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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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Thermodynamics with Chemical Engineering Applications

ELIAS I. FRANSES
Purdue University

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and Ying-Chuen Wang.

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

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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.

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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
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
$\overline{F}$	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
$\mathbf{g}_z$	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
$\mathbf{p}$	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
$\mathbf{p}_{xx}$, $\mathbf{p}_{xy}$, etc.,	components of the pressure matrix
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
$\overline{V}_1$	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, . . .)
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

ε	extent of reaction, equilibrium
ε_{d}	extent of reaction, dynamic, Section 16.4
$\varepsilon_{\mathrm{eq}}$	extent of reaction, equilibrium
θ	angle
θ	empirical temperature, in degrees Celsius (or Fahrenheit)
κ_T	isothermal compressibility, bar^{-1}
λ	distance or thickness, m
λ	Lagrange multiplier, Section 17.4
μ	chemical potential, J/mol
μ	viscosity, poise (C.G.S. units) or Pa · s (S.I. units)
v	Joule–Thomson coefficient, K/atm
v_{JT}	Joule–Thomson coefficient, Eq. (6.72), K/atm
v	stoichiometric coefficient of a reaction, Chapter 16
Π	osmotic pressure, N or atm
ρ	density, $\mathrm{g/cm^3}$ or $\mathrm{kg/m^3}$
ρ_{a}	density of air
ρ_{g}	density of gas phase
ρ_{l}	density of liquid phase
ρ_{s}	density of solid phase
τ	stress, $\mathrm{N/m^2}$
$\boldsymbol{\tau}$	stress tensor
ϕ_i°	fugacity coefficient of pure component *i*
$\hat{\phi}_i$	fugacity coefficient of component *i* in solution
Ω	number of systems in an ensemble, Chapter 14
ω	Pitzer's acentric factor, Eq. (5.79)

Other symbols

$\int_{\mathrm{S}}$	surface integral
$\int_{\mathrm{V}}$	volume integral
$\int_{\mathrm{C}}$	line integral
$\oint_{\mathrm{C}}$	line integral along a closed line