

# Introduction to Metallurgical Thermodynamics

second edition

David R. Gaskell



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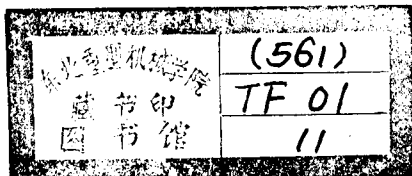
# INTRODUCTION TO METALLURGICAL THERMODYNAMICS

**SECOND EDITION**

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## **INTRODUCTION TO METALLURGICAL THERMODYNAMICS, Second Edition**

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*For Sheena*

*Sarah*

*Claire*

*and Andrew*

CAPIES /

# PREFACE

The major difference between the first and second editions is the adoption of S.I. units in the latter. In addition, Chapter 14 has been revised to include a discussion of the thermodynamics of aqueous solutions and Pourbaix diagrams, the numbers of worked examples and end-of-chapter problems have been increased, and a solutions manual has been prepared.

I wish to acknowledge my gratitude to Professor S. K. Tarby of Lehigh University who provided me with many valuable comments and suggestions, all of which have been incorporated in the later printings of the first edition and in this new edition.

**David R. Gaskell**

# PREFACE TO THE FIRST EDITION

Thermodynamics tends to be a confusing subject to the beginning student. This confusion is caused by the initial conceptual difficulties experienced by the student rather than as a result of the subject being, in any way, inherently "difficult." Indeed the beauty of the subject stems from its simplicity, whereby, from the statement of a few initial laws, there evolves systematically a method of rigorously describing the behavior of matter in a manner which is devoid of temporal theories. The ease with which the average undergraduate begins to understand the thermodynamic method and its applications depends very much on the nature of his introduction to the subject. Although there exist many excellent standard treatises on thermodynamics, these standard works, being written for thermodynamicists by thermodynamicists, are, almost by definition, not suitable as introductory texts for beginning students. There thus exists a need for introductory texts, the prime purpose of which is to render the student more capable of fully utilizing the standard treatises.

At one extreme thermodynamics can be regarded as being a subject which is of sufficient beauty to be worth studying solely for its own sake, and at the other extreme it can be regarded as being simply a tool to be applied for the purposes of solving real problems. Although the ideal introduction to the subject should take some midway path between these extremes, the majority of undergraduates are introduced to the subject near one or the other of its extremes. Traditionally these are the "chemistry" students and the "engineering" students. On the one hand, students who are introduced to thermodynamics by chemists can find themselves rapidly immersed in a pseudoqualitative world inhabited by a countless number of strange equations, among which there appear to be few connections. The student rates the difficulty of the subject as being proportional to the number of equations which he is required to memorize, and the lack of

any apparent *raison d'être* or even application of the subject, as presented, leaves the student thinking that thermodynamics is a subject to be learned solely for reasons of acquiring a feeling of intellectual superiority. On the other hand, the students who are introduced to thermodynamics by the traditional engineers learn the subject purely as a mathematical tool. They learn the minimum possible number of equations which are then available for the "plugging in" of numbers. The subtleties of the subject are all but ignored, as a result of which the arrival of the student at the wrong numerical answer is caused by his plugging the wrong numbers into the wrong places in the wrong equation. A student simultaneously learning thermodynamics from the chemists and the engineers might have difficulty in realizing that the two subjects are, in fact, the same.

As metallurgy can be partially defined as being the meeting point of the physical sciences and engineering, in that a balance is struck between physical principles and practical applications, it is appropriate that a similar balance be obtained in the presentation of metallurgical thermodynamics. In this book an attempt has been made to simultaneously demonstrate the underlying principles and their applicability. Wherever possible an attempt has been made to accompany the normal thermodynamic derivation of an equation with a derivation which illustrates the thermodynamics of the situation, and the order in which the material is presented is such as to attempt to maintain, throughout, a continuity of the development and use of the principles. Also an attempt has been made to illustrate the principles, as they are developed, with quantitative examples of their applicability. It has been stated that thermodynamics is a subject which must be applied with intelligence. In this context the "intelligence" is acquired as a result of an understanding of the principles.

As the treatment of the subject in this book is introductory in nature, its scope is necessarily limited; but, once having read the book, it is hoped that the student of metallurgy will be in a better position than he otherwise would be both for using the thermodynamic method and for going more deeply into the subject with the aid of the standard reference texts.

The author gratefully acknowledges the aid of Dr. Dwarika P. Agarwal, who verified the answers to the problems.

**David R. Gaskell**

# SYSTEM OF UNITS, SYMBOLS, NOTATION, AND SELECTED CONSTANTS

## S.I. UNITS

S.I. units (Système International d'Unités) are arranged in three categories: (1) base units, which are dimensionally independent of one another, (2) derived units, which are obtained by suitable combination of the base units, and (3) supplementary units.\* The six base units and the specially named derived units commonly used in chemical thermodynamics are listed in Tables 1 and 2, respectively.

Fractions and multiples of the basic units are as designated in Table 3.

\*"The International System of Units (SI)," NBS Special Publication 330, U.S. Department of Commerce, 1974 edition.

**Table 1.** The S.I. Base Units

Quantity	Name	Symbol
Length	Meter	m
Mass	Kilogram	kg
Time	Second	s
Electric current	Ampere	A
Thermodynamic temperature	Kelvin	K
Amount of substance	Mole	mol



Table 2. S.I. Derived Units with Special Names

Quantity	Name	Symbol	Expression in terms of other units	Expression in terms of S.I. base units
Force	Newton	N		$\text{m}\cdot\text{kg}\cdot\text{s}^{-2}$
Energy	Joule	J	$\text{N}\cdot\text{m}$	$\text{m}^2\cdot\text{kg}\cdot\text{s}^{-2}$
Pressure	Pascal	Pa	$\text{N}/\text{m}^2$	$\text{m}^{-1}\cdot\text{kg}\cdot\text{s}^{-2}$
Power	Watt	W	$\text{J}/\text{s}$	$\text{m}^2\cdot\text{kg}\cdot\text{s}^{-3}$
Electric charge	Coulomb	C	$\text{A}\cdot\text{s}$	$\text{s}\cdot\text{A}$
Electromotive force	Volt	V	$\text{W}/\text{A}$	$\text{m}^2\cdot\text{kg}\cdot\text{s}^{-3}\cdot\text{A}^{-1}$

An exponent attached to a symbol containing a prefix indicates that the multiple or submultiple of the unit is raised to the power expressed by the exponent. For example,

$$1\text{ cm}^3 = (10^{-2}\text{ m})^3 = 10^{-6}\text{ m}^3$$
$$1\text{ cm}^{-1} = (10^{-2}\text{ m})^{-1} = 10^2\text{ m}^{-1}$$

The S.I. system specifically eliminates the use of such units as

$$\text{erg} \text{ (1 erg = } 10^{-7}\text{ J)}$$

and 
$$\text{dyne} \text{ (1 dyne = } 10^{-5}\text{ N)}$$

and deprecates the use of

$$\text{torr} \left( 1\text{ torr} = 1\text{ mmHg} = \frac{101,325}{760}\text{ Pa} \right)$$

and 
$$\text{calorie} \text{ (1 thermochemical calorie = } 4.184\text{ J)}$$

Table 3. S.I. Prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
$10^1$	Deka	da	$10^{-1}$	Deci	d
$10^2$	Hecto	h	$10^{-2}$	Centi	c
$10^3$	Kilo	k	$10^{-3}$	Milli	m
$10^6$	Mega	M	$10^{-6}$	Micro	$\mu$
$10^9$	Giga	G	$10^{-9}$	Nano	n
$10^{12}$	Tera	T	$10^{-12}$	Pico	p
			$10^{-15}$	Femto	f
			$10^{-18}$	Atto	a

However, the system tolerates, “for the time being,” use of the

standard atmosphere (1 atm = 101,325 Pa)

and bar (1 bar = 10<sup>5</sup> Pa)

In view of the familiarity, on the part of the metallurgist, with the standard atmosphere as the unit of pressure and 1 atm pressure as the standard state for an ideal gas, this unit has been adopted in the present text.

## LIST OF SYMBOLS

$a$	van der Waals constant
$a_i$	the activity of species $i$ with reference to a specified standard state
$A$	Helmholtz free energy (or work function)
$\mathfrak{A}$	Avogadro's number
$b$	van der Waals constant
$C$	the number of components
$C$	heat capacity
$c_p$	constant pressure molar heat capacity
$c_v$	constant volume molar heat capacity
$\mathcal{E}$	electromotive force
$\mathcal{E}_{M/M^{z+}}^0$	standard oxidation potential of species M
$\mathcal{E}_{A/A^{z-}}^0$	standard reduction potential of species A
$E$	electromotive force with sign according to the European convention
$e_j^i$	the interaction parameter of $i$ on $j$
$F$	the number of degrees of freedom of an equilibrium
$\mathcal{F}$	Faraday's constant
$f$	fugacity
$f_i$	the Henrian activity coefficient of the species $i$
$f_{i(\text{wt}\%)}^i$	the activity coefficient of the species $i$ with respect to the 1 weight percent standard state
$f_j^i$	the interaction coefficient of $i$ on $j$
$G$	Gibbs free energy
$H$	enthalpy
$h_i$	the Henrian activity of species $i$

**xx            SYSTEM OF UNITS, SYMBOLS, NOTATION, AND SELECTED CONSTANTS**

$h_{i(\text{wt}\%)}$     the activity of the species  $i$  with respect to the 1 weight percent standard state

$K$             the equilibrium constant

$k$             Boltzmann's constant

$m$             mass

$n$             the number of moles

$n_i$            the number of moles of the species  $i$

$P$             pressure

$P$             partition function

$P$             the number of phases occurring in a system

$p_i$            the partial pressure of the species  $i$

$p_i^0$           the saturated vapor pressure of the species  $i$

$q$             heat

$R$             the Gas Constant

$S$             entropy

$T$             temperature

$T_m$           melting temperature

$T_b$           boiling temperature

$U$             internal energy

$V$             volume

$w$             work

$X_i$           the mole fraction of the species  $i$

$Z$             the compressibility factor

$\alpha$           coefficient of thermal expansion

$\alpha$            the regular solution constant

$\beta$            coefficient of isothermal compressibility

$\gamma$	ratio of $c_p$ to $c_v$
$\gamma_i$	the activity coefficient of the species $i$
$\gamma_i^0$	the Henry's law constant
$\epsilon_i$	the energy of the $i$ th energy level
$\epsilon_j^i$	the interaction parameter of $i$ on $j$
$\mu_i$	the chemical potential of the species $i$
(s)	solid
(l)	liquid
(g)	gas

### NOTATION FOR EXTENSIVE THERMODYNAMIC PROPERTIES (exemplified by $G$ , the Gibbs free energy)

$G'$	the Gibbs free energy of the system containing $n$ moles
$G$	the Gibbs free energy per mole of the system
$\Delta G$	the change in $G$ due to a specified change in the state of the system
$\Delta G^M$	the integral molar Gibbs free energy change due to mixing of the components to form a solution
$\Delta G^{M,id}$	the integral molar Gibbs free energy change due to mixing of the components to form an ideal solution
$G_i$	the molar Gibbs free energy of the species $i$
$G_i^0$	the molar Gibbs free energy of the species $i$ in its designated standard state
$\bar{G}_i$	the partial molar Gibbs free energy of $i$ in some specified solution
$\Delta \bar{G}_i^M$	$= \bar{G}_i - G_i^0$ , the partial molar Gibbs free energy of mixing of $i$
$G^{xs}$	$= \Delta G^M - \Delta G^{M,id}$ , the integral excess molar Gibbs free energy of a solution
$\bar{G}_i^{xs}$	the partial molar excess Gibbs free energy of mixing of $i$
$\Delta G_m$	the molar Gibbs free energy of melting
$\Delta G_b$	the molar Gibbs free energy of boiling

### VALUES OF SELECTED PHYSICAL CONSTANTS

Absolute temperature of the ice point ( $0^\circ\text{C}$ ) = 273.15 K

Absolute temperature of the triple point of  
 $\text{H}_2\text{O}$  (by definition) = 273.16000 K

Thermochemical calorie  
(by definition)

$$1 \text{ calorie} = 4.184 \text{ joules}$$

Faraday's constant

$$\begin{aligned} \mathcal{F} &= 96,487 \text{ coulomb/mole} \\ &= 23,060 \text{ calories/volt}\cdot\text{mole} \end{aligned}$$

Avogadro's number

$$N_A = 6.0232 \times 10^{23} / \text{gram}\cdot\text{mole}$$

Boltzmann's constant

$$k = 1.38054 \times 10^{-23} \text{ joules/degree}$$

Atmosphere

$$\begin{aligned} 1 \text{ atm} &= 1.01325 \times 10^6 \text{ dyne/cm}^2 \\ &= 1.01325 \text{ bar} \\ &= 101.325 \text{ kPa} \\ &= 760 \text{ mmHg} \end{aligned}$$

Gas Constant

$$\begin{aligned} R &= 8.3144 \text{ joules/degree}\cdot\text{mole} \\ &= 1.987 \text{ calories/degree}\cdot\text{mole} \\ &= 82.06 \text{ cm}^3\cdot\text{atm/degree}\cdot\text{mole} \end{aligned}$$

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