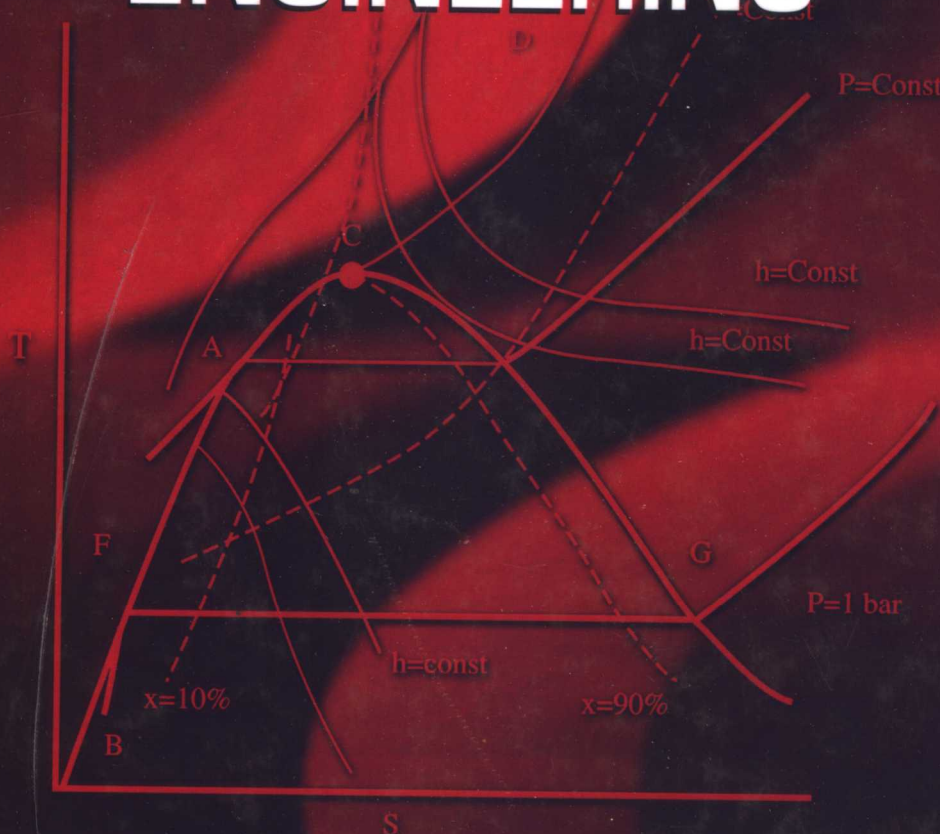


CRC Series in
COMPUTATIONAL MECHANICS and APPLIED ANALYSIS

ADVANCED THERMODYNAMICS ENGINEERING



Kalyan Annamalai • Ishwar K. Puri



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**CRC Series in
COMPUTATIONAL MECHANICS and APPLIED ANALYSIS**

ADVANCED THERMODYNAMICS ENGINEERING

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KA dedicates this text to his mother Kancheepuram Pattammal Sundaram, who could not read or write, and his father, Thakkolam K. Sundaram, who was schooled through only a few grades, for educating him in all aspects of his life. He thanks his wife Vasanthal for companionship throughout the cliff-hanging journey to this land of opportunity and his children, Shankar, Sundhar and Jothi for providing a vibrant source of "energy" in his career.

IKP thanks his wife Beth for her friendship and support and acknowledges his debt to his sons Shivesh, Sunil, and Krishan, for allowing him to take time off from other pressing responsibilities, such as playing catch. His career has been a fortunate journey during which his entire family, including his parents Krishan and Sushila Puri, has played a vital role.

PREFACE

We have written this text for engineers who wish to grasp the *engineering physics* of thermodynamic concepts and *apply* the knowledge in their field of interest rather than merely digest the abstract generalized concepts and mathematical relations governing thermodynamics. While the fundamental concepts in any discipline are relatively invariant, the problems it faces keep changing. In many instances we have included physical explanations along with the mathematical relations and equations so that the principles can be relatively applied to real world problems.

The instructors have been teaching advanced thermodynamics for more than twelve years using various thermodynamic texts written by others. In writing this text, we acknowledge that debt and that to our students who asked questions that clarified each chapter that we wrote. This text uses a “down-to-earth” and, perhaps, unconventional approach in teaching advanced concepts in thermodynamics. It first presents the phenomenological approach to a problem and then delves into the details. Thereby, we have written the text in the form of a self-teaching tool for students and engineers, and with ample example problems. Readers will find the esoteric material to be condensed and, as engineers, we have stressed applications throughout the text. There are more than 110 figures and 150 engineering examples covering thirteen chapters.

Chapter 1 contains an elementary overview of undergraduate thermodynamics, mathematics and a brief look at the corpuscular aspects of thermodynamics. The overview of microscopic thermodynamics illustrates the physical principles governing the macroscopic behavior of substances that are the subject of classical thermodynamics. Fundamental concepts related to matter, phase (solid, liquid, and gas), pressure, saturation pressure, temperature, energy, entropy, component property in a mixture and stability are discussed.

Chapter 2 discusses the first law for closed and open systems and includes problems involving irreversible processes. The second law is *illustrated* in Chapter 3 rather than presenting an axiomatic approach. Entropy is introduced through a Carnot cycle using ideal gas as the medium, and the illustration that follows considers any reversible cycle operating with any medium. Entropy maximization and energy minimization principles are illustrated. Chapter 4 introduces the concept of availability with a simple engineering scheme that is followed by the most general treatment. Availability concepts are illustrated by scaling the performance of various components in a thermodynamic system (such as a power plant or air conditioner) and determining which component degrades faster or outperforms others. Differential forms of energy and mass conservation, and entropy and availability balance equations are presented in Chapters 2 to 4 using the Gauss divergence theorem. The differential formulations allow the reader to determine where the maximum entropy generation or irreversibility occurs within a unit so as to pinpoint the major source of the irreversibility for an entire unit. Entropy generation and availability concepts are becoming more important to energy systems and conservation groups. This is a rapidly expanding field in our energy-conscious society. Therefore, a number of examples are included to illustrate applications to engineering systems. Chapter 5 contains a postulatory approach to thermodynamics. In case the reader is pressed for time, this chapter may be entirely skipped without loss of continuity of the subject.

Chapter 6 presents the state equation for real gases including two and three parameter, and generalized equations of state. The Kessler equation is then introduced and the methodology for determining $Z^{(0)}$ and $Z^{(1)}$ is discussed. Chapter 7 starts with Maxwell's relations followed by the development of generalized thermodynamic relations. Illustrative examples are presented for developing tables of thermodynamic properties using the Real Gas equations. Chapter 8 contains the theory of mixtures followed by a discussion of fugacity and activity. Following the methodology for estimating the properties of steam from state equations, a methodology is presented for estimating partial molal properties from mixture state equations. Chapter 9 deals with phase equilibrium of multicomponent mixtures and vaporization and boiling. Applications to engineering problems are included. Chapter 10 discusses the regimes

of stable and metastable states of fluids and where the criteria for stability are violated. Real gas state equations are used to identify the stable and unstable regimes and illustrative examples with physical explanation are given.

Chapter 11 deals with reactive mixtures dealing with complete combustion, flame temperatures and entropy generation in reactive systems. In Chapter 12 criteria for the direction of chemical reactions are developed, followed by a discussion of equilibrium calculations using the equilibrium constant for single and multi-phase systems, as well as the Gibbs minimization method. Chapter 13 presents an availability analysis of chemically reacting systems. Physical explanations for achieving the work equivalent to chemical availability in thermodynamic systems are included. The summary at the end of each chapter provides a brief review of the chapter for engineers in industry.

Exercise problems are placed at the end. This is followed by several tables containing thermodynamic properties and other useful information.

The field of thermodynamics is vast and all subject areas cannot be covered in a single text. Readers who discover errors, conceptual conflicts, or have any comments, are encouraged to E-mail these to the authors (respectively, kannamalai@tamu.edu and ikpuri@uic.edu). The assistance of Ms. Charlotte Sims and Mr. Chun Choi in preparing portions of the manuscript is gratefully acknowledged. We wish to acknowledge helpful suggestions and critical comments from several students and faculty. We specially thank the following reviewers: Prof. Blasiak (Royal Inst. of Tech., Sweden), Prof. N. Chandra (Florida State), Prof. S. Gollahalli (Oklahoma), Prof. Hernandez (Guanajuato, Mexico), Prof. X. Li. (Waterloo), Prof. McQuay (BYU), Dr. Muyschondt. (Sandia National Laboratories), Prof. Ochterbech (Clemson), Dr. Peterson, (RPI), and Prof. Ramaprabhu (Anna University, Chennai, India).

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NOMENCLATURE*

<i>Symbol</i>	<i>Description</i>	<i>SI</i>	<i>English</i>	<i>Conversion</i>
				<i>SI to English</i>
A	Helmholtz free energy	kJ	BTU	0.9478
A	area	m ²	ft ²	10.764
a	acceleration	m s ⁻²	ft s ⁻²	3.281
a	specific Helmholtz free energy	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
\bar{a}	attractive force constant			
\bar{a}	specific Helmholtz free energy	kJ kmole ⁻¹	BTU lbmole ⁻¹	0.4299
\bar{b}	body volume constant	m ³ kmole ⁻¹	ft ³ lbmole ⁻¹	16.018
c	specific heat	kJ kg ⁻¹ K ⁻¹	BTU/lb R	0.2388
COP	Coefficient of performance			
E	energy, (U+KE+PE)	kJ	BTU	0.9478
E _T	Total energy (H+KE+PE)	kJ	BTU	0.9478
e	specific energy	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
c _T	methalpy = h + ke + pe	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
F	force	kN	lb _f	224.81
f	fugacity	kPa(or bar)	lb _f in ⁻²	0.1450
G	Gibbs free energy	kJ	BTU	0.9478
g	specific Gibbs free energy	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
(mass basis)				
g	gravitational acceleration	m s ⁻²	ft s ⁻²	3.281
g _c	gravitational constant			
\bar{g}	Gibbs free energy (mole basis)	kJ kmole ⁻¹	BTU lbmole ⁻¹	0.4299
\hat{g}	partial molal Gibb's function,	kJ kmole ⁻¹	BTU lbmole ⁻¹	0.4299
H	enthalpy	kJ	BTU	0.9478
h _{fg}	enthalpy of vaporization	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
h	specific enthalpy (mass basis)	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
h _{o,h} *	ideal gas enthalpy	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
I	irreversibility	kJ	BTU	0.9478
I	irreversibility per unit mass	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
I	electrical current	amp		
J	Joules' work equivalent of heat	(1 BTU = 778.14 ft lb _f)		
J _k	fluxes for species, heat etc	kg s ⁻¹ , kW	BTU s ⁻¹	0.9478
J _k	fluxes for species, heat etc	kg s ⁻¹ , kW	lb s ⁻¹	0.4536
K	equilibrium constant			
KE	kinetic energy	kJ	BTU	0.9478
ke	specific kinetic energy	kJ kg ⁻¹	BTU lb _m ⁻¹	0.4299
k	ratio of specific heats			
L	length, height	m	ft	3.281
l	intermolecular spacing	m	ft	3.281
l _m	mean free path	m	ft	3.281
LW	lost work	kJ	BTU	0.9478
LW	lost work	kJ	ft lb _f	737.52
M	molecular weight, molal mass	kg kmole ⁻¹	lb _m lbmole ⁻¹	
m	mass	kg	lb _m	2.2046

* Lower case (lc) symbols denote values per unit mass, lc symbols with a bar (e.g., \bar{h}) denote values on mole basis, lc symbols with a caret and tilde (respectively, \hat{h} and \tilde{h}) denote values on partial molal basis based on moles and mass, and symbols with a dot (e.g. \dot{Q}) denote rates.

Y	mass fraction			
N	number of moles	kmole	lbmole	2.2046
N _{Avag}	Avogadro number	molecules kmole ⁻¹	molecules lbmole ⁻¹	0.4536
n	polytropic exponent in $PV^n = \text{constant}$			
P	pressure	kN m ⁻²	kPa lb _r in ⁻²	0.1450
PE	potential energy	kJ	BTU	0.9478
pe	specific potential energy			
Q	heat transfer	kJ	BTU	0.9478
q	heat transfer per unit mass	kJ kg ⁻¹	BTU lb ⁻¹	0.4299
q _c	charge			
R	gas constant	kJ kg ⁻¹ K ⁻¹	BTU lb ⁻¹ R ⁻¹	0.2388
\bar{R}	universal gas constant	kJ kmole ⁻¹ K ⁻¹	BTU lbmole ⁻¹ R ⁻¹	0.2388
S	entropy	kJ K ⁻¹	BTU R ⁻¹	0.5266
\bar{s}	specific entropy (mass basis)	kJ kg ⁻¹ K ⁻¹	BTU lb ⁻¹ R ⁻¹	0.2388
\bar{s}	specific entropy (mole basis)	kJ kmole ⁻¹ K ⁻¹	BTU lbmole ⁻¹ R ⁻¹	0.2388
T	temperature	°C, K	°F, °R	(9/5)T+32
T	temperature	°C, K	°R	1.8
t	time	s	s	
U	internal energy	kJ	BTU	0.9478
\bar{u}	specific internal energy	kJ kg ⁻¹	BTU lb ⁻¹	0.4299
\bar{u}	internal energy (mole basis)	kJ kmole ⁻¹	BTU lbmole ⁻¹	0.4299
V	volume	m ³	ft ³	35.315
V	volume	m ³	gallon	264.2
V	velocity	m s ⁻¹	ft s ⁻¹	3.281
\bar{v}	specific volume (mass basis)	m ³ kg ⁻¹	ft ³ lb _m ⁻¹	16.018
\bar{v}	specific volume (mole basis)	m ³ kmole ⁻¹	ft ³ lbmole ⁻¹	16.018
W	work	kJ	BTU	0.9478
W	work	kJ	ft lb _r	737.5
w	work per unit mass	kJ kg ⁻¹	BTU lb ⁻¹	0.4299
w	Pitzer factor			
ω	specific humidity	kg kg ⁻¹	lb _m lb _m ⁻¹	
x	quality			
x _k	mole fraction of species k			
Y _k	mass fraction of species k			
z	elevation	m	ft	3.281
Z	compressibility factor			

Greek symbols

$\hat{\alpha}_k$	activity of component k, γ_k / f_k			
β_p, β_T	compressibility	K ⁻¹ , atm ⁻¹	R ⁻¹ , bar ⁻¹	0.555, 1.013
β_s		atm ⁻¹	bar ⁻¹	1.013
γ_k	activity coefficient, $\hat{\alpha}_k / \hat{\alpha}_k^{\text{id}}$			
$\hat{\phi}_k / \phi_k$	Gruneisen constant			
λ	thermal conductivity	kW m ⁻¹ K ⁻¹	BTU ft ⁻¹ R ⁻¹	0.1605
η	First Law efficiency			
η _r	relative efficiency			

ω	specific humidity			
ρ	density	kg m^{-3}	$\text{lb}_m \text{ft}^{-3}$	0.06243
ϕ	equivalence ratio, fugacity coefficient			
ϕ	relative humidity,			
Φ	absolute availability(closed system)	kJ	BTU	0.9478
Φ'	relative availability or exergy	kJ kg^{-1}	BTU lb^{-1}	0.4299
ϕ	fugacity coefficient			
J_T	Joule Thomson Coefficient	K bar^{-1}	$^{\circ}\text{R atm}^{-1}$	1.824
μ	chemical potential	kJ kmole^{-1}	BTU lbmole^{-1}	0.4299
ν	stoichiometric coefficient			
σ	entropy generation	kJ K^{-1}	BTU R^{-1}	0.2388
Ψ	absolute stream availability	kJ kg^{-1}	BTU lb^{-1}	0.2388
Ψ'	relative stream availability or exergy			

Subscripts

a	air
b	boundary
c	critical
chem	chemical
c.m.	control mass
c.v.	control volume
e	exit
f	flow
f	saturated liquid (or fluid)
f	formation
fg	saturated liquid (fluid) to vapor
g	saturated vapor (or gas)
H	high temperature
I	inlet
inv	inversion
id	ideal gas
iso	isolated (system and surroundings)
L	low temperature
max	maximum possible work output between two given states (for an expansion process)
m	mixture
min	minimum possible work input between two given states
net	net in a cyclic process
p	at constant pressure
p,o	at constant pressure for ideal gas
R	reduced, reservoir
rev	reversible
r	relative pressure, relative volume
s	isentropic work, solid
sf	solid to fluid (liquid)
sh	shaft work
Th	Thermal
TM	Thermo-mechanical
TMC	Thermo-mechanical-chemical
w	wet mixture

v	at constant volume
v,o	at constant volume for ideal gas
v	vapor (Chap. 5)
0 or o	ambient, ideal gas state

Superscripts

(0)	based on two parameters
(1)	Pitzer factor correction
α	alpha phase
β	beta phase
id	ideal mixture
ig	ideal gas
P	liquid
g	gas
l	liquid
res	residual
sat	saturated
o	pressure of 1 bar or 1 atm
-	molal property of k, pure component
^	molal property when k is in a mixture

Mathematical Symbols

$\delta()$	differential of a non-property, e.g., δQ , δW , etc.
d()	differential of property, e.g., du, dh, dU, etc.
Δ	change in value

Acronyms

CE	Carnot Engine
c.m.	control mass
c.s	control surface
c.v	control volume
ES	Equilibrium state
HE	Heat engine
IPE,ipe	Intermolecular potential energy
IRHE	Irreversible HE
KE	Kinetic energy
ke	kinetic energy per unit mass
LHS	Left hand side
KES	Kessler equation of state
MER	Mechanical energy reservoir
mph	miles per hour
NQS/NQE	non-equilibrium
PC	piston cylinder assembly
PCW	piston cylinder weight assembly
PE	Potential energy
pe	potential energy per unit mass
PR	Peng Robinson
RE, re	Rotational energy
RHE	Reversible HE
RHS	Right hand side
RK	Redlich Kwong

RKS	Redlich Kwong Soave
QS/QE	Quasi-equilibrium
ss	steady state
sf	steady flow
TE, te	translational
TER	Thermal energy reservoir
TM	thermo-mechanical equilibrium
TMC	Thermo-mechanical-chemical equilibrium
uf	uniform flow
us	uniform state
VE,ve	Vibrational energy
VW	Van der Waals

Laws of Thermodynamics in Lay Terminology

First Law: It is impossible to obtain something from nothing, but one may break even

Second Law: One may break even but only at the lowest possible temperature

Third Law: One cannot reach the lowest possible temperature

Implication: It is impossible to obtain something from nothing, so one must optimize resources

The following equations, sometimes called the accounting equations, are useful in the engineering analysis of thermal systems.

Accumulation rate of an extensive property B: $dB/dt = \text{rate of B entering a volume } (\dot{B}_i) - \text{rate of B leaving a volume } (\dot{B}_e) + \text{rate of B generated in a volume } (\dot{B}_{\text{gen}}) - \text{rate of B destroyed or consumed in a volume } (\dot{B}_{\text{des/cons}})$.

Mass conservation: $dm_{\text{cv}}/dt = \dot{m}_i - \dot{m}_e$.

First law or energy conservation: $dE_{\text{cv}}/dt = \dot{Q} - \dot{W} + \dot{m}_i e_{T,i} - \dot{m}_e e_{T,e}$,

where $e_T = h + ke + pe$, $E = U + KE + PE$, $\delta w_{\text{rev, open}} = -v dP$, $\delta w_{\text{rev, closed}} = P dv$.

Second law or entropy balance equation: $dS_{\text{cv}}/dt = \dot{Q}/T_b + \dot{m}_i s_i - \dot{m}_e s_e + \dot{\sigma}_{\text{cv}}$,

where $\dot{\sigma}_{\text{cv}} > 0$ for an irreversible process and is equal to zero for a reversible process.

Availability balance: $d(E_{\text{cv}} - T_0 S_{\text{cv}})/dt = Q(1 - T_0/T_R) + \dot{m}_i \psi_i - \dot{m}_e \psi_e - \dot{W} - T_0 \dot{\sigma}_{\text{cv}}$,

where $\psi = (e_T - T_0 s) = h + ke + pe - T_0 s$, and $E = U + KE + PE$.

Third law: $S \rightarrow 0$ as $T \rightarrow 0$.

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