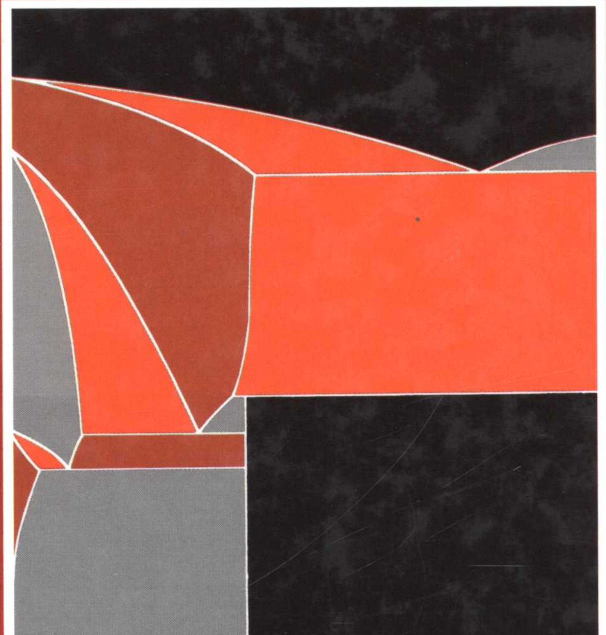
INTRODUCTION TO THE THERMODYNAMICS OF MATERIALS

Fourth Edition



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Introduction to the Thermodynamics of Materials

Fourth Edition

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Taylor & Francis
Taylor & Francis Group

New York • London

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Published in 2003 by
Taylor & Francis
29 West 35th Street
New York, NY 10001

Published in Great Britain by
Taylor & Francis
11 New Fetter Lane
London EC4P 4EE

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10 9 8 7 6 5 4 3 2 1

Library of Congress Cataloging-in-Publication Data

Gaskell, David R., 1940-
Introducion to the thermodynamics of materials/David R. Gaskell.— 4th ed.
p. cm
Includes index.
Rev. ed. of: Introduction to metallurgical thermodynamics. 2nd ed. c1981.
ISBN 1-56032-992-0 (alk. paper)
1. Metallurgy. 2. Thermodynamics. 3. Materials — Thermal properties. I. Gaskell, David R., 1940- Introduction to metallurgical thermodynamics. II. Title.

TN673 .G33 2003
620.1'1296—dc21

2002040935

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For Sheena
Sarah and Andy,
Claire and Kurt,
Jill and Andrew

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Preface

The fourth edition of this text is different from the third edition in three ways. First, there is an acute emphasis on typographical and mathematical accuracy. Second, a new chapter, Chapter 14, has been added, which presents and discusses equilibria in binary systems in temperature-pressure-composition space. An understanding of the influence of pressure on phase equilibria is particularly necessary given the increase in the number of methods of processing materials systems at low pressures or in a vacuum.

The major improvement, however, is the inclusion of a CD-Rom to supplement the text. This work, which is titled "Examples of the Use of Spreadsheet Software for Making Thermodynamic Calculations" is a document produced by Dr. Arthur Morris, Professor Emeritus of the Department of Metallurgical Engineering at the University of Missouri—Rolla. The document contains descriptions of 22 practical examples of the use of thermodynamic data and typical spreadsheet tools. Most of the examples use the spreadsheet Microsoft® Excel* and others make use of a software package produced by Professor Morris called THERBAL. As Professor Morris states, "The availability of spreadsheet software means that more complex thermodynamics problems can be handled, and simple problems can be treated in depth."

I express my gratitude to Professor Morris for providing this supplement.

David R. Gaskell
Purdue University

A Word on the CD-Rom

The CD contains data and descriptive material for making detailed thermodynamic calculations involving materials processing. The contents of the CD are described in the text file, *CD Introduction.doc,* which you should print and read before trying to use the material on the CD.

There are two Excel workbooks on the disk: ThermoTables.xls and ThermoXmples.xls. They contain thermodynamic data and examples of their use by Excel to solve problems and examples of a more extended nature than those in the text. The CD also contains a document describing these examples, XmpleExplanation.doc, which is in Microsoft® Word* format. You will need Word to view and print this document.

Dr. Arthur E. Morris
Thermart Software
http://home.att.net/~thermart

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Fourth Edition

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Chapter 1

INTRODUCTION AND DEFINITION OF TERMS

1.1 INTRODUCTION

Thermodynamics is concerned with the behavior of matter, where matter is anything that occupies space, and the matter which is the subject of a thermodynamic analysis is called a *system*. In materials science and engineering the systems to which thermodynamic principles are applied are usually chemical reaction systems. The central aim of applied thermodynamics is the determination of the effect of environment on the state of rest (equilibrium state), of a given system, where environment is generally determined as the pressure exerted on the system and the temperature of the system. The aim of applied thermodynamics is thus the establishment of the relationships which exist between the equilibrium state of existence of a given system and the influences which are brought to bear on the system.

1.2 THE CONCEPT OF STATE

The most important concept in thermodynamics is that of *state*. If it were possible to know the masses, velocities, positions, and all modes of motion of all of the constituent particles in a system, this mass of knowledge would serve to describe the *microscopic state* of the system, which, in turn, would determine all of the properties of the system. In the absence of such detailed knowledge as is required to determine the microscopic state of the system, thermodynamics begins with a consideration of the properties of the system which, when determined, define the *macroscopic state* of the system; i.e., when all of the properties are fixed then the macroscopic state of the system is fixed. It might seem that, in order to uniquely fix the macroscopic, or thermodynamic, state of a system, an enormous amount of information might be required; i.e., all of the properties of the system might have to be known. In fact, it is found that when the values of a small number of properties are fixed then the values of all of the rest are fixed. Indeed, when a simple system such as a given quantity of a substance of fixed composition is being considered, the fixing of the values of two of the properties fixes the values of all of the rest. Thus only two properties are independent, which, consequently, are called the independent variables, and all of the other properties are dependent variables. The thermodynamic state of the simple system is thus uniquely fixed when the values of the two independent variables are fixed.

In the case of the simple system any two properties could be chosen as the independent variables, and the choice is a matter of convenience. Properties most amenable to control are the pressure P and the temperature T of the system. When P and T are fixed, the state of the simple system is fixed, and all of the other properties have unique values corresponding to this state. Consider the volume V of a fixed quantity of a pure gas as a property, the value of which is dependent on the values of P and T. The relationship between the dependent variable V and the independent variables P and T can be expressed as

$$V = V(P,T) \tag{1.1}$$

The mathematical relationship of V to P and T for a system is called an *equation of state* for that system, and in a three-dimensional diagram, the coordinates of which are volume, temperature, and pressure, the points in P-V-T space which represent the equilibrium states of existence of the system lie on a surface. This is shown in Fig. 1.1 for a fixed quantity of a simple gas. Fixing the values of any two of the three variables fixes the value of the third variable. Consider a process which moves the gas from state 1 to state 2. This process causes the volume of the gas to change by

$$\Delta V = V_2 - V_1$$

This process could proceed along an infinite number of paths on the P-V-T surface, two of which, $1 \rightarrow a \rightarrow 2$ and $1 \rightarrow b \rightarrow 2$, are shown in Figure 1.1. Consider the path $1 \rightarrow a \rightarrow 2$. The change in volume is

$$\begin{aligned}\Delta V &= V_2 - V_1 \\ &= (V_a - V_1) + (V_2 - V_a)\end{aligned}$$

where $1 \rightarrow a$ occurs at the constant pressure P_1 and $a \rightarrow 2$ occurs at the constant temperature T_2:

$$(V_a - V_1) = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT$$

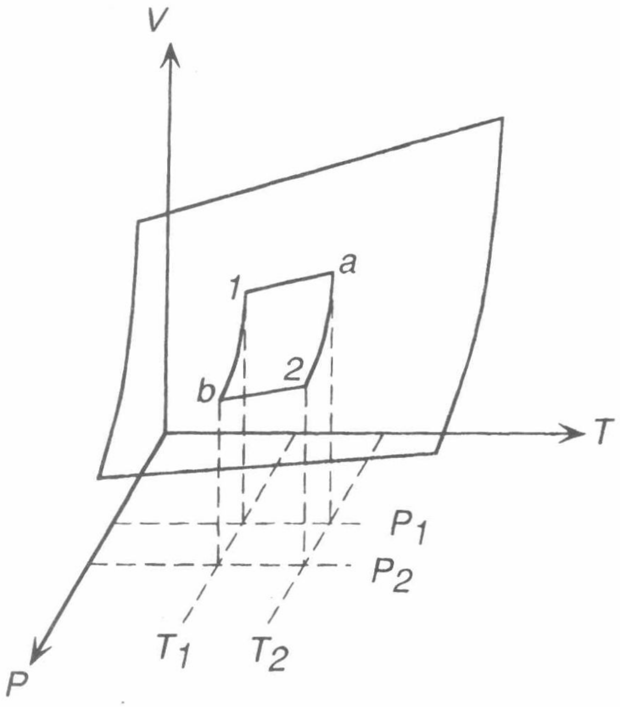

Figure 1.1 The equilibrium states of existence of a fixed quantity of gas in *P-V-T* space.

and

$$(V_2 - V_a) = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$$

Thus

$$\Delta V = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP \tag{1.2}$$

Similarly for the path $1 \rightarrow b \rightarrow 2$,

$$(V_b - V_1) = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_1} dP$$

and

$$(V_2 - V_b) = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_2} dP$$

and, hence, again

$$\Delta = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_2} dT \tag{1.3}$$

Eqs. (1.2) and (1.3) are identical and are the physical representations of what is obtained when the complete differential of Eq. (1.1), i.e.,

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \tag{1.4}$$

is integrated between the limits P_2, T_2 and P_1, T_1.

The change in volume caused by moving the state of the gas from state 1 to state 2 depends only on the volume at state 1 and the volume at state 2 and is independent of the path taken by the gas between the states 1 and 2. This is because the volume of the gas is a *state function* and Eq. (1.4) is an exact differential of the volume V.*

1.3 SIMPLE EQUILIBRIUM

In Figure 1.1 the state of existence of the system (or simply the state of the system) lies on the surface in P-V-T space; i.e., for any values of temperature and pressure the system is at equilibrium only when it has that unique volume which corresponds to the particular values of temperature and pressure. A particularly simple system is illustrated in Figure 1.2. This is a fixed quantity of gas contained in a cylinder by a movable piston. The system is at rest, i.e., is at equilibrium, when

1. The pressure exerted by the gas on the piston equals the pressure exerted by the piston on the gas, and

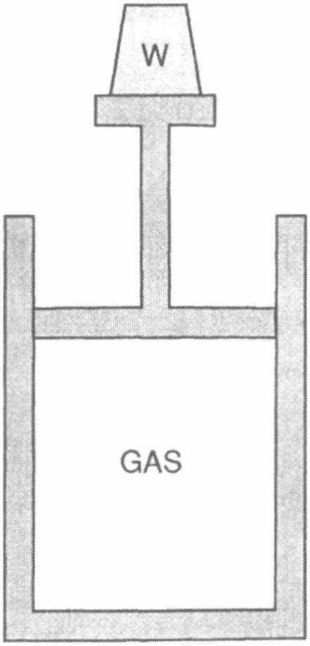

Figure 1.2 A quantity of gas contained in a cylinder by a piston.

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*The properties of exact differential equations are discussed in Appendix B.

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