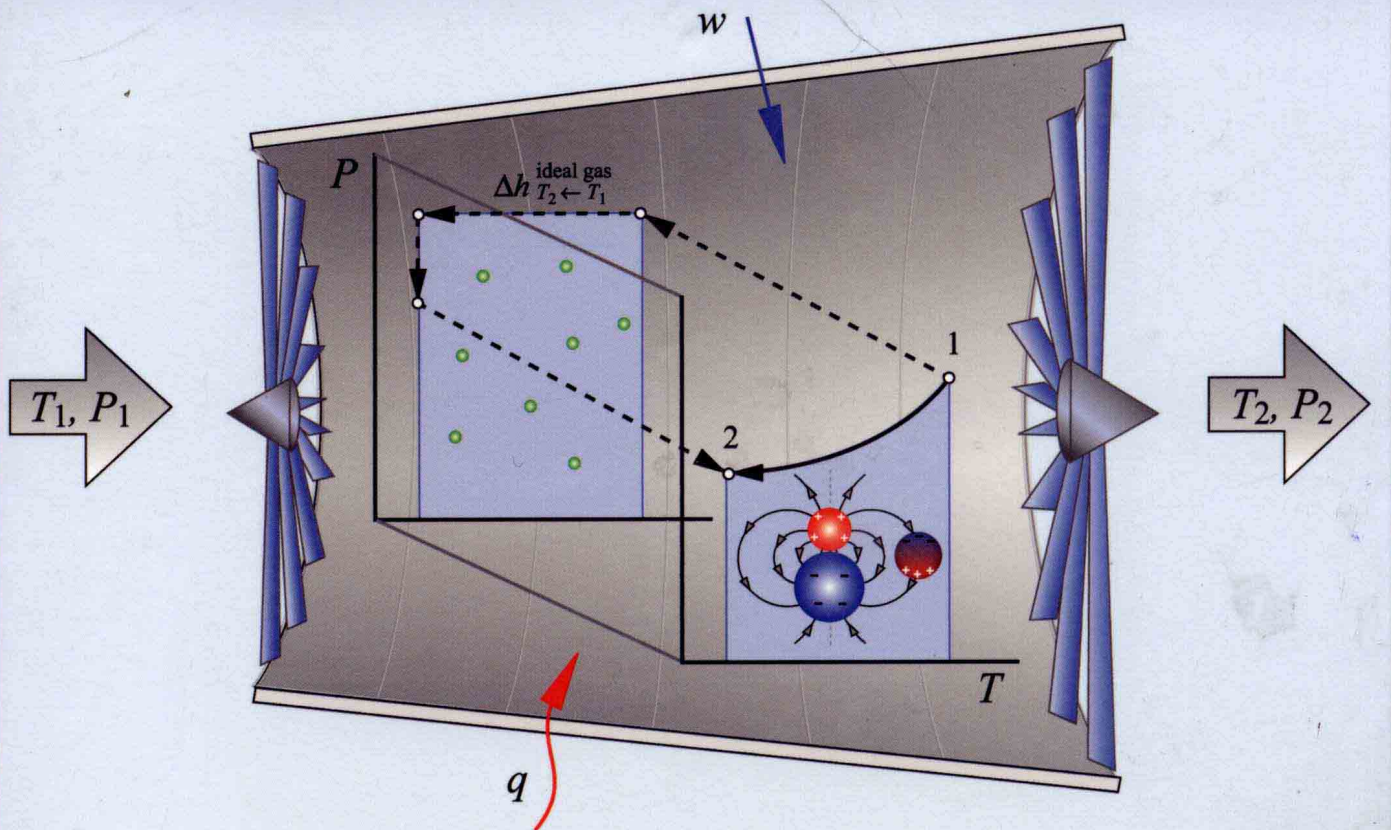


Engineering and Chemical Thermodynamics

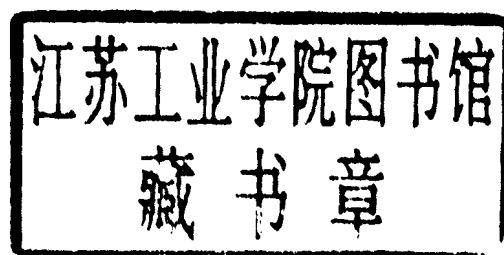


Milo D. Koretsky

Engineering and Chemical Thermodynamics

Milo D. Koretsky

*Department of Chemical Engineering
Oregon State University*



WILEY

JOHN WILEY & SONS, INC.

Executive Editor *Bill Zobrist*
Project Editor *Jenny Welter*
Marketing Manager *Ilsa Wolfe*
Senior Production Editor *Norine M. Pigliucci*
Design Director *Maddy Lesure*
Editorial Assistant *Mary Moran*
Production Management Services *Hermitage Publishing Services*

The cover depicts a turbine, a common process that is analyzed using thermodynamics. A cutaway of the physical apparatus reveals the conceptual tools that will be developed in this text. This includes a hypothetical thermodynamic pathway marked by dashed arrows. You will learn how to construct such pathways to solve a variety of problems. The figure also contains a “molecular dipole,” which is drawn in the *PT* plane associated with the real fluid. This conceptually illustrates the use of molecular concepts to reinforce thermodynamic principles as they are developed, another important thematic link to the text.

The book was set in New Caledonia by Hermitage Publishing Services and printed and bound by Hamilton Printing. The cover was printed by Phoenix Color Corp.

This book is printed on acid free paper. ∞

Copyright © 2004 John Wiley & Sons, Inc. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc. 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201)748-6011, fax (201)748-6008, E-Mail: PERMREQ@WILEY.COM. To order books or for customer service please call 1-800-CALL WILEY (225-5945).

Library of Congress Cataloging in Publication Data:

Koretsky, Milo D.

Engineering and chemical thermodynamics / Milo D. Koretsky.

p. cm.

Includes bibliographical references.

ISBN 0-471-38586-7 (cloth: acid-free paper)

1. Thermodynamics. 1. Title

TP155.2.T45K67 2004

660'.2969-dc21

2003053848

ISBN 0-471-38586-7

WIE ISBN: 0-471-45237-8

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

FUNDAMENTAL PHYSICAL CONSTANTS

Speed of light in vacuum	c	$2.997\,924\,58 \times 10^8$	[m/s]
Avagadro's number	N_A	$6.022\,141\,99 \times 10^{23}$	[molecule/mol]
Gas constant	R	8.314 472	[J/(mol K)]
Boltzmann's constant (R/N_A)	k	$1.380\,650\,3 \times 10^{-23}$	[J/(molecule K)]
Faraday's constant	F	$9.648\,534\,15 \times 10^4$	[C/(mole)]
Elementary charge	Q	$1.602\,176\,46 \times 10^{-19}$	[C]
		$4.803\,204\,19 \times 10^{-10}$	[esu]
Mass of a proton	m	$1.672\,621\,58 \times 10^{-27}$	[kg]
Atomic mass unit	AMU	$1.660\,538\,73 \times 10^{-27}$	[kg]
Atmospheric pressure (sea level)	P	$1.013\,25 \times 10^5$	[Pa]
Gravitational acceleration (sea level)	g	9.806 55	[m ² /s]
Pi	π	3.141 592 65	

CONVERSION FACTORS

$$1 \text{ [m]} = 10^2 \text{ [cm]} = 10^{10} \text{ [\AA]} = 39.370 \text{ [in]} = 3.2808 \text{ [ft]}$$

$$1 \text{ [kg]} = 10^3 \text{ [g]} = 2.2046 \text{ [lb}_m\text{]} = 0.068522 \text{ [slug]}$$

$$[\text{K}] = [^\circ\text{C}] + 273.15 = (5/9) [^\circ\text{R}]; [^\circ\text{R}] = [^\circ\text{F}] + 459.67$$

$$1 \text{ [m}^3\text{]} = 10^{-3} \text{ [L]} = 10^{-6} \text{ [cm}^3\text{]} = 35.315 \text{ [ft}^3\text{]} = 264.17 \text{ [gal] (U.S.)}$$

$$1 \text{ [N]} = 10^5 \text{ [dyne]} = 0.22481 \text{ [lb}_f\text{]}$$

$$1 \text{ [atm]} = 1.01325 \text{ [bar]} = 1.01325 \times 10^5 \text{ [Pa]} = 14.696 \text{ [psi]} = 760 \text{ [torr]}$$

$$1 \text{ [J]} = 10^7 \text{ [erg]} = 0.23885 \text{ [cal]} = 9.4781 \times 10^{-4} \text{ [BTU]} = 6.242 \times 10^{18} \text{ [eV]}$$

For electric and magnetic properties see Appendix D: Table D.2.

COMMON VALUES FOR THE GAS CONSTANT, R

8.314	[J/(mol K)]
0.08314	[(L bar)/(mol K)]
1.987	[cal/(mol K)]
1.987	[BTU/(lbmol °R)]
0.08206	[(L atm)/(mol K)]

SPECIAL NOTATION

Properties

Uppercase	Extensive	$K: V, G, U, H, S, \dots$
Lowercase	Intensive (molar)	$k = \frac{K}{n} = v, g, u, h, s, \dots$
Circumflex, lowercase	Intensive (specific)	$\hat{k} = \frac{K}{m} = \hat{v}, \hat{g}, \hat{u}, \hat{h}, \hat{s}, \dots$

Mixtures

Subscript i	Pure species property	$K_i: V_i, G_i, U_i, H_i, S_i, \dots$
		$k_i: v_i, g_i, u_i, h_i, s_i, \dots$
Bar, subscript i	Partial molar property	$\bar{K}_i: \bar{V}_i, \bar{G}_i, \bar{U}_i, \bar{H}_i, \bar{S}_i, \dots$
As is	Total solution property	$K: V, G, U, H, S, \dots$
		$k: v, g, u, h, s, \dots$
Delta, subscript mix	Property change of mixing:	$\Delta K_{mix}: \Delta V_{mix}, \Delta H_{mix}, \Delta S_{mix}, \dots$
		$\Delta k_{mix}: \Delta v_{mix}, \Delta h_{mix}, \Delta s_{mix}, \dots$

Other

Dot	Rate of change	$\dot{Q}, \dot{W}, \dot{n}, \dot{V}, \dots$
Overbar	Average	$\bar{\bar{V}}^2, \bar{\bar{c}}_P, \dots$

A complete set of notation used in this text can be found on page (ix)

Engineering and Chemical Thermodynamics

For Nicole and Moses



Preface

You see, I have made contributions to biochemistry. There were no courses in molecular biology. I had no courses in biology at all, but I am one of the founders of molecular biology. I had no courses in nutrition or vitaminology. Why? Why am I able to do these things? You see, I got such a good basic education in the fields where it is difficult for most people to learn by themselves.

Linus Pauling
On his ChE education

► AUDIENCE

Engineering and Chemical Thermodynamics is intended for use in the undergraduate thermodynamics course(s) taught in the sophomore or junior year in most Chemical Engineering (ChE) Departments. For the majority of ChE undergraduate students, chemical engineering thermodynamics, concentrating on the subjects of phase equilibria and chemical reaction equilibria, is one of the most abstract and difficult core courses in the curriculum. In fact, it has been noted by more than one thermodynamics guru (e.g., Denbigh, Sommerfeld) that this subject cannot be mastered in a single encounter. Understanding comes at greater and greater depths with every skirmish with this subject. Why another textbook in this area? This textbook is targeted specifically at the sophomore or junior undergraduate who must, for the first time, grapple with the treatment of equilibrium thermodynamics in sufficient detail to solve the wide variety of problems that chemical engineers must tackle. It is a *conceptually* based text, meant to provide students with a solid foundation in this subject in a single iteration. Its intent is to be both *accessible* and *rigorous*. Its accessibility allows students to retain as much as possible through their first pass while its rigor provides them the foundation to understand more advanced treatises and forms the basis of commercial computer simulations such as ASPEN®, HYSIS®, and CHEMCAD®.

► GOALS AND METHODOLOGY

The text was developed from course notes that have been used in the undergraduate chemical engineering classes at Oregon State University since 1994. It uses a logically consistent development whereby each new concept is introduced in the context of a framework laid down previously. This textbook has been specifically designed to accommodate students with different learning styles. Its conceptual development, worked-out examples, and numerous end-of-chapter problems are intended to promote *deep learning* and provide students the ability to apply thermodynamics to real-world engineering problems. Two major threads weave throughout the text: (1) a common methodology for approaching topics, be it enthalpy or fugacity, and (2) the reinforcement of classical thermodynamics with molecular principles. Whenever possible, intuitive and qualitative arguments complement mathematical derivations.

The basic premise on which the text is organized is that *student learning is enhanced by connecting new information to prior knowledge and experiences*. The approach is to introduce new concepts in the context of material that students *already know*. For example, the second law of thermodynamics is formulated analogously to the first law, as a generality to many observations of nature (as opposed to the more common approach of using specific statements about obtaining work from heat through thermodynamic cycles). Thus, the experience students have had in learning about the thermodynamic property energy, which they have already encountered in several classes, is applied to introduce a new thermodynamic property, entropy. Moreover, the underpinnings of the second law—reversibility, irreversibility, and the Carnot cycle—are introduced with the first law, a context with which students have more experience; thus they are not new when the second law is introduced.

► LEARNING STYLES

There has been recent attention in engineering education to crafting instruction that targets the many ways in which students learn. For example, in their landmark paper “Learnings and Teaching Styles in Engineering Education,”¹ Richard Felder and Linda Silverman define specific dimensions of learning styles and corresponding teaching styles. In refining these ideas, the authors have focused on four specific dimensions of learning: sequential vs. global learners; active vs. reflective learners; visual vs. verbal learners; and sensing vs. intuitive learners. This textbook has been specifically designed to accommodate students with different learning styles by providing avenues for students with each style and, thereby, reducing the mismatches between its presentation of content and a student’s learning style. The objective is to create an effective text that enables students to access new concepts. For example, each chapter contains learning objectives at the beginning and a summary at the end. These sections do not parrot the order of coverage in the text, but rather are presented in a *hierarchical* order from the most significant concepts down. Such a presentation creates an effective environment for global learners (who should read the summary before embarking on the details in a chapter). On the other hand, to aid the sequential learner, the chapter is developed in a logical manner, with concepts constructed step by step based on previous material. Identified key concepts are presented schematically to aid visual learners. Questions about key points that have been discussed previously are inserted periodically in the text to aid both active and reflective learners. Examples are balanced between those that emphasize concrete, numerical problem solving for sensing learners and those that extend conceptual understanding for intuitive learners.

In the cognitive dimension, we can form a taxonomy of the hierarchy of knowledge that a student may be asked to master. For example, a modified Bloom’s taxonomy includes: remember, understand, apply, analyze, evaluate, and create. The tasks are listed from lowest to highest level. To accomplish the lower-level tasks, surface learning is sufficient, but the ability to perform at the higher levels requires *deep learning*. In deep learning, students look for patterns and underlying principles, check evidence and relate it to conclusions, examine logic and argument cautiously and critically, and through this process become actively interested in course content. In contrast, students practicing surface learning tend to memorize facts, carry out procedures algorithmically, find it difficult to make sense of new ideas, and end up seeing little value in a thermodynamics course. While it is reinforced throughout the text, promotion of deep learning is most significantly influenced by what a student is expected to do. End-of-chapter problems have been constructed to cultivate a deep understanding of the material. Instead of merely finding the right equation to “plug and chug,” the student is asked to search for connections and patterns in the material, understand the physical meaning of the equations, and creatively apply the fundamental principles that have been covered to entirely new problems. The belief is that only through this deep learning is a student able to synthesize information from the university classroom and creatively apply it to new problems in the field.

► SOLUTION MANUAL

The Solutions Manual is available for instructors who have adopted this book for their course. Please visit the Instructor Companion site located at www.wiley.com/college/koretsky to register for a password.

► MOLECULAR CONCEPTS

While outside the realm of classical thermodynamics, the incorporation of molecular concepts is useful on many levels. In general, by the time undergraduate thermodynamics is taught, the chemical engineering student has had many chemistry courses, so why not take advantage of this experience! Thermodynamics is inherently abstract. Molecular concepts reinforce the text’s

¹Felder, Richard M., and Linda K. Silverman, *Engr. Education*, **78**, 674 (1988).

intuitive approach, providing more access to the typical undergraduate student than could a mathematical derivation alone. A molecular approach is also becoming important on a technological level, with the increased development of molecular-based simulations. Finally, molecular understanding allows the student to form a link between the understanding of equilibrium thermodynamics and other fundamental engineering sciences, such as transport processes.

► THERMOSOLVER SOFTWARE

The accompanying ThermoSolver software has been specifically designed to complement the text. This integrated, menu-driven program is easy to use and learning-based. ThermoSolver readily allows students to perform more complex calculations, giving them opportunity to explore a wide range of problem solving in thermodynamics. Equations used to perform the calculations can be viewed within the program and use nomenclature consistent with the text. Since the equations from the text are integrated into the software, students are better able to connect the concepts to the software output, reinforcing learning. The ThermoSolver software may be downloaded for free from the student companion site located at www.wiley.com/college/koretsky.

► ACKNOWLEDGMENTS

I would like to acknowledge and offer thanks to those individuals who have provided thoughtful input: Wayne Anderson, Connelly Barnes, Hugo Caran, Chih-hung (Alex) Chang, John Falconer, Dennis Hess, P. K. Lim, Erik Muehlenkamp, Jeff Reimer, Skip Rochefort, Wyatt Tenhaeff, Darrah Thomas, and David Wetzel. Last, but not least, I am tremendously grateful to the students with whom, over the years, I have shared the thermodynamics classroom.

► NOTATION

The study of thermodynamics inherently contains detailed notation. Below is a summary of the notation used in this text. The list includes: special notation, symbols, Greek symbols, subscripts, superscripts, operators and empirical parameters. Due to the large number of symbols as well as overlapping by convention, the same symbol sometimes represents different quantities. In these cases, you will need to deduce the proper designation based on the context in which a particular symbol is used.

Special Notation

Properties

Uppercase	Extensive	$K : V, G, U, H, S, \dots$
Lowercase	Intensive (molar)	$k = \frac{K}{n} = v, g, u, h, s, \dots$
Circumflex, lowercase	Intensive (specific)	$\hat{k} = \frac{K}{m} = \hat{v}, \hat{g}, \hat{u}, \hat{h}, \hat{s}, \dots$

Mixtures

Subscript i	Pure species property	$K_i : V_i, G_i, U_i, H_i, S_i, \dots$ $k_i : v_i, g_i, u_i, h_i, s_i, \dots$
Bar, subscript i	Partial molar property	$\bar{K}_i : \bar{V}_i, \bar{G}_i, \bar{U}_i, \bar{H}_i, \bar{S}_i, \dots$
As is	Total solution property	$K : V, G, U, H, S, \dots$ $k : v, g, u, h, s, \dots$
Delta, subscript mix	Property change of mixing:	$\Delta K_{mix} : \Delta V_{mix}, \Delta H_{mix}, \Delta S_{mix}, \dots$ $\Delta k_{mix} : \Delta v_{mix}, \Delta h_{mix}, \Delta s_{mix}, \dots$

Other

Dot	Rate of change	$\dot{Q}, \dot{W}, \dot{n}, \dot{V}, \dots$
Overbar	Average	$\bar{\bar{V}}^2, \bar{\bar{c}}_P, \dots$

Symbols

a, b, \dots, i, \dots	Generic species in a mixture	K_i	K-value
a, A	Helmholtz energy	L	Flow rate of liquid
A, B	Labels for processes to be compared	m	Number of chemical species
A	Area	m	Mass
a_i	Activity of species i	MW	Molecular weight
A_i	Species i in a chemical reaction	n	Number of moles
b_j	Element vector	n	Concentration of electrons in a semiconductor
c_P	Heat capacity at constant pressure	n_i	Intrinsic carrier concentration
c_v	Heat capacity at constant volume	N	Number of molecules in the system or in a given state
c_i	Molal concentration of species i	N_A	Avagadro's number
C_i	Mass concentration of species i	OF	Objective function
$[i]$	Molar concentration of species i	p	Concentration of holes in a semiconductor
COP	Coefficient of performance	P	Pressure
D_{i-j}	Bond $i-j$ dissociation energy	p_i	Partial pressure of species i in an ideal gas mixture
e, E	Energy	P_i^{sat}	Saturation pressure of species i
e_k, E_K	Kinetic energy	q, Q	Heat
e_p, E_P	Potential energy	Q	Electric charge
\vec{E}	Electric field	r	Distance between two molecules
F	Force	R	Gas constant
F	Flow rate of feed	R	Number of independent chemical reactions
F	Faraday's constant	s	Stoichiometric constraints
\mathfrak{F}	Degrees of freedom	s, S	Entropy
f_i	Fugacity of pure species i	t	Time
\hat{f}_i	Fugacity of species i in a mixture	T	Temperature
f	Total solution fugacity	T_b	Temperature at the boiling point
g, G	Gibbs energy	T_m	Temperature at the melting point
g	Gravitational acceleration	T_u	Upper consolute temperature
h, H	Enthalpy	u, U	Internal energy
$\Delta \tilde{h}_s$	Enthalpy of solution	v, V	Volume
\mathcal{H}_i	Henry's law constant of solute i	V	Flow rate of vapor
i	Interstitial	V	Vacancy
I	Ionization energy	\vec{V}	Velocity
I	Ionic strength	w, W	Work
k, K	Generic representation of any thermodynamic property except P or T	w_{flow}, W_{flow}	Flow work
k	Boltzmann's constant	w_s, W_s	Shaft work
k	Heat capacity ratio (c_P/c_v)	w^*, W^*	Non- Pv work
k	Spring constant	w_i	Weight fraction of species i
K	Equilibrium constant	x	Quality (fraction vapor)
k_{ij}	Binary interaction parameter between species i and j	x	Position along x -axis
		x_i	Mole fraction of liquid species i

X_i	Mole fraction of solid species i	z	Valence of an ion in solution
y_i	Mole fraction of vapor species i	1, 2 ...	Labels of specific states of a system
z	Compressibility factor		
z	Position along z -axis	1, 2 ...	Generic species in a mixture

Greek Symbols

α_i	Polarizability of species i	η	Efficiency factor
β	Thermal expansion coefficient	λ_i	Lagrangian multiplier
β_{ij}	Formula coefficient matrix	Γ	Molecular potential energy
E	Electrochemical potential	Γ_i	Activity coefficient of solid species i
φ_i	Fugacity coefficient of pure species i	Γ_{ij}	Molecular potential energy between species i and j
$\hat{\varphi}_i$	Fugacity coefficient of species i in a mixture	κ	Isothermal compressibility
φ	Total solution fugacity coefficient	μ_i	Dipole moment of species i
γ_i	Activity coefficient of species i	μ_i	Chemical potential of species i
$\gamma_i^{\text{Henry's}}$	Activity coefficient using a Henry's law reference state	μ_{JT}	Joule-Thomson coefficient
γ_i^m	Molality based activity coefficient	π	Phases
γ_{\pm}	Mean activity coefficient of anions and cations in solution	Π	Osmotic pressure
		ρ	Density
		ν_i	Stoichiometric coefficient
		ω	Pitzer acentric factor
		ξ	Extent of reaction

Subscripts

a, b, \dots, i, \dots	Generic species in a mixture	net	Net heat or work transferred
atm	Atmosphere	out	Flow stream out of the system
c	Critical point	products	Products of a chemical reaction
C	Cold thermal reservoir	pc	Pseudocritical
calc	Calculated	r	Reduced property
cycle	Property change over a thermodynamic cycle	reactants	Reactants in a chemical reaction
exp	Experimental	real gas	Real gas
f	Property value of formation (with Δ)	rev	Reversible process
fus	Fusion	rxn	Reaction
E	External	sub	Sublimation
H	Hot thermal reservoir	surr	Surroundings
high	High value (e.g. in interpolation)	sys	System
ideal gas	Ideal gas	univ	Universe
in	Flow stream into the system	v	Vapor
inerts	Inerts in a chemical reaction	vap	Vaporization
irrev	Irreversible process	z	In the z direction
l	Liquid	1, 2 ...	Labels of specific states of a system
low	Low value (e.g. in interpolation)	1, 2 ...	Generic species in a mixture
mix	Equation of state parameter of a mixture		

Superscripts

dep	Departure function (with Δ)	s	Solid
E	Excess property	sat	At saturation
ideal	Ideal solution	v	Vapor
ideal gas	Ideal gas	α, β	Generic phases (in equilibrium)
molecular	Molecular	γ	Volume exponential of a polytropic process
l	Liquid	∞	At infinite dilution
o	Value at the reference state	(0)	Simple fluid term
real	Real fluid with intermolecular interactions	(1)	Correction term

Operators

d	Total differential	δ	Inexact (path dependent) differential
∂	Partial differential	\ln	Natural (base e) logarithm
Δ	Difference between the final and initial value of a state property	\log	Base 10 logarithm
∇	Gradient operator	\prod	Cumulative product operator
\int	Integral	\sum	Cumulative sum operator

Empirical parameters

a, b	van der Waals or Redlich-Kwong attraction and size parameter, respectively
$a, b, \alpha, \kappa \dots$	Empirical parameters in various cubic equations of state
A	Two-suffix Margules activity coefficient model parameter
A_{ij}	Three-suffix Margules activity coefficient model parameters (one form)
A, B	Three-suffix Margules or van Laar activity coefficient model parameters
A, B	Debye-Huckel parameters
A, B, C	Empirical constants for the Antoine equation
A, B, C, D, E	Empirical constants for the heat capacity equation
B, C, D	Second, third and fourth virial coefficients
B', C', D'	Second, third and fourth virial coefficient in the pressure expansion
C_6	Constant of van der Waals or Lennard-Jones attraction
C_n	Constant of intermolecular repulsion potential of power r^{-n}
ε	Lennard-Jones energy parameter
Λ_{ij}	Wilson activity coefficient model parameters
σ	Distance parameter in hard sphere, Lennard-Jones and other potential functions

Engineering and Chemical Thermodynamics

Period	1
--------	---

18 He 0.00260 2

18 He 0.00260 2

18 He 0.00260 2

*The systematic names and symbols for elements of atomic numbers above 109 will be used until the approval of trivial names by IUPAC.

*The systematic names and symbols for elements of atomic numbers above 109 will be used until the approval of trivial names by IUPAC.

*The systematic names and symbols for elements of atomic numbers above 109 will be used until the approval of trivial names by IUPAC.



Contents

►CHAPTER 1

Measured Thermodynamic Properties And Other Basic Concepts 1

Learning Objectives 1

- 1.1 Thermodynamics 2
- 1.2 Preliminary Concepts—The Language of Thermo 3
- 1.3 Measured Thermodynamic Properties 7
 - Volume (Extensive or Intensive) 7
 - Temperature (intensive) 8
 - Pressure (intensive) 11
- 1.4 Equilibrium 12
- 1.5 Independent and Dependent Thermodynamic Properties 15
- 1.6 The PvT Surface and Its Projections for Pure Substances 17
- 1.7 Thermodynamic Property Tables 23
- 1.8 The Ideal Gas 26
- 1.9 Summary 28
- 1.10 Problems 29

►CHAPTER 2

The First Law Of Thermodynamics 31

Learning Objectives 31

- 2.1 The First Law of Thermodynamics 32
 - Forms of Energy 32
 - Work and Heat: Transfer of Energy Between the System and the Surroundings 37
- 2.2 Construction of Hypothetical Paths 41
- 2.3 Reversible and Irreversible Processes 42
- 2.4 The First Law of Thermodynamics for Closed Systems 49
 - Integral Balances 49
 - Differential Balances 51
- 2.5 The First Law of Thermodynamics for Open Systems 52
- 2.6 Thermochemical Data for U and H 58
 - Heat Capacity: c_v and c_p 58
 - Latent Heats 67
 - Enthalpy of Reactions 70
- 2.7 Reversible Processes in Closed Systems 76
 - Reversible, Isothermal Expansion (Compression) 76
 - Adiabatic Expansion (Compression) with Constant Heat Capacity 78
 - Summary 79

- 2.8 Open-System Energy Balances on Process Equipment 80

- 2.9 Thermodynamic Cycles and the Carnot Cycle 86

- 2.10 Summary 92

- 2.11 Problems 93

►CHAPTER 3

Entropy And The Second Law Of Thermodynamic 103

Learning Objectives 103

- 3.1 Directionality of Processes/Spontaneity 104
- 3.2 Reversible and Irreversible Processes (Revisited) and Their Relationship to Directionality 105
- 3.3 Entropy, the Thermodynamic Property 107
- 3.4 The Second Law of Thermodynamics 115
- 3.5 Other Common Statements of the Second Law of Thermodynamics 117
- 3.6 The Second Law of Thermodynamics for Closed and Open Systems 118
 - Calculation of Δs for Closed Systems 119
 - Calculation of Δs for Open Systems 123
- 3.7 Calculation of Δs for an Ideal Gas 126
- 3.8 The Mechanical Energy Balance and the Bernoulli Equation 135
- 3.9 Vapor-Compression Power and Refrigeration Cycles 138
 - The Rankine Cycle 138
 - The Vapor-Compression Refrigeration Cycle 143
- 3.10 Molecular View of Entropy 146
 - Maximizing Molecular Configurations over Space 148
 - Maximizing Molecular Configurations over Energy 149
- 3.11 Summary 152
- 3.12 Problems 154

►CHAPTER 4

Equations Of State And Intermolecular Forces 164

Learning Objectives 164

- 4.1 Introduction 165
 - Motivation 165
 - The Ideal Gas 166
- 4.2 Intermolecular Forces 166
 - Internal (Molecular) Energy 166
 - Attractive Forces 168
 - Intermolecular Potential Functions and Repulsive Forces 177

- Principle of Corresponding States 180
- Chemical Forces 182
- 4.3 Equations of State 186
 - The Van Der Waals Equation of State 186
 - Cubic Equations of State 192
 - The Virial Equation of State 194
 - Equations of State for Liquids and Solids 196
- 4.4 Generalized Compressibility Charts 197
- 4.5 Determination of Parameters for Mixtures 200
- 4.6 Summary 204
- 4.7 Problems 205

►CHAPTER 5

The Thermodynamic Web 211

Learning Objectives 211

- 5.1 Types of Thermodynamic Properties 211
- 5.2 Thermodynamic Property Relationships 212
 - Dependent and Independent Properties 212
 - Fundamental Property Relations 214
 - Maxwell Relations 216
 - Other Useful Mathematical Relations 217
 - Using the Thermodynamic Web to Access Reported Data 218
- 5.3 Calculation of Δs , Δu , and Δh Using Equations of State 220
 - Relation of ds in Terms of Independent Variables T and v and Independent Variables T and P 220
 - Relation of du in Terms of Independent Variables T and v 221
 - Relation of dh in Terms of Independent Variables T and P 224
- 5.4 Departure Functions 230
- 5.5 Joule–Thomson Expansion and Liquefaction 237
- 5.6 Summary 243
- 5.7 Problems 243

►CHAPTER 6

Phase Equilibria I: Problem Formulation 250

Learning Objectives 250

- 6.1 Introduction 250
- 6.2 Pure Species Phase Equilibrium 253
 - Gibbs Energy as a Criterion for Chemical Equilibrium 253
 - Roles of Energy and Entropy in Phase Equilibria 255
 - The Relationship Between Saturation Pressure and Temperature: The Clapeyron Equation 258
 - Pure Component Vapor–Liquid Equilibrium: The Clausius–Clapeyron Equation 260
- 6.3 Thermodynamics of Mixtures 263
 - Introduction 263

- Partial Molar Properties 264
- The Gibbs–Duhem Equation 269
- Summary of the Different Types of Thermodynamic Properties 270
- Property Changes of Mixing 271
- Determination of Partial Molar Properties 280
- Relations Among Partial Molar Quantities 288
- 6.4 Multicomponent Phase Equilibria 289
 - The Chemical Potential—The Criteria for Chemical Equilibrium 289
 - Temperature and Pressure Dependence of μ_i 292
- 6.5 Summary 293
- 6.6 Problems 294

►CHAPTER 7

Phase Equilibria II: Fugacity 302

Learning Objectives 302

- 7.1 Introduction 302
- 7.2 The Fugacity 303
 - Definition of Fugacity 303
 - Other Forms of Fugacity 305
 - Criteria for Chemical Equilibria in Terms of Fugacity 306
- 7.3 Fugacity in the Vapor Phase 307
 - Fugacity and Fugacity Coefficient of Pure Gases 307
 - Fugacity and Fugacity Coefficient of Species i in a Gas Mixture 313
 - The Lewis Fugacity Rule 319
 - Property Changes of Mixing for Ideal Gases 320
- 7.4 Fugacity in the Liquid Phase 322
 - Reference States for the Liquid Phase 322
 - Thermodynamic Relations Between γ_i 330
 - Models for γ_i Using g^E 336
 - Equation of State Approach to the Liquid Phase 353
- 7.5 Fugacity in the Solid Phase 353
 - Pure Solids 353
 - Solid Solutions 353
 - Interstitials and Vacancies in Crystals 353
- 7.6 Summary 354
- 7.7 Problems 356

►CHAPTER 8

Phase Equilibria III: Phase Diagrams 364

Learning Objectives 364

- 8.1 Vapor–Liquid Equilibrium (VLE) 365
 - Raoult's Law (Ideal Gas and Ideal Solution) 365
 - Nonideal Liquids 372
 - Azeotropes 381
 - Fitting Activity Coefficient Models with VLE Data 386