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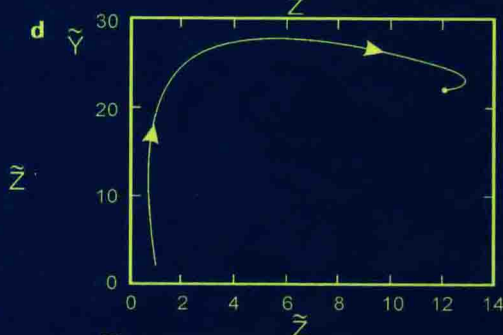visit our web site at books.elsevier.com
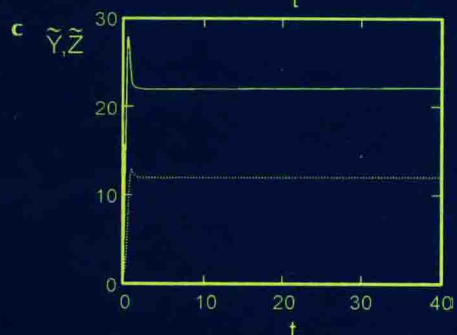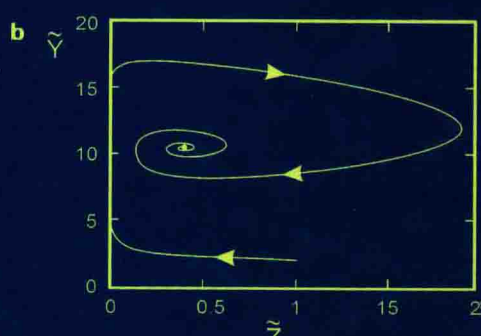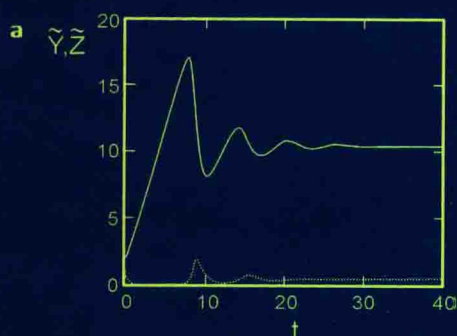
Thermodynamics of Non-Equilibrium Processes for Chemists with a Particular Application to Catalysis

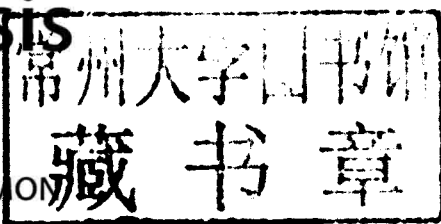To my scientific parents, Kirill Zamaraev and Georgij Zhidomirov

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.

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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.

CONTENTS

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)
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