PHYSICAL CHEMISTRY

AN ADVANCED TREATISE

Edited by
HENRY EYRING
DOUGLAS HENDERSON
WILHELM JOST

VOLUME VIIIA

PHYSICAL CHEMISTRY

An Advanced Treatise

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Edited by

DOUGLAS HENDERSON
IBM Research Laboratories
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List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

J. A. Barker, IBM Research Laboratories, San Jose, California (377)

R. J. Baxter, Research School of Physical Sciences, The Australian National University, Canberra, Australia (267)

Sow-Hsin Chen, Department of Nuclear Engineering, Massachusets Institute of Technology, Cambridge, Massachusetts (85)

Henry Eyring, Departments of Chemistry and Metallurgy, University of Utah, Salt Lake City, Utah (335)

Douglas Henderson, IBM Research Laboratories, San Jose, California (377)

Mu Shik Jhon, Korea Institute of Science and Technology, Seoul, Korea (335)

Francis H. Ree, Lawrence Livermore Laboratory, University of California, Livermore, California (157)

Robert L. Scott, Department of Chemistry, University of California, Los Angeles, California (1)

Foreword

In recent years there has been a tremendous expansion in the development of the techniques and principles of physical chemistry. As a result most physical chemists find it difficult to maintain an understanding of the entire field.

The purpose of this treatise is to present a comprehensive treatment of physical chemistry for advanced students and investigators in a reasonably small number of volumes. We have attempted to include all important topics in physical chemistry together with borderline subjects which are of particular interest and importance. The treatment is at an advanced level. However, elementary theory and facts have not been excluded but are presented in a concise form with emphasis on laws which have general importance. No attempt has been made to be encyclopedic. However, the reader should be able to find helpful references to uncommon facts or theories in the index and bibliographies.

Since no single physical chemist could write authoritatively in all the areas of physical chemistry, distinguished investigators have been invited to contribute chapters in the field of their special competence.

If these volumes are even partially successful in meeting these goals. we will feel rewarded for our efforts.

We would like to thank the authors for their contributions and to thank the staff of Academic Press for their assistance.

HENRY EYRING
DOUGLAS HENDERSON
WILHELM JOST

Preface

The prediction of the properties of liquids has been one of the classic problems of physical chemistry. Until very recently, it was an unsolved problem. Even now it is widely so regarded. Fortunately, this is no longer true. The equilibrium properties of simple liquids, except in the neighborhood of the critical point, are now well understood.

This volume is restricted to simple liquids because the theory is most developed for these liquids. The term simple liquid has been interpreted broadly. Thus, a chapter is devoted to liquid helium. Nonsimple liquids, such as water, are of great practical interest. Such liquids are, in general, not considered in this volume because the theory of such liquids is not well developed. However, the techniques which have proved so useful for simple liquids will form the basis of the theory of complex liquids. It is our aim that through the study of these techniques, which are described in this volume, a student will be able to read and contribute to the current literature on both simple and complex liquids.

There are four main techniques in the theory of liquids: simulation studies, integral equation methods, lattice theories, and perturbation theories. Each of these methods is treated in this volume. The only lattice theory which has received attention during the past decade is the significant structure theory and, as a result, that is the only lattice theory considered in this volume.

As has been mentioned, the critical point and nonequilibrium properties of liquids are not so well understood. Introductions to these fields, which the student should find useful, are included.

The editor would like to thank the authors for their contributions. Thanks are also due to Drs. J. A. Barker and H. L. Frisch for many valuable suggestions relating to the organization of this volume.

DOUGLAS HENDERSON

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Douglas Henderson and J. A. Barker

Chapter 1

Introduction

ROBERT L. SCOTT

I. Introduction

A. Definition

Although the area labeled "liquid" on a pressure–temperature phase diagram is usually small compared with that occupied by "gas" and by various crystalline modifications, for many substances that area lies near the usual convenient pressures and temperatures and is of major importance. Nonetheless, it is not always easy to define the liquid state, either experimentally or theoretically, in a way which clearly includes highly viscous fluids but excludes glasses and crystalline solids, or which distinguishes it unequivocally from the less dense fluids which we prefer to call gases.

Experimentally, the most obvious way to distinguish[1] between two "states of aggregation" is to observe a phase transition between them. In a typical isothermal expansion of a pure substance, a graph of the variation of pressure p with volume V may look like that shown in Fig. 1. As one increases the volume isothermally (line a), one finds two regions in which

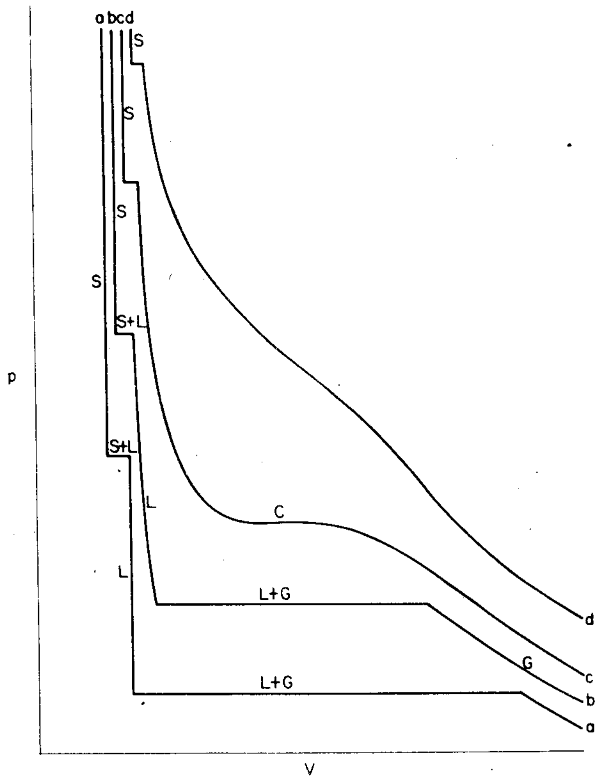

FIG. 1. Schematic pressure–volume behavior for a one-component system at a series of constant temperatures (isotherms). Lines a and b are for $T < T_c$; line c is the critical isotherm ($T = T_c$). Line d is for $T > T_c$. Here, S, L, and G denote solid, liquid, and gas phases, respectively; $S + L$ and $L + G$ denote two coexisting phases; C denotes the critical point.