dynamic solution of a particular initial state of an ensemble of particles is a fluctuation, while the evolution of instability upon destruction of this solution is a relaxation of this fluctuation.

The ability of a system to possess simultaneously statistical and deterministic properties is identical to its ability to have both strongly unstable and stable degrees of freedom. For example, a vessel that holds a gas can be considered as a system that is far from thermodynamic equilibrium in respect to comparatively stable degrees of freedom (this is a subsystem of the vessel walls), while the statistical properties are determined by the unstable degrees of freedom (a subsystem of the gas molecules).

The unstable degrees of freedom determine the number of various allowed microstates that are responsible for creating the given macrostate. This is namely the number of the microstates, or their thermodynamic probability $\boldsymbol{\Omega}_\Sigma$, which determines a total of entropy S of the system. According to the Boltzmann formula,

$$S = k_B \ln \boldsymbol{\Omega}_\Sigma,$$

where k_B is the Boltzmann constant. When the system stratifies into several allowed microstates to be assembled to macroscopic (quasi)stationary states, then

$$\boldsymbol{\Omega}_\Sigma = \boldsymbol{\Omega}_{\text{micro}} \cdot \boldsymbol{\Omega}_{\text{stat}},$$

where $\boldsymbol{\Omega}_{\text{micro}}$ is the number of ways to produce microstates in the stationary state, and $\boldsymbol{\Omega}_{\text{stat}}$ is the allowed number of stationary states. Hence, a total of the system entropy here is

$$S = S_{\text{micro}} + S_{\text{stat}}.$$

In the fully stable systems, there is an only one dynamic solution—one macrostate: $\boldsymbol{\Omega}_{\text{stat}} = 1$.

In the real systems beyond the full equilibrium, only unstable degrees of freedom are characteristics of the entropy, because the concept of entropy is the statistical description of the system, while the unstable degrees of freedom usually imply the occurrence of thermodynamic equilibrium in respect to them. At the same time, the system can be out of the thermodynamically equilibrium state in respect to strongly deterministic (mechanistic) degrees of freedom. Moreover, the concept of entropy per se is only applicable to the degrees of freedom that become unstable during the system monitoring. The stable degrees of freedom do not contribute to the statistical weight of the system and are not taken into account in its total entropy. From this viewpoint, the solid walls of the gas vessel behave as a giant thermodynamic fluctuation to be relaxed for the time of the vessel existence—that is, much longer than the time of the system monitoring. Therefore, in the strongly nonequilibrium and heterogeneous systems, the concept of entropy is only applicable to the individual statistical degrees of freedom. For example, in biological systems the concept of entropy can only be applied to particular metabolic processes. Neglecting this problem may cause serious errors in interpreting the *life* phenomenon in pure thermodynamics terms.

6.3. THE RELATIONSHIP BETWEEN ENTROPY AND INFORMATION

A relationship between the concepts of entropy and information was established mostly while studying information processes in biology. One of the principal and most essential specific features of living biological objects is known to be the presence of very peculiar molecular systems engaged in recording, transferring, processing, and accepting hereditary biological information that is most important to the functioning of the living objects. As soon as a researcher gets the information on the actual system state, the initial uncertainty of his knowledge on the system decreases. Obviously, the more uncertainty that is characteristic of the initial state of the system, the larger the quantity of information that can be acquired.

Let the number of states, which allow the given system to be realized, be equal to Ω, while the probabilities of each of them are identical and equal to $p = 1/\Omega$. Let us assume in the simplest case that we acquire a message on the sole and actual state of the system. In the information theory, the quantity I of the information comprised in this accepted message is equal to

$$I = -\log_2 p = \log_2 \Omega. \tag{6.1}$$

The information comprised in a reliable message at the initial number of potential events equal to $\Omega = 2$ (a priori probability of the event equals $p = 1/2$) is taken as a unit of the information quantity (bit). Hence,

$$I = \log_2 2 = 1 \text{ bit}.$$

This is the information quantity comprised, for example, in the report on the results of a coin toss (heads or tails).

Similarly, the information on which of 64 chessboard squares is occupied by a selected piece comprises

$$I = \log_2 64 = 6\ \text{bit}.$$

Formula (6.1) is valid for the case when all $\boldsymbol{\Omega}$ events are equiprobable. In a more general situation, when there are initially N events with the probabilities $p_1, p_2, \ldots, p_N$, the relevant information quantity is defined as

$$I = -\sum_{j=1}^{N} p_j \log_2 p_j. \qquad (6.2)$$

Expressions (6.1) and (6.2) were proposed by C. Shannon for estimating the absolute quantity of information at transferring the message on the event that must occur a priori at a certain probability.

While comparing formula (6.1) to the Boltzmann formula for a physical system with the identical number of microstates $\boldsymbol{\Omega}$, one can easily discover a formal relationship between entropy and information:

$$S(J/K) = k_B \ln\Omega = k_B \ln 2 \cdot I\ (\text{bit}) \approx 0.96 \cdot 10\ ^{24}\ I\ (\text{bit}). \qquad (6.3)$$

Hence, a unit of physical entropy 1 J/K equals approximately 10^{24} bit, or 1 bit of information is identical to $k_B \ln 2 \approx 10\ ^{24}$ J/K.

There is a comprehensive sense in this coincidence (with the accuracy of coefficients) of expressions that derive the quantities of entropy and information: The entropy of a system and the information on the system are interrelated. One can consider the information to be identical to that difference between the maximal possible entropy of the system and the entropy actually inherent in the system at the moment of time under consideration, or vice versa, entropy is identical to the information missing for the full system description. The latter becomes clear after the information on the system has been received.

The following example illustrates this. While real systems usually are not in total equilibrium but in some dynamically stable (e.g., stationary) state, then

$$\boldsymbol{\Omega}_\Sigma = \boldsymbol{\Omega}_{\text{micro}} \cdot \boldsymbol{\Omega}_{\text{stat}}.$$

Let the system under discussion be a specific ensemble of atoms with the possible number of states equal to Ω. While the system exists actually in only one of the possible states, the number of state provided by the atom assemblage appears lower and equal to Ω_{micro}. Therefore, the difference ΔS between the maximal and actual entropy of the system equals

$$\Delta S = k_B(\ln \Omega_\Sigma - \ln \Omega_{\text{actual state}}) = k_B \cdot \ln \Omega_{\mathrm{stat}}.$$

In this case, the information quantity I corresponds to ΔS:

$$I = \log_2 \Omega_{\mathrm{stat}}.$$

In virtue of the similarity of entropy and the measure of the information quantity, the information quantity determined by expression (6.2) often is called the Shannon entropy.

Another significant similarity exists between information and entropy. The interrelation between the entropy and information quantities argues, formally, for the identity of I and S values through expressions (6.1)–(6.3). This interrelation was discovered by L. Brillouin and formulated as the *negentropy principle of information.* If negentropy N is defined as a reversed sign function to entropy S ($N \equiv -S$), then, in accordance to the Second Law of thermodynamics, a dissipation (a decrease in the value) is characteristics of negentropy upon each spontaneous irreversible transformation in the system. The information can also be lost—that is, dissipate—upon each spontaneous failure in the information transfer system. Hence, the information quantity follows the generalized Carnot principle and tends to dissipate at each spontaneous transformation. For this reason, one can consider the problem of identity of parameters I (bit) and S (J/K) to be in some respect similar to the problem of the mass to energy correlation according to the Einstein relation $E = mc^2$.

It is important that the preceding speculations are true only for macroinformation—that is, information on the occurrence of one of many possible system macrostates at a given moment of time. As to microinformation, it cannot be fixed in principle, since any microstate may turn rapidly to another microstate due to the strong instability of microscopic motion and heat fluctuations. For example, biological and computational systems store only macroinformation (see following for details on some its properties). For this reason, the Brillouin relation does not give correlation between macroinformation and physical entropy of dynamically unstable degrees of freedom.

6.4. THE QUANTITY OF BIOLOGICAL INFORMATION

The preceding expressions of the information theory can be used for estimating the information quantity inherent in a living organism that is constituted by individual cells. There are approximately 10^{13} cells in a human body. Let us suppose that all of them are unique and not allowed to be transposed in order to preserve the organism integrity. A priori, the methods to arrange a structure by the given number of cells is $\Omega = 10^{13}!$. Therefore, the quantity of information comprised in the message on building the required particular human structure equals

$$I = \log_2(10^{13}!) \approx 10^{13} \log_2 10^{13} \approx 4 \cdot 10^{14} \text{ bit.}$$

When an ordered human organism is built by the system of chaotically arranged 10^{13} cells, a decrease in entropy is

$$\Delta S = 10^{\;\;24} \cdot 4 \cdot 10^{14} \text{J/K} \approx 4 \cdot 10^{\;\;10} \text{J/K.}$$

In the human organism, the estimated quantity of the captured biological information is indeed much greater if the unique arrangement of aminoacid residues in the DNA molecules is taken into account, too. Any adult organism comprises more than150 g of DNA—that is, $3 \cdot 10^{24}$ amino acid residues. The information quantity related to their regular arrangement will be $I = \log_2(3 \cdot 10^{24})! = 1.3 \cdot 10^{26}$ bit, which means a decrease in entropy by $\Delta S \approx 1200$ J/K in comparison to a fully chaotic mixture of amino acid residues.

One can see that only a minor decrease in physical entropy is observed upon the formation of the most complex biological structure—a human organism—the decrease being identical to the decrease in entropy during condensation of 170 cm^3 of water vapor. In the metabolic processes, the entropy decrease by 1200 J/K is easily balanced by an increase in entropy due to the oxidation of 900 g of glucose. Thus, the formalistic application of equations (6.1) and (6.3) demonstrated that the substance ordering degree and, as a consequence, the quantity of information in a biological system is small and not larger than the entropy of a solid, with the mass equal to that of the system.

6.5. THE VALUE OF INFORMATION

In the preceding speculations, we assumed that the ordering of structural units in a living object is of the same significance through the whole system to be built. However, the information encoded in biological structures may differ in value at certain organization levels of the living matter. A complication of a biological system occurs due to the increase of dissimilar structural units in number and of their interrelations in the system. When the system structural units become more essential, this implies an increase in value of the inherent information.

Surely, only irredundant information related to irreplaceable elements of the system is valuable. The redundant (replicated or duplicated) information also is of vital importance to minimize the probability of destructing the valuable information as it is transferred. In this viewpoint, any aperiodic system contains a much larger number of irreplaceable units and, therefore, a greater quantity of irredundant information than a periodic system of the same gross composition with the interchangeable elements (see Figure 6.1).

The information value is determined by the degree of irredundancy, or irreplaceability, of the message. For example, the quantity of information encoded by the coding sequence of *n* general type nucleotides (adenine, guanine, thymine, and cytosine) in a DNA chain equals

$$I_1 = \log_2 4^n = 2n \text{ bit.}$$

However, at the next level of the biological system, the information quantity decreases in the protein chain against that at the DNA level because each of 20 amino acid residues is encoded by three nucleotides (codon).

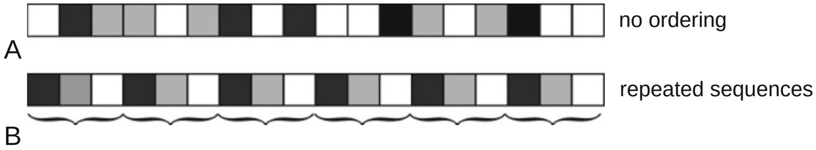

Figure 6.1 Regarding the information value of a chain constructed by inserted locuses that differ in their nature: (A) aperiodic locuses in the chain, a unique sequence; and (B) repetition of short sequences, less valuable information on the locus arrangement in the chain.

For this reason, the actual quantity of information in the protein chain synthesized on *n* nucleotides equals

$$I_2 = \log_2 20^{n/3} = 1.44n \text{ bit.}$$

Thus, the initial quantity of the lower level information (DNA) decreases on transferring to a higher level (protein). In the case under consideration, this is accounted for by the particular triplet code of living organisms on Earth. The same amino acid residue is encoded by different codons consisting of a three nucleotide sequence, a total of codons, $4^3 = 64$, being more than the amino acid number (only 20). At the next level, some of the amino acids may be substituted for by others without considerable changes in the protein properties to reduce the number of the actually irreplaceable amino acids ($N < 20$), and, as a result, the information quantity I_3 at this level equals

$$I_3 = \log_2 N^{n/3} < \log_2 20^{n/3} = I_2.$$

For example, a DNA fragment of 600 nucleotides comprises the information in the amount $I_{DNA} = \log_2 4^{600} = 1200$ bit, while the information I_P in the primary protein sequence synthesized on this fragment and containing 20 amino acids is smaller: $I_P = \log_2 20^{200} = 860$ bit.

The difference $\Delta I = I_{DNA} - I_P = 340$ bit is redundant and of no self value. Each next level of arranging the structure that stores biological information reduces the quantity of the irreplaceable information. Hence, the information comprised in its molecular carriers' elements increases in value at higher organization levels in comparison to the primary information at the lower level. Such a decrease in the information quantity contained at the first lowest level may be substituted for by a decrease in the number of elements at the next level. So the value of an element in the information message is higher at the higher level than at the lower level; that can be defined as an increase in the irreplaceability degree of this element.

It is commonly accepted that Darwin's theory of evolution of living organisms is based directly on the capability of storing the valuable (for example, for the system survival) biological information that has appeared in the course of spontaneous molecular scale mutations of the hereditary apparatus of the organism. An interesting fact revealed by studying genomes of man and other living organisms is that full genomes (i.e., carriers of the valuable irreplaceable biological information) in humans and far lower organized organisms like worms are only slightly different and contain in both cases approximately 30,000–40,000 genes. It is also established that numerous "sleeping locuses" exist in DNA and genomes of all living organisms, the role of them in the hereditary information being not as yet understood.

6.6. RECEPTION AND EXPRESSION OF INFORMATION IN DYNAMIC SYSTEMS

To perform the reception of the information, a dynamic receptor system must be capable of transferring to one of several allowed stable states according to the acquired information. In other words, the information system must be multistationary. The number of stable stationary states Ω_{stat} determines the information capacity of the system—that is, the maximal information quantity I_{max} to be accepted by the system equals

$$I_{max} = \log_2 \Omega_{stat}.$$

It is important that a system of ordinary unstable physical microstates is incapable of remembering and storing information for a long time because as soon as it falls into any particular microstate, the system escapes it immediately due to the instability. Therefore, reception, fixing, and storing of the transmitted information needs certain work to be done to change the system state to any great extent. The work done will allow the system to transfer to one of several dynamically stable states, with the energy partly lost through the dissipation processes. The work done on the system will cause an increase in the entropy of the whole system by the quantity larger than the quantity of the stored information.

Thus, all information systems possess dissipative properties due to the necessary transfer to the particular deterministic degrees of freedom that are capable of storing their parameters for a long time. This is namely what causes emergence of the macroinformation to be stored by the system and then transferred to other acceptor systems. In real information systems, the characteristic storing time depends on the system design, the capacity of the memory units, and the temperature. Of particular importance to biology is the possibility of acquiring and storing the information in molecular systems—that is, the systems where heat fluctuations even at ambient temperatures usually lead to an instability in the microscale motion.

As a simple example of the reception phenomenon, one can consider the behavior of moving balls in a lottery basket. The basket has several holes in it, and the win is determined by the ball that falls stochastically into one of them. In the system, physical entropy relates only to quickly relaxing degrees of freedom, while their behavior is determined by the nature of the ball in the basket but independent of whether the ball is in a hole. However, while for the physical entropy the information quantity is zero, for the second situation, when the ball is already in a given hole, the information equals I_{max}. Thus, the reception of information arises when the ball hits the hole. This event required some work W to be done and is accompanied by the mechanical energy to heat transfer to make the reception irreversible. The physical entropy of the system increases by W/T, which is much larger than the quantity of the appeared information: $W/T \gg I_{max}$.

The information storage time is determined by the time of the ball residence in the hole, which depends in turn on both the barrier height and on spontaneous thermal oscillations of the ball inside the hole (in view of the ball approaching the hole walls). Apparently, when the hole is deep enough ($\gg k_BT$), heat fluctuations are not sufficient for the ball to escape it. At short observation times, an increase in thermal oscillation frequency of the ball inside the hole—that is, an increase of the energy factor in power to initiate the ball jumping over to another hole—can result in the information loss even though the hole is deep enough (see Section 3.5).

Now if the ball is actually a molecule in a potential energy well of depth *E*, the occurrence of heat oscillations at the frequency k_BT / h allows an estimation of the limit storage time in terms of the theory of monomolecular reactions:

$$\tau_{storage} \leq \left(\frac{k_BT}{h}\right)^{\ 1} \cdot \exp\left(\frac{E}{k_BT}\right) \approx 10^{\ 12} \exp\left(\frac{E}{k_BT}\right), \mathrm{s}.$$

Hence, to ensure storing the received information for a time that is longer than the given time τ, we need the energy well with the depth $E > k_BT \ln(\tau k_BT/h) \approx k_BT \ln(10^{12} \cdot \tau)$.

What this means is that at temperature T = 300 K, the well depth *E* must be longer than 89 kJ/mol for the information storage for an hour, 112 kJ/mol for a year, 118 kJ/mol for 10 years, 146 kJ/mol for 10^6 years, and 164 kJ/mol for 10^9 years. The elevation of temperature results in more severe requirements for the energetic barrier height. For example, storage of geochemical information for 10^9 years at the temperature 300°C = 573 K (typical of abyssal rocks) needs $E > 312$ kJ/mol that is close to the energy of the strongest bonds in saturated hydrocarbon molecules.

The preceding relations provide, in particular, a semiquantitative estimation of the strength of chemical compounds that can be used as chemical markers of a variety of geological processes in nature. The limitations for the minimal energetic barrier, which is necessary for storing and reading the information, bring about limitations for the maximal achievable productivity of computers due to an increase in the specific power of the heat release by their units at the increase in the frequency of logical operations—in other words, of the computer productivity.

In molecular systems, storage of a certain sequence of nucleotides (amount of stored information I_{max}) depends mainly on the chemical stability of the DNA molecule. The information capacity is determined by the number of certain combinations of nucleotides but not by the number of microstates, including accounting the vibrations of all of the atoms in the DNA chain. The formation of macroinformation is coupled here with the work and energy consumption in the course of biosynthesis of the DNA molecule. Similarly, the information can be implemented by consuming energy for the processes of the information translation and synthesis of the protein chain.

An interesting fact is that the synthesis and replication of DNA is based on the cleavage of hydrogen bonds (their energy, which equals 15–60 kJ/mol, is optimal for recording biological information). The codons used by living beings contain each of three nucleotides, the "hole" depth being trebled that is enough for storing the biological information for the whole life of the living organism. If there were stronger (covalent) bonds, then the hole would be too deep, and reading and reproducing the information during a reasonable (in view of the organism life) amount of time would be too difficult. As for weaker (Van der Waals) bonds, they would rapidly lose the information.

Thus, any information system must comprise statistical and dynamic subsystems. The physical entropy is the measure of numerous nonstored system microstates that are related to statistical subsystem, while macroinformation is the measure of numerous states to be stored in the dynamic subsystem.

Emergence of the primary information may be stochastic in nature (e.g., the number of holes, the combination of nucleotides, etc.). However, the stochastic information, should it appear in the system, is stored and thus acquires the value and meaning. The principle of remembering a stochastic choice underlies the appearance of mutations and biological information. These receive the information involved in biopolymers and its application for real biological processes that impart the biological value to it and define the role of the biological ordering and organization. In the course of natural selection and competition, the organism replication may, in turn, select and fix the valuable information that is necessary for the vital activity. There may exist a kind of "training," as well—that is, an extraction (from the environment) of the vitally important information that is not inherited through the organism replication. The training is provided by a special structure of the receptor systems: They transfer the "valuable" information but prevent undesirable reactions of the organism by stopping the value free information.

Some diseases that occur as the organism ages are caused by the disordered action of the synthetic apparatus of the organism and may result from failures in the processes of transferring and storing the biological information, while the information is selected by nature for the nonfailure use of it during a finite time needed for engendering the like progeny.

6.7. BIOINFORMATICS AND ITS APPLICATION TO BIOLOGY AND BIOCHEMISTRY

The modern methods for identification of the primary structure (sequenation[*]) of DNA allowed genomes of many living organisms to be decoded, including the genomes of humans, animals, plants, and a variety of microorganisms. While there is an unambiguous compatibility of the DNA structure and the structure of the protein synthesized thereon, the information on the amino acid sequence in more than 1 million proteins has been obtained to date. Except for the primary structure of the overwhelming majority of the proteins, not much more is known. However, the primary structure is responsible for all of the further protein structures, such as spatial stacking of polypeptide chains, spatial arrangement of atoms, and so forth. For this reason, many characteristics of sequenated proteins

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[*] From *sequence*.

can be theoretically predicted, even though they are not characterized by other methods.

The huge quantity of genetic information that has been decoded as well as the potentialities of modern computers have given rise to a new scientific area: bioinformatics. *Bioinformatics* is a science related to the computer aided analysis of genetic texts, amino acid sequences, spatial structures, and the functions of proteins. It supplies solutions to problems like understanding the formation of the protein spatial structure, analyzing the protein molecules' interactions, understanding the evolutionary interrelations on both molecular and whole organism scales, predicting the structure and function of genes and proteins, searching for potential targets for medical substances and predicting feasible activities of these substances, and studying the exoelectron structure of genes, to name a few.

For example, identifying a group of proteins that have similar primary structures allows them to be classified into generic groups (proteins usually are supposed to be cogeneric if their homology exceeds 30%). The application of computer programs makes it possible to collate homologous proteins into clusters and to construct the so called *phylogenetic tree*—that is, to order the proteins in the series following the principle of least changes. Figure 6.2 shows, as a typical example, the phylogenetic relations of

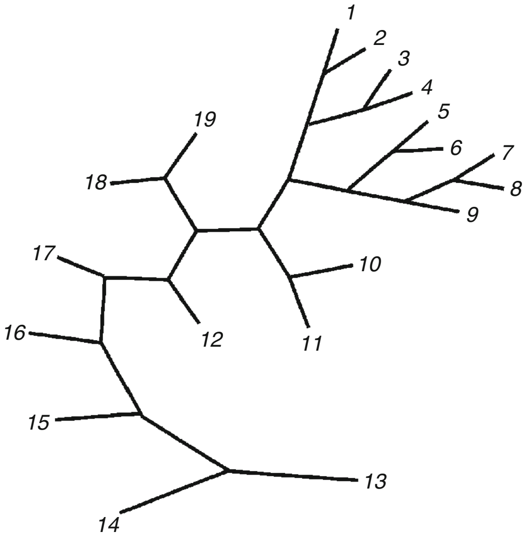

Figure 6.2 An example of the phylogenetic tree derived for peroxidase enzymes extracted from various plants. The digits refer to the particular plant species for which the DNA sequencing was carried out [1].

"relatives" of peroxidase enzymes identified in the genomes of various plants. The "leaves" at the ends of the "branches" of tree are sequenated proteins of particular plant strains, and the "branch" intersections are the hypothetic structures that are common in the family.

In bioinformatics, the so called alignment procedure is widely used to compare sequences of amino acids and to identify closely related proteins. The procedure is most often used for modeling the protein spatial structure based on homologous analogues, as well as for searching in databases for objects that would be similar to the amino acid sequence under study in order to predict functions of the latter. The alignment procedure is the computer aided comparison of amino acid sequences aimed at identifying common invariant chain fragments or amino acid positions. While comparing, it is easy to detect the skip (deletion) or insertion of some chain fragments that are caused by mutation processes or gene exchanges between DNA fragments.

The procedure of alignment of a group of related proteins with respect to a chosen protein is as follows: The primary structure of the reference protein is taken as a matrix whereon the rest of the family proteins are "stacked." Some of the amino acids will be identical in certain positions throughout the family, while other positions bear different amino acids. If a large number of proteins are present in the protein family under consideration (a large sampling), the probability p_{ji} of residing amino acid *j* at each *i* position in accordance to a "reference" template can be calculated. One should calculate how many times the given amino acid is in the given position throughout the whole family, the result being divided by the total number of proteins in the family.

In bioinformatics, the invariance (or conservatism) of the position of amino acid *j* in a polypeptide chain is typically estimated using the Shannon entropy as an integral characteristic of the probabilistic (stochastic) process (see also equation (6.2)):

$$H_j = -\sum_i (p_{ji} \log_2 p_{ji}), \tag{6.4}$$

where p_{ji} is the probability of amino acid *j* residing at position *i* in the polypeptide chain (a stochastic event).

When the probability of an event tends to unit or zero, the Shannon entropy is close or equal to zero. Thus, if probability p_{ji} of localization of amino acid *j* in position *i* equals unit (an absolutely certain event), then one should suppose that these amino acids occupy their absolutely constant positions and the related Shannon entropy is zero.

Let us imagine a family of homologous proteins aligned with respect to a certain "reference" protein of the family. The probability of the localization of one or another amino acid can be determined for each position in the amino acid sequence in this protein. For example, if 100 proteins are compared and combined into one group through the alignment procedure, and 98 glycines are in position *i*, then the probability for glycine to occupy this position equals 0.98. Therefore, entropy H can be calculated by equation (6.4) for each *i* position. If there is glycine in this position in almost all of the proteins (98 of 100), the Shannon entropy of glycine will tend to zero. The positions of amino acids, which are common for the given protein family, can be identified this way. Positions of this kind and the amino acids that correspond to them are referred to as conservative.

Figure 6.3 illustrates typical results of calculations of the Shannon entropy for the family of 184 proteins close in properties to the pepsin enzyme. All of the proteins of this family demonstrate enzymatic activity to hydrolysis of proteins and peptides. The Shannon entropy of some amino acids (G21, T33, S35, Y75, G78, G82, D87, G119, G122, G168, D215, G217, G302, F305, A323) is seen to be almost zero. Hence,

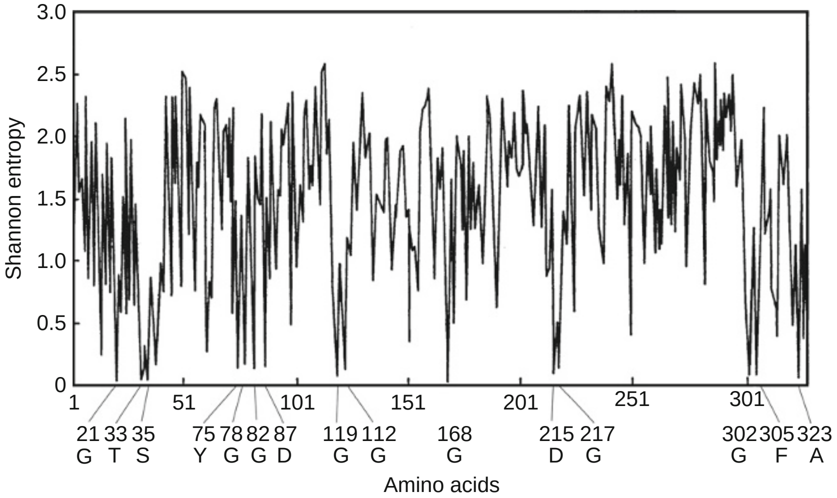

Figure 6.3 An example of the Shannon entropy calculated for 184 proteins of the pepsin family, which are aligned in respect of pepsin (the conservative amino acids are indicated) [1].

we should suppose that these are conservative amino acids in this protein family which bear an important function in the pepsin type enzymes. Thus, the alignment operation and calculation of the residence probability of a certain amino acid can be used, for example, for understanding the mechanisms of the operation of active centers of some enzymes.

6.8. CHAPTER EXERCISES

1. In DNA, the biological information is encoded by codons, each of which contains three nucleotides. Assuming that all opposite nucleo tides are stacked through identical chemical bonds in the duplex DNA, estimate the energy of these bonds to ensure the information storage for the period not shorter than 30 years. What type of chemical bonds are characterized by this energy?
2. In an integral semiconductor circuit unit for the information storage and processing, there are as many as 10^6 electronic triggers per 1 cm^3. Estimate the minimal specific heat power released in the unit at its operation frequency 20 MHz and the required time of no less than one year for the information storage.

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