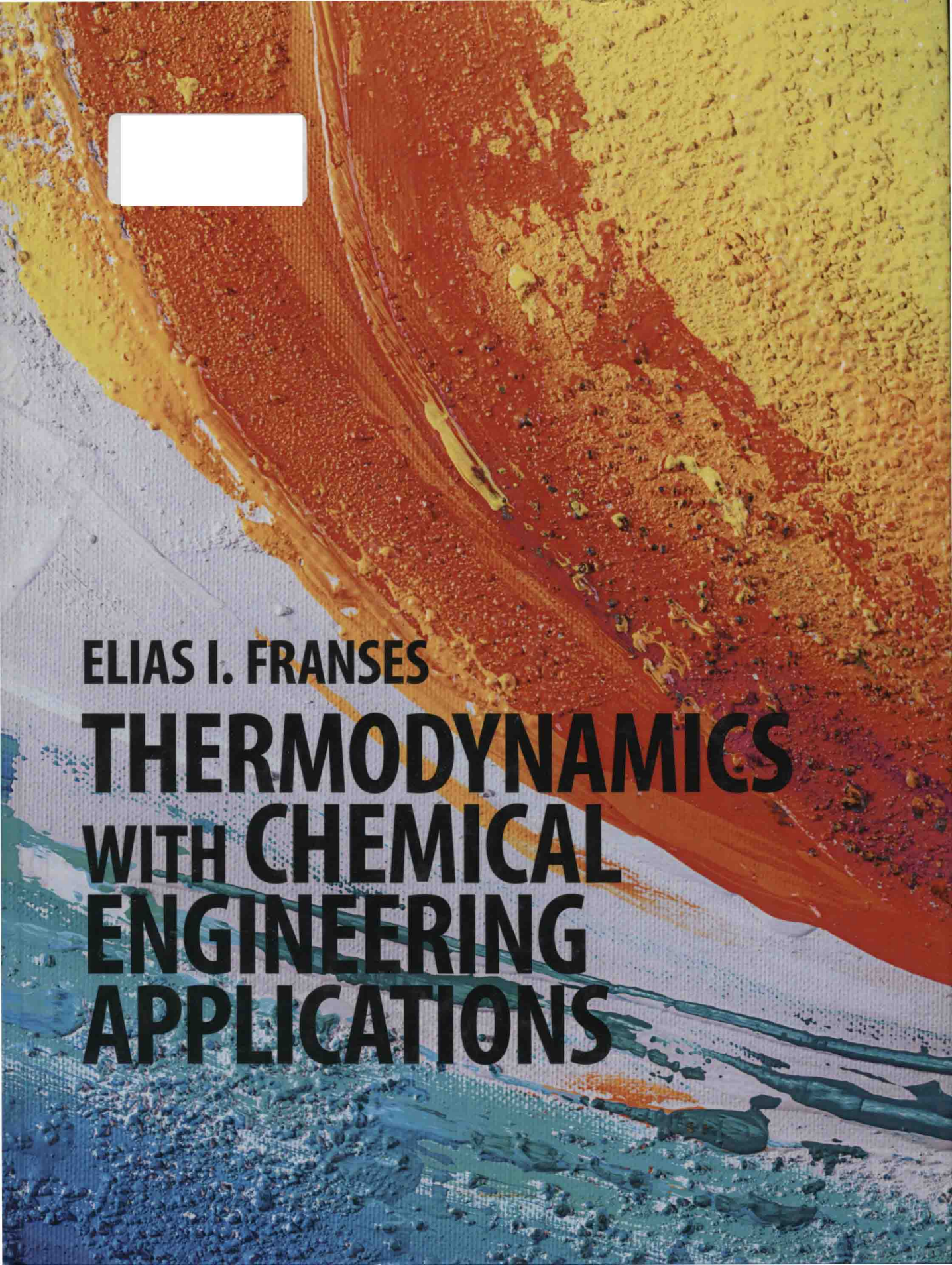
ELIAS I. FRANSES
THERMODYNAMICS
WITH CHEMICAL
ENGINEERING
APPLICATIONS

Thermodynamics with Chemical Engineering Applications

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Elias I. Franses has been a Professor of Chemical Engineering at Purdue University for over 30 years. An expert in thermodynamics, he has taught numerous courses on this topic to chemical engineering students of all levels.

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Jochen Lauterbach
University of South Carolina

In loving memory of Iosafat S. Franses, Linda I. Franses,
and Ying-Chuen Wang.

And to Linda, Joseph, Nikki, Alex, and William,
who liven up my life every day.

PREFACE AND ACKNOWLEDGMENTS

This book should be used primarily as a textbook. It is also designed to be used for self-study, including many essay-style sections, which may be appropriate for a more general audience. Over the last 30 years I have taught thermodynamics, chemical reaction engineering, and surface thermodynamics in courses for sophomores, juniors, seniors, and graduate students in chemical engineering at Purdue University. On the basis of such experiences, I believe that this book may be used either for sophomore/junior courses in thermodynamics in chemical engineering or as a reference for graduate thermodynamics courses.

I am grateful to many of my previous teachers and mentors. As an undergraduate student at the National Technical University of Athens, Greece, I took valuable courses on the thermodynamic theory and on laboratory measurements of thermodynamic quantities from Professors Theodoros Skoulikidis and Nicolaos Koumoutsos. As a graduate student at the University of Minnesota, I benefited greatly from the courses given by, and discussions with, Professors L. E. (Skip) Scriven and H. Ted Davis. I also got valuable lessons in solution thermodynamics, phase behavior, and experimental methods from Professor Wilmer G. Miller.

Most of the chapters of this book were typed by Ms. Karen Heide; some were typed by Dr. Jiannan Dong. I have appreciated their work. Several graduate students from Purdue University, namely Dr. Jiannan Dong, Dr. Yoonjee Park, Dr. Hung-Wei Tsui, Ms. Betty Yang, and my son, Dr. Joseph W. Franses, helped prepare many figures and did some of the calculations for these figures. I am indebted to them for their help. I thank Professor Arvind Varma, who is the Chemical Engineering series editor of Cambridge University Press, and Head of the School of Chemical Engineering at Purdue University, for his support. Professor Chongli Yuan provided valuable comments on some of the chapters. Throughout the writing, my wife, Professor Nien-Hwa Linda Wang, provided support, inspiration, and invaluable criticisms.

I am grateful to the staff of Cambridge University Press for their hard and careful work in producing this book. I am particularly thankful to Dr. Michelle Carey, who undertook the project and provided valuable advice and encouragement. Ms. Elizabeth Horne and Ms. Sarah Payne provided additional advice and support; and Dr. Steven Holt guided the final editing with patience, diligence, thoroughness, and expert technical feedback when needed.

This book is dedicated to the loving memory of my parents, Iosafat S. Franses and Linda I. Franses, and of my father-in-law Ying-Chuen Wang. It is also dedicated to my dear family

members: my wife Nien-Hwa Linda Wang; her mother Yun Lan Wang; my brother Simon I. Franses; my sister-in-law, Roula Atoun Franses; my sister, Nelli I. Franses; my brother-in-law, Paul Zadik; my sister-in-law, Nellie Lin; my brother-in-law, Shengyen Lin; and my son Joseph W. Franses, his wife Nicole A. C. W. Franses, and our two lovely grandsons Alex and William Franses.

LIST OF SYMBOLS

A	area, m^2
A	area of heat exchanger, Section 6.6.7
A_i	inside area of heat exchanger, Section 6.6.7
A_o	outside area of heat exchanger, Section 6.6.7
A	Helmholtz free energy, J
A	specific Helmholtz free energy, J/kg, or molar Helmholtz free energy in J/mol
A	constant in heat capacity of ideal gas, liquid, or solid, Eqs. (4.123)–(4.126)
A	constant in Antoine's equation, Eq. (5.57)
A	constant in Clausius–Clapeyron equation, Eq. (5.63)
A	constant in virial equation of state Eq. (5.70)
A	constant in regular solution model Eq. (9.74)
A	constant in Redlich–Kister equation, Eq. (9.77)
A_{12}, A_{21}	constants in Margules equation, Eq. (9.78)
A	Poynting factor, Eq. (10.15)
A	constant in heat capacity equation, Eq. (14.4)
A	correction term in pressure for van der Waals equation in Section 5.3
a	constant in van der Waals equation, Eq. (5.34)
a	constant in Redlich–Kwong Eq. (5.65)
a_1	activity coefficient of component 1
$\mathbf{a}$	acceleration, m/s^2
a_o	area per molecule, $Å^2$/molecule
B	constant defined in Eq. (2.26)
B	second virial coefficient constant in virial equation of state Eq. (5.70)
B'	second virial coefficient constant in Eq. (5.72)
B'	second virial coefficient constant in Eq. (13.28) for osmotic pressure
B	constant in heat capacity of ideal gas, liquid, or solid, Eqs. (4.123)–(4.126), K^{-1}
B	constant in Antoine's equation, Eq. (5.57)
B	constant in Clausius–Clapeyron equation, Eq. (5.63)
B	constant in Redlich–Kister equation, Eq. (9.77)
b	excluded molar volume, m^3/mol
b	constant in van der Waals equation of state Eq. (5.34)
b	constant in Redlich–Kwong equation of state Eq. (5.65)
C	number of components in the Gibbs phase rule Eq. (8.89)

C	integration constant
C	heat capacity, J/K
C	constant in heat capacity of ideal gas, liquid, or solid, Eqs. (4.123)–(4.126), K^{-2}
C	constant in Antoine's equation, Eq. (5.57)
C	constant in virial equation of state Eq. (5.70)
C'	constant in Eq. (5.72)
C	constant in Redlich–Kister equation, Eq. (9.77)
C_p	specific or molar heat capacity at constant pressure, J/K · mol, Eq. (4.104)
$\overline{C}_p$	specific heat capacity per unit mass at constant pressure, J/K · kg, Eq. (4.104)
$\overline{C}_p$	molar heat capacity of a mixture, Eq. (4.127)
C_v	specific or molar heat capacity at constant volume, J/K · mol, Eq. (4.98)
$\overline{C}_v$	specific heat capacity per unit mass at constant volume, J/K · kg, Eq. (4.98)
c	concentration, in gas or liquid phase, mol/l or mol/m^3, Section 16.13
c	speed of light, 3×10^8 m/s
D	constant in Section 2.1.2
D	constant in heat capacity of ideal gas, liquid, or solid, Eqs. (4.123)–(4.126), K^2
D	constant in virial equation of state Eq. (5.70)
D'	constant in Eq. (5.72)
d	thickness, m or cm
d	differential, exact
$\overline{\mathrm{d}}$	differential, inexact
E	energy, J
E	electric field, V/m, Eq. (2.74)
E_k	kinetic energy, J
$\overline{E}_k$	specific kinetic energy, J/kg
E_p	potential energy, J
$\overline{E}_p$	specific potential energy, J/kg
E_T	total energy, J
$\mathbf{e}_x$	unit vector in x-direction
$\mathbf{e}_y$	unit vector in y-direction
$\mathbf{e}_z$	unit vector in z-direction
F	number of degrees of freedom in the Gibbs phase rule Eq. (8.89)
F	function in Section 17.4
F	force, N or dyn
$\overline{\mathbf{F}}$	force per unit mass N/kg
F_b	buoyancy force, Section 2.3
F_compress	compressive force
F_g	gravity force, N
F_p	pressure force, N
F_pul	tensile force, N
F_γ	surface tension force, N
f	function, generally
f	function in Section 17.4

f	function in Eq. (7.9)
f	fugacity, atm or bar
f_i°	fugacity of pure component i, atm or bar
$\hat{f}_i$	fugacity of component i in a solution, atm or bar
f	efficiency of a real engine divided by the efficiency of an ideal heat engine, Eq. (7.24)
G	Gibbs free energy, J
$\overline{G}$	specific Gibbs free energy, J/kg; or molar Gibbs free energy in J/mol
G	universal gravitational constant, 6.674×10^{-10} N m^2/kg^2
G	function defined in Eq. (14.35), related to the probabilities of various states
g or g_0	acceleration due to gravity, m/s^2
$\mathbf{g}$	gravity vector
g_z	component of gravity vector in the z-direction
g	function in Eq. (7.11)
H	enthalpy, J
$\overline{H}$	specific enthalpy in J/kg or molar enthalpy, J/mol
H	Henry's law constant, Eq. (11.6)
h	height, m
I	electric current, Eq. (2.76)
K	dimensionless Henry's law constant, Eq. (11.9)
K	Nernst partition coefficient, Eq. (12.6)
K	equilibrium constant of reaction, Eq. (16.74), dimensionless
K_f	equilibrium constant of reaction in terms of fugacities, in Eq. (16.76), dimensionless
K_p	equilibrium constant of reaction in terms of partial pressures in the gas phase, in Eq. (16.75), dimensionless
K_x	equilibrium constant of reaction in terms of mole fractions, Eq. (16.76), dimensionless
K_x	mass transfer coefficient in the liquid phase, Eq. (11.11)
K_y	equilibrium constant of reaction in terms of mole fractions in gas phase, Eq. (16.78)
K_y	mass transfer coefficient in the liquid phase, Eq. (11.10)
K_ϕ	equilibrium constant of reaction in terms of fugacity coefficients, Eq. (16.79)
k_B	Boltzmann's constant, 1.38×10^{-23} J/K
k	reaction equilibrium constant; may have dimensions; see Section 16.13
L	length, m
L_x	length in x-direction, m
l	length, m
M	molecular mass (or molecular weight)
M	function of two or three variables, Chapter 4
M	number of systems in an ensemble, Chapter 14
$\overline{M}_n$	number-average molecular mass (or molecular weight)
m	mass, kg
$\dot{m}$	mass flow rate, kg/s
$\mathbf{m}$	unit vector

N	number of moles
N	number of molecules, Chapter 14
N	number of components
N	function of two or three variables
N_A	Avogadro's number, 6.023×10^{23} molecules/mol
N_i	number of moles of component i
N_s	number of molecules at surface
n	number of molecules
n	number of moles
n	efficiency of a heat engine, Chapter 7
n	number of systems with the same properties, Chapter 14
$\mathbf{n}$	unit vector
n_p	efficiency of a heat pump
n_R	efficiency of a refrigerator or air-conditioner
P	number of phases in the Gibbs phase rule Eq. (8.89)
P_i	probability of a state or of a configuration, Chapter 14
p	pressure, Pa, atm, psi, or cm of water
$\boldsymbol{p}$	pressure matrix
$\boldsymbol{p}$	pressure tensor
$\overline{p}$	ensemble-average pressure, atm
p_c	critical pressure, Pa, bar, or atm
p°	vapor pressure, Pa, bar, or atm
p_0	reference or atmospheric pressure, atm, or Pa
p_r	reduced or dimensionless pressure, p/p_c
p_{ext}	external pressure outside a system
p_f	pressure in film
p_g	gauge pressure, atm, or Pa, $p - p_0$
p_{int}	internal pressure, atm
p_i	pressure inside a spherical drop or bubble, Eq. (15.35)
p_o	pressure outside a spherical drop or bubble, Eq. (15.35)
p_r	pressure for a spherical interface
p_∞	pressure for a flat interface (infinite radius of curvature)
p_v	vacuum pressure, atm, or Pa, $p_0 - p$
p_x	pressure in the x-direction
p_y	pressure in the y-direction
p_z	pressure in the z-direction
p_{xx},	components of the pressure matrix
p_{xy}, etc.,	
p_1	partial pressure of component 1 in a gas mixture, atm
Q	heat, J
$\dot{Q}$	heat flow rate, J/s
$\overline{Q}$	heat per mol or per unit mass, J/mol or J/kg or (J/s)/(kg/s)
Q	canonical partition function, Eq. (14.24)

Q_{rev} reversible heat
q electric charge, Eq. (2.74)
R universal gas constant, 8.314 J/mol/K
R radius, m
R electrical resistance, Ω
r radius, m
r_i inside radius in heat exchanger, Section 6.6.7
r_o outside radius in heat exchanger, Section 6.6.7
r radial coordinate
S area, m^2
S entropy, J/K
$\overline{S}$ specific entropy in J/K · kg or molar entropy in J/K · mol
S selectivity, Eq. (10.1)
T absolute temperature, K
T_c critical temperature, K
T_C cold fluid temperature in heat exchanger
T_H hot fluid temperature in heat exchanger
T_{id} ideal gas temperature, K
T_r reduced or dimensionless temperature, T/T_c
T_r temperature of surroundings, K
t time, s
$\mathbf{t}$ unit tangent
U internal energy, J
$\overline{U}$ specific internal energy, J/kg, or molar internal energy, J/mol
U overall heat transfer coefficient, in J/s · K · m^2, Eq. (6.32)
U_i overall heat transfer coefficient, in J/s · K · m^2 based on inside area
U_o overall heat transfer coefficient, in J/s · K · m^2 based on outside area
$\overline{U}_{tr}$ translational kinetic energy, Eq. (5.13)
u velocity of molecule, m/s
V voltage, V, Eq. (2.76)
V volume, m^3
$\overline{V}_c$ critical molar volume, m^3/mol
V_r reduced or dimensionless molar volume, $\overline{V}/\overline{V}_c$
V_l volume of liquid phase, m^3
$\overline{V}$ specific molar volume, m^3/kg, or molar volume, m^3/mol
$\overline{V}_l$ partial molar volume, m^3/mol
v velocity, m/s
w steam quality, no units
W work, J
W rate of work, J/s
$\dot{W}$ rate of total work, J/s
W_{el} electrical work, Eq. (2.74)
W_{irrev} irreversible work

W_{rev}	reversible work
W_s	shaft work
$\dot{W}_s$	rate of shaft work
W_T	total work
x	displacement or distance, m
x	mole fraction in mixture, usually in a liquid phase, x_1 or x_2
x^A	mole fraction of A in mixture
x_1^A	binodal mole fraction
y	mole fraction in a mixture, usually in a gas or vapor phase
y	coordinate, or distance
Z	compressibility factor,
$\overline{Z}_1$	partial molar compressibility factor
z	coordinate or height or depth, m
z	concentration, Section 16.13, mol/l

Superscripts

E	excess property over the ideal solution
∞	at infinite dilution as the mole fraction of the solute goes to zero
L	liquid phase
mix	after mixing, or of mixing, two or more components to form a solution
V	vapor phase

Subscripts

b	binodal, Section 9.5
sp	spinodal, Section 9.5

Greek symbols

α	Lagrange multiplier in Section 14.4
β	Lagrange multiplier in Section 14.4, equal to $1/(k_B T)$, Eq. (14.36)
β_p	Volume expansivity, K^{-1}
Γ or Γ_2^*	surface excess molar density, mol/m^2, Eq. (15.35)
Γ_c	surface density of component i ($i = 1, 2, \ldots$)
γ	surface tension, mN/m or dyn/cm, Eq. (15.28)
γ_o	surface tension of solvent, mN/m
γ	ratio of heat capacities, C_p/C_v
Δ	difference or sum
δ	thickness, m
δ_n	small quantity of n
ε	height, m or cm