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0521330416 - Thermodynamics of Chemical Systems
Scott E. Wood and Ruben Battino
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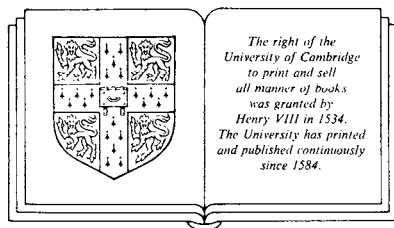
Thermodynamics of CHEMICAL SYSTEMS

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CAMBRIDGE UNIVERSITY PRESS

Cambridge

New York Port Chester Melbourne Sydney

Cambridge University Press
0521330416 - Thermodynamics of Chemical Systems
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Published by the Press Syndicate of the University of Cambridge
The Pitt Building, Trumpington Street, Cambridge CB2 1RP
40 West 20th Street, New York NY 10011, USA
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1990

First published 1990

Library of Congress Cataloging in Publication Data

Wood, Scott E. (Scott Emerson), 1910–

Thermodynamics of chemical systems / Scott E. Wood, Rubín Battino.

p. cm.

Includes index.

ISBN 0–521–33041–6

1. Thermodynamics. I. Battino, Rubín. II. Title.

QD504.W66 1989

541.3'69–dc20

89-32580

CIP

British Library Cataloguing in Publication Data

Wood, Scott E.

Thermodynamics of chemical systems.

1. Chemical reactions. Thermodynamics

I. Title II. Battino, Rubín

541.3'69

ISBN 0–521–33041–6 hard covers

Transferred to digital printing 2004

Cambridge University Press
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To Our Sons

Edward S. Wood
David Rubin Battino
Benjamin Sadik Battino

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Preface

The systems to which thermodynamics have been applied have become more and more complex. The analysis and understanding of these systems requires a knowledge and understanding of the methods of applying thermodynamics to multiphase, multicomponent systems. This book is an attempt to fill the need for a monograph in this area.

The concept for this book was developed during several years of teaching a one-year advanced graduate course in chemical thermodynamics at the Illinois Institute of Technology. Students who took the course were studying chemistry, chemical engineering, gas technology, or biochemistry. During those years we came to believe that the major difficulty that students have is not with the numerical solution of a problem; the difficulty is with the development of the pertinent relations in terms of experimentally determinable quantities. Moreover, during the initial writing of the book, it became evident that chemical thermodynamics was being applied in many new fields and to systems having more than two or three components. These new fields are so numerous that any attempt to illustrate the application of thermodynamics to each of them would make this book much too long. Therefore, the aim of the book is to develop in a *general* way the concepts and relations that are pertinent to the solution of many thermodynamic problems encountered in multiphase, multicomponent systems. *The emphasis is on obtaining exact expressions in terms of experimentally determinable quantities.* Simplifying assumptions can be made as necessary after the exact expression has been obtained. It is expected that users of this book have some knowledge of physical chemistry and elementary thermodynamics. It is hoped that, once these basic concepts have been developed, the users will be able to apply chemical thermodynamics to any specific problem in their particular field.

The methods of Gibbs are used throughout with emphasis on the chemical potential. The material is presented in a rigorous and mathematical manner. Several topics that are presented briefly or omitted entirely in more-elementary texts are introduced. Among these topics are: the requirements

xiv *Preface*

that must be satisfied to define the state of a thermodynamic system, particularly indifferent systems; the use of the Gibbs–Duhem equation in the solution of problems associated not only with simple phase equilibria, but also with phase equilibria in which chemical reactions may occur in one or more phases; the conditions of stability for single-phase, multicomponent systems; and the graphical representation of the thermodynamic functions. Because of the importance of reference states and standard states, special attention is given to their definition and use.

The subject matter is divided into two parts. The first part is devoted to defining the thermodynamic functions and to developing the fundamental relations relevant to chemical systems at equilibrium. The second part is devoted to the application of these relations to real systems and the methods that can be used to obtain additional relations.

The introductory material (Chapters 1–4) is treated briefly. The basic concepts, which are always so difficult to define, are approached from an operational viewpoint and in the classical manner. No attempt is made to use a more general approach.

A bibliography is given after the appendices. The first section lists those books to which reference is made in the text and a few of the more recent and relevant advanced texts in chemical thermodynamics. The other sections give references to data compilations and sources. An abbreviated set of thermodynamic data are given in the appendices for quick reference.

The notation and symbolism used in this text are a combination of those recommended by IUPAC and variations chosen by us for ease and clarity of use. We have chosen the tilde over a symbol, such as \tilde{V}_1 , to represent the molar volume of component 1, rather than the more cumbersome IUPAC notation of $V_{m,1}$ for the same quantity. Similarly, although the IUPAC notation elegantly represents a partial molar volume, for example, as V_1 , we chose the redundant but unambiguous notation of placing a bar over a symbol to indicate this quantity: \bar{V}_1 . IUPAC recommends the phrase ‘amount of substance’ for n which is commonly called the number of moles. We chose to describe n as the ‘mole number,’ for ease of writing, even though we (and our readers) know that n refers to a quantity or amount of substance. In any case, we have been consistent in our usage, and a list of our notation is given after this Preface.

In concluding this Preface, we wish to make some separate and some joint acknowledgments. First, SEW wishes to express his appreciation to those who were influential in stimulating his interest in thermodynamics, and to others who helped in the development of this book: first, to Professors George Scatchard, James A. Beattie, and Louis J. Gillespie, for developing his interest in thermodynamics and for introducing him to the work of J. Willard Gibbs; second, to his many colleagues, but, particularly Dr. Russell K. Edwards, Professor Harry E. Gunning, and Professor Ralph J.

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Preface

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Tykodi, for many long, arduous, and helpful discussions; and third, to the many students who took his course and taught him while they were being taught. RB wishes to express his appreciation to his teachers of thermodynamics: Professors Mark W. Zemansky and John H. Saylor, and to the senior author, Professor Scott E. Wood. We thank Henry E. Sostman for helpful comments and Dr. Thomas W. Listerman for carefully reading Chapter 14. We both express our indebtedness to Dr. Stanley Weissman, who read and critiqued most of the book, and to the secretaries who typed it: Alice Capp, Claudia Hillard, and Mary Alspaugh. Some of the book was written while the senior author was a Senior Fulbright Scholar at the Department of Chemistry at University College, Dublin. Finally, we wish to thank our wives for the patience and encouragement that they showed during the writing of this book.

Scott E. Wood
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September 1989

Notation

- a* area
- a* activity
- A* area
- A* Helmholtz energy
- B** magnetic induction
- B* 1 mole of an unspecified substance
- c* molarity
- c* specific heat capacity
- C* number of components
- C* heat capacity
- C_p* heat capacity at constant pressure
- C_v* heat capacity at constant volume
- d* inexact differential
- D** electric displacement
- E* energy
- E** electric field strength
- ℰ* electromotive force (emf)
- f* fugacity
- F** force, generalized force
- F_e** external force
- ℱ* Faraday constant
- g* gaseous state
- g** acceleration due to gravity
- G* Gibbs energy
- h* height
- H* enthalpy
- H** magnetic field strength
- i* current
- I* integration constant

Notation

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- k Henry's law constant
- k distribution coefficient
- K equilibrium constant
- l length
- ℓ liquid state
- L liter
- L length
- m mass
- m number of units of mass
- m molality
- \mathbf{m} magnetic moment per unit volume
- M molecular mass
- \mathbf{M} total magnetic moment
- n amount of substance/mole numbers
- niA magnetic moment
- \mathbf{p} polarization of the medium per unit volume
- P pressure
- P number of phases
- P_k partial pressure of component k
- \mathbf{P} total polarization ($= V_c \mathbf{p}$)
- Q heat
- Q electrical charge
- r distance
- r radius
- R gas constant
- R number of independent chemical reactions
- s solid state
- s displacement
- S entropy
- S number of species
- t time
- t temperature
- t transference number
- T Kelvin or thermodynamic temperature
- T_i inversion temperature (Joule–Thomson)
- \mathbf{v} velocity
- v specific volume
- V volume
- V number of variances or number of degrees of freedom
- W work
- x mole fraction
- X_i generalized coordinate
- \tilde{X}_i molar property

\bar{X}_i partial molar property
 y mole fraction, gas phase
 z mole fraction, solid phase
 z electrical charge on ion
 Z compressibility factor

Greek

α deviations of the real gas or gas mixture from ideal behavior
 γ activity coefficient
 γ surface tension or interfacial tension
 γ fugacity coefficient
 Γ surface concentration
 ε permittivity
 ε_0 permittivity of empty space
 $\varepsilon/\varepsilon_0$ dielectric constant
 η efficiency of a heat engine
 θ arbitrary temperature
 μ chemical potential
 μ permeability
 μ_0 permeability of vacuum
 μ/μ_0 relative permeability
 μ_{JT} Joule–Thomson coefficient
 ν stoichiometric coefficient
 π osmotic pressure
 ρ density
 τ arbitrary temperature
 ϕ electrical potential
 ϕ function of T, P, μ_1, n_2, \dots
 ϕ osmotic coefficient
 ϕX apparent molar quantity
 Φ gravitational potential, centrifugal potential
 Φ electrostatic potential
 χ_M magnetic susceptibility
 χ_e electric susceptibility
 ψ electrical potential
 ω angular velocity
 ω acentric factor

Superscripts

E excess change on mixing
 M mixture or mixing
 P planar
 σ defined surface

Notation

xix

- \ominus standard state
- \cdot pure component
- \sim molar property
- $-$ partial molar property
- $*$ reference state
- ∞ infinite dilution

Subscripts

- 1, 2, 3, ... component 1, 2, 3, ...
- b boiling point
- c condenser
- c critical property
- D dimer
- E excess
- f formation
- mp melting point
- mix for the mixing process
- M monomer
- r reduced property, as in $T_r = T/T_c$
- s mixed solvent (pseudobinary system)
- S space
- sat saturated
- tr transition