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*Book Review*

# **Molecular, Quantum and Evolution Thermodynamics: Development and Specialization of the Gibbs Method.** By E. S. Rudakov. Donetsk State University Press, Donetsk (Ukraine). 1998, 139 pp, in Russian. ISBN 966-02-0708-5.

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Recently Professor E. S.Rudakov has written a new book which might have attracted the attention of many peoples interested in thermodynamics. From previous experience it can be anticipated, however, that its impact on the majority of international scientific community would be substantially delayed because this book was published by an Ukrainian publisher in Russian. The main aim of this book can be understood as further development and "specialization" of the Gibbs method by combining the equations of Gibbs thermodynamics with those of quantum mechanics. The classical Gibbs equation is complemented by new terms accounting for motions of, and interaction between, particles. This approach proved applicable to some simple model systems (such as the ideal gas, systems of point rotators and vibrators, systems with central interparticle interactions, including those in external field, photon gas, etc.). New solution of these problems are made possible within the frame of the mathematical formalism of characteristic functions. This provides a unified approach to the derivation of equations and inequalities specifying conditions of equilibrium, stability criteria, parameters of mutual convexity and fluctuations of variables.

The so called "Specialized Thermodynamics" is, in fact, a generalization of the method of thermodynamic potentials by introduction of molecular-quantum variables. In this way, the information on a specific class of molecular systems is directly introduced into the Gibbs equation as non-classical molecular-quantum bifunctions derived from corresponding Hamiltonian. The new equations and inequalities proved to be symmetric with respect to permutation of conjugated intensive and extensive variables. In the spirit of the Gibbs model, a non-equilibrium state is assumed to be a combination of intensive and extensive variables for two different equilibrium states; the stability is characterized by a new parameter, baptized as "Work Production Capacity (WPC)" and defined as "the minimum work spent for creation of a given non-equilibrium state in a reversible process, or the maximum work recovered in the course of equilibration".

A feeling of the importance of kinetic energy in *Molecular Thermodynamics* can be assessed from the general treatment of intermolecular interactions (yielding, *inter alia*, a novel look at the compensation effect). A further important Step is the development of *Quantum Thermodynamics* which addresses the same issue as traditional thermodynamics both in form and aims but differ in contents. In this respect, *quantum thermodynamics* is basically different from *statistical thermodynamics* as soon as the main target of the latter is the modeling (by canonical or grand canonical ensembles) the properties of a system via its energy spectrum. It is to be emphasized that quantum thermodynamics is in no way the alternative to the classical thermodynamics; the former is assumed to be the extension of the latter to those specific cases when it becomes possible to build the quantum models of bifunctions of motion and interactions between particles from the existing solutions of quantum equations and/or structure of a hamiltonian for a given energy component.

The theory of evolution of signs of thermodynamic inequalities was built along essentially similar lines. The main idea is the conservation of signs of inequalities attending their transformation from the differential form to the rate (evolution) one. In other words, the differentials of intensive and extensive variables are substituted by their time derivatives. In this way, the sign of an inequality is determined by the direction of system evolution. In a reversible process the WPC (positive by sign) smoothly decreased with time to a definite minimum value at infinite time. The notion of the minimum WPC serves as a basis for generalization of the Gibbs extremum principle and of the Gibbs-Duhem equation, for a more general formulation of the universal criterion of evolution, etc.

The analysis has been given for closed systems consisting of two subsystems. Two extreme cases of evolution are fully arbitrary process (without work production) and "regulated" arbitrary process producing the work. The author develops the "two-times" model of the evolution direction, which gives the new possibility to describe the chemical reactions in the framework of the Gibbs-Duhem equation. The evolution theory of the inequality signs is an important general result both in classical end quantum the modynamics. The second and the third thermodynamic laws and also Gibbes-Duhem and Gibbs-Bogolyubov relations are also considered and generalized. It is important that the author gives some examples of quantum statistical analogues of the model relations developed in the book.

In this short review it is very difficult to present all the new results and approaches developed by the author and we have only done an attempt to mention the most important problems discussed in the book. The book is supplied with a highly developed mathematical formalism. To substantiate his point of view, the author introduced into consideration new concepts and definitions, among them the principle of the minimum of the work production capacity playing the most important role. The book consists of 9 chapters. Chapter one is introduction, chapter 2 considers the principles of molecular thermodynamics. In Chapter 3 thermodynamics of nonequilibrium states is considered, whereas in chapter 4, thermodynamics of intermolecular interactions. In chapter 5 the problems of system symmetry are discussed. Principles of quantum thermodynamics are presented in chapter 6 and analysis of the systems of particles with central interactions in external scalar field- in chapter 7. The most important chapters are chapter 8, where the general discussion of quantum thermodynamics is presented, and chapter 9 that considers the evolution thermodynamics and symmetry and generalization of the Gibbs method and Gibbs-Duhem equation. The book has three appendices, where quantum statistical analogues of relation of specialized thermodynamics, statistical thermodynamics of gases in external field and specialized thermodynamics and compensation effects in liquids of thermodynamic interaction functions are presented. In such a way the possibility and utility of combination of classical thermodynamics and quantum mechanics seem to be evident. Specialization of the Gibbs method presented by E. S.Rudakov, does not replace the classical thermodynamics but extends it on the model and real systems whose energy (hamiltonian) is bilinear function of variables. This circumstance confines the field of application of quantum thermodynamics, although leaves a great room for the analysis of many thermodynamic systems.