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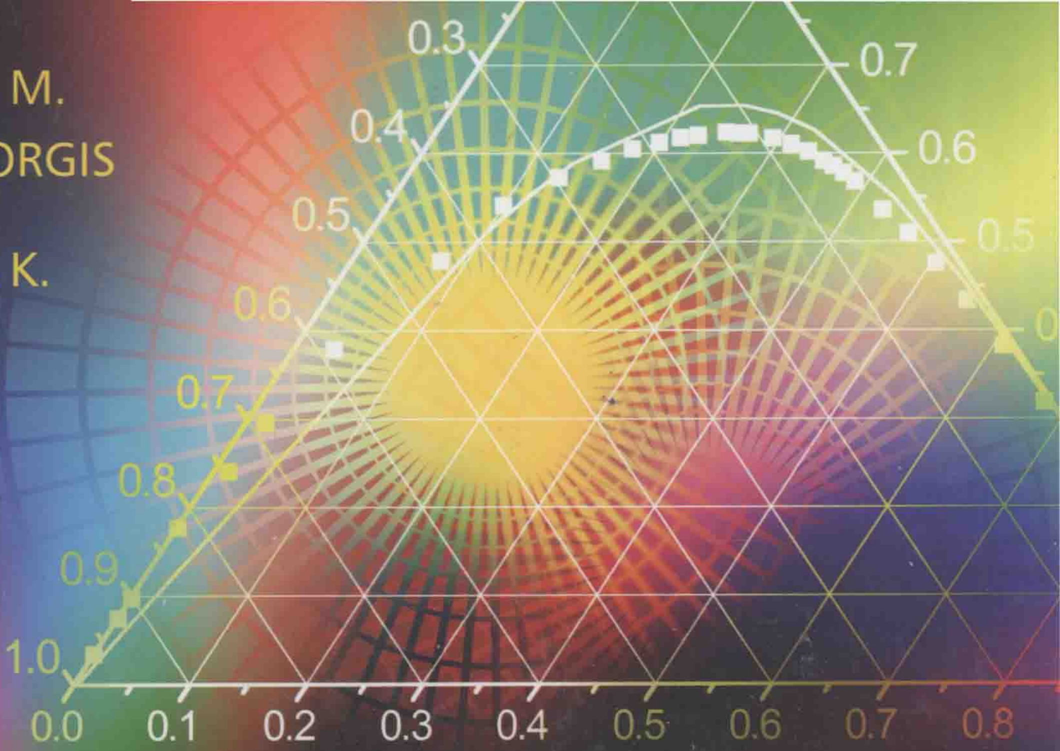

THERMODYNAMIC MODELS FOR INDUSTRIAL APPLICATIONS

FROM CLASSICAL AND ADVANCED MIXING RULES TO ASSOCIATION THEORIES

WILEY

Thermodynamic Models for Industrial Applications

From Classical and Advanced Mixing Rules to Association Theories

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Thermodynamic Models for Industrial Applications

No man lives alone and no books are written in a vacuum either.
Our families especially (in Denmark, The Netherlands and Greece)
have deeply felt the consequences of the process of writing this book.

I (Georgios Kontogeorgis) would like to dedicate the book to my wife
Olga for her patience, support, love and understanding – especially as,
during the period of writing of this book, our daughter,
Elena, was born.

I (Georgios Folas) would like to thank Georgios Kontogeorgis for
our excellent collaboration in writing this monograph during the past
two years. I am grateful to my family and wish to dedicate this book to
my wife Athanasia for always inspiring and supporting me.

Preface

Thermodynamics plays an important role in numerous industries, both in the design of separation equipment and processes as well as for product design and optimizing formulations. Complex polar and associating molecules are present in many applications, for which different types of phase equilibria and other thermodynamic properties need to be known over wide ranges of temperature and pressure. Several applications also include electrolytes, polymers or biomolecules. To some extent, traditional activity coefficient models are being phased out, possibly with the exception of UNIFAC, due to its predictive character, as advances in computers and statistical mechanics favor use of equations of state. However, some of these 'classical' models continue to find applications, especially in the chemical, polymer and pharmaceutical industries. On the other hand, while traditional cubic equations of state are often not adequate for complex phase equilibria, over the past 20–30 years advanced thermodynamic models, especially equations of state, have been developed.

The purpose of this work is to present and discuss in depth both 'classical' and novel thermodynamic models which have found or can potentially be used for industrial applications. Following the first introductory part of two short chapters on the fundamentals of thermodynamics and intermolecular forces, the second part of the book (Chapters 3–6) presents the 'classical' models, such as cubic equations of state, activity coefficient models and their combination in the so-called EoS/G^E mixing rules. The advantages, major applications and reliability are discussed as well as the limitations and points of caution when these models are used for design purposes, typically within a commercial simulation package. Applications in the oil and gas and chemical sectors are emphasized but models suitable for polymers are also presented in Chapters 4–6.

The third part of the book (Chapters 7–14) presents several of the advanced models in the form of association equations of state which have been developed since the early 1990s and are suitable for industrial applications. While many of the principles and applications are common to a large family of these models, we have focused on two of the models (the CPA and PC–SAFT equations of state), largely due to their range of applicability and our familiarity with them. Extensive parameter tables for the two models are available in the two appendices on the companion website at www.wiley.com/go/Kontogeorgis. The final part of the book (Chapters 15–20) illustrates applications of thermodynamics in environmental science and colloid and surface chemistry and discusses models for mixtures containing electrolytes. Finally, brief introductions about the thermodynamic tools available for mixtures with biomolecules as well as the possibility of using quantum chemistry in engineering thermodynamics conclude the book.

The book is based on our extensive experience of working with thermodynamic models, especially the association equations of state, and in close collaboration with industry in the petroleum, energy, chemical and polymer sectors. While we feel that we have included several of the exciting developments in thermodynamic models with an industrial flavor, it has not been possible to include them all. We would like, therefore, to apologize in advance to colleagues and researchers worldwide whose contributions may not have been included or adequately discussed for reasons of economy. However, we are looking forward to receiving comments and suggestions which can lead to improvements in the future.

The book is intended both for engineers wishing to use these models in industrial applications (many of them already available in commercial simulators, as stand-alone or in CAPE-Open compliant format) and for students, researchers and academics in the field of applied thermodynamics. The contents could also be used in graduate courses on applied chemical engineering thermodynamics, provided that a course on the fundamentals of applied thermodynamics has been previously followed. For this reason, problems are provided on the companion website at www.wiley.com/go/Kontogeorgis. Answers to selected problems are available, while a full solution manual is available from the authors.

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About the Authors

Georgios M. Kontogeorgis has been a professor at the Technical University of Denmark (DTU), Department of Chemical and Biochemical Engineering, since January 2008. Prior to that he was associate professor at the same university, a position he had held since August 1999. He has an MSc in Chemical Engineering from the Technical University of Athens (1991) and a PhD from DTU (1995). His current research areas are energy (especially thermodynamic models for the oil and gas industry), materials and nanotechnology (especially polymers – paints, product design, and colloid and surface chemistry), environment (design CO_2 capture units, fate of chemicals, migration of plasticizers) and biotechnology. He is the author of over 100 publications in international journals and co-editor of one monograph. He is the recipient of the Empirikion Foundation Award for 'Achievements in Chemistry' (1999, Greece) and of the Dana Lim Price (2002, Denmark).

Georgios K. Folas was appointed as technologist in the distillation and thermal conversion department, Shell Global Solutions (The Netherlands) in January 2009. He previously worked as Senior Engineer (Facilities and Flow Assurance) in Aker Engineering & Technology AS (Oslo, Norway). He has an MSc in Chemical Engineering from the Technical University of Athens (2000) and an industrial PhD from DTU (2006), in collaboration with Statoilhydro (Norway). He is the author of 15 publications in international journals and the recipient of the Director Peter Gorm-Petersens Award for his PhD work.

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We wish to thank all our students and colleagues and especially the faculty members of IVC-SEP Research Center, at the Department of Chemical and Biochemical Engineering of the Technical University of Denmark (DTU), for the many inspiring discussions during the past 10 years which have largely contributed to the shaping of this book. Our very special thanks go to Professor Michael L. Michelsen for the endless discussions we have enjoyed with him on thermodynamics.

In the preparation of this book we have been assisted by many colleagues, friends, current and former students. Some have read chapters of the book or provided material prior to publication, while we have had extensive discussions with others. We would particularly like to thank Professors J. Coutinho, G. Jackson, I. Marrucho, J. Mollerup, G. Sadowski, L. Vega and N. von Solms, Doctors M. Breil, H. Cheng, Ph. Coutsikos, J.-C. de Hemptinne, I. Economou, J. Gabrielsen, A. Grenner, E. Karakatsani I. Kouskoumvekaki, Th. Lindvig, E. Solbraa, N. Sune, A. Tihic, I. Tsivintzelis and W. Yan, as well as the current PhD and MSc students of IVC-SEP, namely A. Avlund, J. Christensen, L. Faramarzi, F. Leon, B. Maribo-Mogensen and A. Sattar-Dar.

All contributions have been highly valuable and we are deeply grateful for them.

List of Abbreviations

AAD %	percentage average absolute deviation: $AAD\,\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{x_{\exp,i} - x_{calc,i}}{x_{\exp,i}}\right) \cdot 100$ for a property x
AM	arithmetic mean rule (for the cross co-volume parameter, b_{12})
AMP	2-amino-2-methyl-1-propanol
ATPS	aqueous two-phase systems
BCF	bioconcentration factor
BR	butadiene rubber (polybutadiene)
BTEX	benzene–toluene–ethylbenzene–xylene
CCC	critical coagulation concentration
CDI	chronic daily intake
CK–SAFT	Chen–Kreglewski SAFT
CMC	critical micelle concentration
Comb-FV	combinatorial free volume (effect, term, contributions)
COSMO	conductor-like screening model
CPA	cubic-plus-association
CPP	critical packing parameter
CS	Carnahan–Starling
CSP	corresponding states principle
CTAB	hexadecyl trimethylammonium bromide
DBE	dibutyl ether
DDT	dichlorodiphenyltrichloroethane
DEA	diethanolamine
DEG	diethylene glycol
DFT	density functional theory
DH	Debye–Hückel
DiPE	diisopropyl ether
DIPPR	Design Institute for Physical Property (database)
DLVO	Derjaguin–Landau–Verwey–Overbeek (theory)
DME	dimethyl ether
DPE	dipropyl ether
ECR	Elliott's combining rule
EoS	Equation of state
EPA	Environmental Protection Agency
EPE	ethyl propyl ether
ESD	Elliott–Suresh–Donohue (EoS)
EU	European Union
FCC	Face-centered cubic structure (close packed, $Z = 12$)

FH	Flory–Huggins
FOG	first-order groups
FV	Free volume
GC	group contribution (methods, principle)
GCA	group contribution plus association
GCVM	group contribution of Vidal and Michelsen mixing rules
GERG	Group Européen de Recherche Gazière
GLC	gas–liquid chromatography
GLE	gas–liquid equilibria
GM	geometric mean rule (for the cross-energy parameter, a_{12})
HB	hydrogen bonds/bonding
HCB	hexachlorobenzene
HF	Hartree–Fock
HIC	hydrophobic interaction chromatography
HLB	hydrophilic–lipophilic balance
HSP	Hansen solubility parameters
HV	Huron–Vidal mixing rule
IEC	ion-exchange chromatography
LALS	low-angle light scattering
LC	local composition (models, principle, etc.)
LCST	lower critical solution temperature
LCVM	linear combination of Vidal and Michelsen mixing rules
LGT	linear gradient theory
LJ	Lennard-Jones
LLE	liquid–liquid equilibria
LR	Lewis–Randall; long range
mCR-1	modified CR-1 combining rule (for the CPA EoS), equation (9.10)
MC–SRK	Mathias–Copeman SRK
MDEA	methyl diethanolamine
MEA	monoethanolamine
MEG	(mono)ethylene glycol
MEK	methyl ethyl ketone
MHV1	modified Huron–Vidal first order
MHV2	modified Huron–Vidal second order
MM	McMillan–Mayer
MO	molecular orbital
MSA	mean spherical approximation
MW	molecular weight
NLF–HB	lattice–fluid hydrogen bonding (EoS)
NP	number of experimental points
NRHB	non-random hydrogen bonding (EoS)
NRTL	non-random two liquid
PAHs	polynuclear aromatic hydrocarbons
PBA	poly(butyl acrylate)
PBD	polybutadiene
PBMA	poly(butyl methacrylate)
PCBs	polychlorinated biphenyls

PC–SAFT	perturbed-chain SAFT
PDH	Pitzer–Debye–Hückel
PDMS	poly(dimethyl siloxane)
PEA	poly(ethyl acrylate)
PEG	(poly)ethylene glycol
PIB	polyisobutylene
PIPMA	poly(isopropyl methacrylate)
PM	primitive model
PMA	poly(methyl acrylate)
PMMA	poly(methyl methacrylate)
PP	polypropylene
PPA	poly(propyl acrylate)
PR	Peng–Robinson
PS	polystyrene
PSRK	predictive Soave–Redlich–Kwong
PVAc	poly(vinyl acetate)
PVAL	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
PVT	pressure, volume, temperature
PZ	piperazine
QC	quantum chemistry
QM	quantum mechanics
QSAR	quantitative structure–activity relationships
RDF	radial distribution function
RK	Redlich–Kwong
RP-HPLC	reversed-phase high-pressure liquid chromatography
RPM	restrictive primitive model
RST	regular solution theory
SAFT	statistical associating fluid theory
SCFE	supercritical fluid extraction
SDS	sodium dodecyl sulfate
SGE	solid–gas equilibria
SL	Sanchez–Lacombe
SOG	second-order groups
SLE	solid–liquid equilibria
SR	short range
SRK	Soave–Redlich–Kwong (EoS)
SVC	second virial coefficients
SWP	Sako–Wu–Prausnitz (EoS)
TEG	triethylene glycol
THF	tetrahydrofurane
UCST	upper critical solution temperature
UMR–PR	universal mixing rule (with the PR EoS)
UNIFAC	universal quasi-chemical functional group activity coefficient
UNIQUAC	universal quasi-chemical
vdW	van der Waals (EoS)
vdW1f	vdW one-fluid (mixing rules)

VLE	vapor–liquid equilibria
VLLE	vapor–liquid–liquid equilibria
VOR	volatile organic compound
VR	variable range
VTPR	volume-translated Peng–Robinson (EoS)
WHO	World Health Organization
WS	Wong–Sandler
WWF	World Wide Fund for Nature
$\Delta P\%$	average absolute percentage error: $\Delta P\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{P_{exp,i}-P_{calc,i}}{P_{exp,i}}\right)\cdot 100$ in bubble point pressure P of component i
Δy	average absolute percentage deviation: $\Delta y = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(y_{exp,i}-y_{calc,i}\right)$ in the vapor phase mole fraction of component i
$\Delta\rho\%$	average absolute percentage deviation: $\Delta\rho\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{\rho_{exp,i}-\rho_{calc,i}}{\rho_{exp,i}}\right)\cdot 100$ in the liquid density of component i

List of Symbols

a	energy term in the SRK term (bar l^2/mol^2) *or* activity *or* particle radius
a_0	surfactant head area
a_{ij}	non-randomness parameter of molecules of type i around a molecule of type j
a_{mk}, $a_{mk,1}$, $a_{mk,2}$, $a_{mk,3}$	UNIFAC temperature-dependent parameters, K
A	surface area *or* Helmholtz energy *or* Hamaker constant
A_{eff}	effective Hamaker constant
A_i	site A in molecule i
A_{ii}	Hamaker constant of particle/surface i–i
$A_{m,i}$	parameter in Langmuir constant, K/bar
A_{spec}	specific surface area, typically in m^2/g
A_0	area occupied by a gas molecule
$\tilde{a}$	reduced Helmholtz energy
a_0	parameter in the energy term of CPA (bar L^2/mol^2) *or* area of the head of a surfactant molecule
A_1, A_2, A_3	parameters in GERG model for water
A_{123}	Hamaker constant between particles (or surfaces) 1 and 3 in medium 2
b	co-volume parameter (l/mol) of cubic equations of state
B	second virial coefficient
B_j	site B in molecule j
$B_{m,i}$	parameter in Langmuir constant, K
C	molar concentration (often in mol/l or mol/m^3) *or* concentration (in general) *or* the London coefficient
c_1	parameter in the energy term of CPA
$C_{m,i}$	Langmuir constant for component i in cavity m
d	density (eq. 4.29) *or* temperature-dependent diameter
D	Diffusion coefficient *or* dielectric constant
E	modulus of Elasticity
f	fugacity, bar
f	fugacity, bar
F	Force
G	Gibbs energy
G^E, g^E	excess Gibbs energy
g_{ji}/R	Huron–Vidal energy parameter, characteristic of the $j-i$ interaction, K
g	radial distribution function
h	Planck's constant, 6.626×10^{-34} J s
H	enthalpy
H	interparticle or interface distance *or* (H_i) Henry's law constant
I	first ionization potential, J *or* ionic strength

k	Boltzmann's constant, J/K
K_i	Distribution factor e.g. Table 1.3
K	chemical equilibrium constant
k_{12}, k_{ij}	binary interaction parameter (in equations of state)
K_{OW}	octanol–water partition coefficient
K^{ref}	chemical equilibrium constant at the reference temperature
l	parameter in the Hansen–Beerbower–Skaarup equation (eq. 18.8) *or* distance between charges in a molecule (eq. 2.2a or 2.2b)
l_c	length of a surfactant molecule
m	segment number *or* molality
MW, M	molecular weight (molar mass)
N_A	Avogadro's number $= 6.0225 \times 10^{23}$ mol/mol
N_{agg}	aggregation (or aggregate) number
n	refractive index
n_T	true number of moles
n_o	apparent number of moles
P	pressure, bar
P^{sat}	saturated vapor pressure
q	charge
Q	quadrupole moment, C m^2
Q_k	surface area parameter for group k
Q_w	van der Waals surface area
R	gas constant, bar l/mol/K *or* molecular radius
r	radial distance from the center of the cavity, Å *or* intermolecular distance
R_i	the radius of cage i, Å
R_k	volume parameter for group k
S	Harkins spreading coefficient *or* entropy
T	temperature, K
T_c	critical temperature, K
$T_{m,i}$	melting temperature of the component i, K
T_r	reduced temperature
T^{ref}	reference temperature, K
T_0	arbitrary temperature for linear UNIFAC (in the temperature dependency of the energy parameters), see Table 5.7
U	composition variable *or* internal energy
V_A	(van der Waals) potential energy
$\tilde{V}$	reduced volume
V^*	hard-core volume
V	volume
V_c	critical volume
V_f	free volume
V_g	gas volume at STP conditions ($= 22\,414$ cm^3/mol)
$\bar{V}_i$	partial molar volume
V_m	molar volume (L mol^{-1}) *or* maximum volume occupied by a gas (in adsorption in a solid)
V_W^{ICE}	molar volume of ice, l mol^{-1}
V_w	van der Waals volume
$W(r)$	cell potential function, J

X	monomer fraction
X_{A_i}	fraction of A-sites of molecule i that are not bonded
x_i	liquid mole fraction of component i
y	reduced density, eq. 2.11 *or* 9.12
y_i	vapor mole fraction of component i
Z	compressibility factor *or* co-ordination number
Z_i	ionic valence
ΔCp_i	heat capacity change of the component i at the melting temperature, J/mol/K
ΔG	Gibbs free energy change (also of micellization)
ΔH	enthalpy change (also of micellization)
$\Delta h_w^{EH-L_0}$	enthalpy differences between the empty hydrate lattice and liquid water, J/mol
ΔH_i^{fus}	heat of fusion of the component i at the melting temperature, J/mol
$\Delta\mu_w^0$	chemical potential difference between the empty hydrate and pure liquid water, J/mol
ΔS	entropy change (also of micellization)
$\Delta V_w^{EH-L_0}$	molar volume differences between the empty hydrate lattice and liquid water, J/mol

Greek letters

α_0	electronic polarizability
α	polarizability *or* Kamlet acid parameter *or* distance of closest approach (Chapter 15)
α	reduced energy $(=\frac{\alpha}{bRT})$, eq. (3.16) & Table 6.3
β	Kamlet base parameter
$\beta^{A_iB_j}$	association volume parameter between site A in molecule i and site B in molecule j (dimensionless) [in CPA]
γ	mole-based activity coefficient *or* surface *or* interfacial tension
γ_i^C	combinatorial part of activity coefficient for the component i
γ_i^r	residual part of activity coefficient for the component i
γ^∞	infinite dilution coefficient
$\Gamma(r)$	potential energy–distance function
Γ_k	activity coefficient of group k at mixture composition *or* adsorption of compound (k)
Γ_k^i	activity coefficient of group k at a group composition of pure component i
$\Gamma_{\max}$	maximum adsorption (often in mol/g)
δ	solubility parameter, $(\mathrm{J/cm^3})^{1/2}$
Δ	association strength, l/mol
ε	dispersion energy parameter, association energy, J
ε_0	permittivity of vacuum (free space), $8.854 \times 10^{-12}\,\mathrm{C^2/J/m}$
ε_r	dielectric constant (dimensionless)
$\varepsilon^{A_iB_j}$	association energy parameter between site A in molecule i and site B in molecule j, bar l/mol
ζ	partial volume fraction *or* zeta potential
η	the reduced fluid density of CPA *or* volume fraction of PC–SAFT
ϑ	contact angle *or* surface area fraction
θ_i	surface area fraction for component i in the mixture
Θ	occupancy of cavity m by component i
κ	association volume of PC–SAFT *or* Debye screening length, eq. 15.25
μ	dipole moment in Debye *or* (μ_i) chemical potential
v	main electronic absorption frequency in the UV region (about 3×10^{15} Hz)
ν_i	number of cavities of type i

ν_{ki}	number of groups of type k in molecule i
π	surface pressure ($= \gamma_w - \gamma$)
$\Delta\varphi$	electrical potential difference, eq. 19.35
ψ_0	surface potential
ρ	molar density, mol/l
σ	segment diameter, Å
τ_{ji}	Boltzmann factor (in local composition models), eq. (5.1)
Φ	(volume/segment) fraction
$\hat{\varphi}_i$	fugacity coefficient of component i in a mixture
ω	acentric factor
χ_{12}	Flory-Huggins (interaction) parameter
Ω	weight-based activity coefficient
Ω_1^∞	infinite dilution weight-based activity coefficient

Superscripts and subscripts

AB	site A–site B
A_iB_j	site A in molecule i with site B in molecule j
A, B, C, D	site indicators
A	anion or attractive
AB	acid–base interactions
Adh, A	adhesion
attr	attractive
assoc	association
b	boiling point/temperature
c or *crit*	critical
C	cation or combinational
chem	chemical
cal	calculated value
Coh	cohesion
comb	combinatorial
comb-fv	combinatorial free volume
d or *disp*	dispersion
DP	data points
DH	Debye-Hückel
E	excess
EH	empty hydrate
eq	equilibrium
excl	excluded
exp	experimental value
fv, FV	free volume
f,*fus*	fusion
FH	Flory-Huggins
g or *gas*	gas
H	hydrate
h or *hb, HB*	hydrogen bonding
hc	hard chain