

# PREFACE

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This monograph is a continuation of the book. 'Thermodynamics of the Critical State of Individual Substances' published by Energoizdat in 1990 and translated into English in 1994. Our original idea was to present the behavior of equilibrium and nonequilibrium properties of individual substances and mixtures in the critical region in a consistent manner in three books. By now, only the second book has been prepared for publication. Its scheme and structure can be inferred from the contents.

Unlike equilibrium properties, the experimental determination of the transport coefficients for liquids and gases encounters some difficulties because of effects caused by deviation of a system from the thermodynamic equilibrium. The transport coefficients in the system are well known to determine the relation between pressure, temperature and concentration gradients and the corresponding flows. The response of the system to the presence of finite gradients is extremely intricate; therefore, in certain cases the experimenter faces a complicated problem of taking into account all of the corrections that strongly affect the precision of measurements.

The pressure gradient, for example, which is bound to be present in investigations of dynamic viscosity, induces secondary flows and energy dissipation in addition to laminar flows of liquids and gases. The temperature gradient usually induces not only thermal conductivity but convection and radiation as well. To take account of these and other side effects, a special technique should be developed for measuring the transport coefficients, which

would minimize the effects that tend to increase as the critical point is approached.

In view of this fact, the first chapter deals with the most widely used techniques for measuring viscosity and thermal conductivity of liquids and gases, taking into account the specific features of their behavior in the critical region. The theoretical foundation for equations used to calculate transport coefficients, based on the results of measurements, is discussed, and possible errors in the final values are estimated for each of the measuring techniques. A list of works is given, which report experimental data on numerous individual substances and binary mixtures near liquid-liquid and liquid-gas critical points.

As experimental data accumulated, a theory of dynamic phenomena near the critical point was being developed. By now, some advances have been made in this field that allow one to calculate transport coefficients in the critical region. However, the accuracy of calculated data depends, to some extent, on the choice of equations and values of dynamic critical exponents. Moreover, an excess 'theoretization' brings about unwarranted difficulties, which can be avoided if a calculation procedure is chosen such as to give reliable final results in a simplest way.

Therefore, problems related to theoretical estimation of critical exponents for viscosity and thermal conductivity are discussed in the second chapter and the estimates are compared with experimental data. An outline of modern theory of transport phenomena near the critical point and procedures of calculating viscosity and thermal conductivity is presented. Some recommendations as to the analysis and processing of experimental data, based on modern theoretical approaches, are given. Special attention is paid to the theories of crossover phenomena and dynamic 'pseudospinodal' scaling, because these theories are competitive for describing anomalous behavior of different substances in the vicinity of the critical point.

An attractive idea of unifying the thermophysics of equilibrium and non-equilibrium phenomena in substances, because they are naturally interconnected, is steadily gaining recognition. This universality is most conspicuous in the behavior of substances as a critical point is approached. It can be hoped, therefore, that a description of this behavior by equations, that connect statistical and dynamic properties of liquids and gases near critical points, would provide further support to the idea and stimulate search for their rational interdependence in the whole region where liquids and gases exist.

The accuracy and self-consistency of equilibrium and nonequilibrium properties is central in developing tables of thermophysical properties. Therefore, in Chapter 3 we briefly present the theoretical principles that establish the connections between the equation of state and transport coefficients. The basic types of parametric equations of state are discussed that can be used in calcu-

lating thermodynamic properties of individual substances near the critical point, the equations following from the crossover theory and 'pseudospinodal' hypothesis included.

Tables of viscosity and thermal conductivity values in the vicinity of the liquid–gas critical point were calculated for some commercially important substances (such as benzene, toluene, ethylbenzene, *o*-xylene, chlorobenzene, fluorobenzene and carbon dioxide). The reliability of the calculated values is estimated. The results obtained are based on the data from numerous theoretical and experimental works of researchers in this country and abroad. The list of the works is presented.

When working at this book, we kept in mind what Einstein once noted. He said that no scientist thinks in formulas. Before starting calculations, a physicist should have a course of reasoning in his mind, and this, in most cases, can be formulated in simple words. Calculations and formulas are the next step.

Whether we succeeded in following this is for our readers to judge. We ourselves are far from considering the work a complete success lacking shortcomings. Therefore, we would greatly appreciate any comments and proposals, which can be used in our future work.

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