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Thermodynamic Equilibria and Extrema

Analysis of Attainability Regions and Partial Equilibria

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

Preface

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

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

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

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

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

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

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

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

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

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

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

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

E.G. Antsiferov created the first algorithms for calculation of partial equilibria that correspond to extreme concentrations of given substances [7]. Further

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

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

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

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