# Thermodynamic Models for Industrial Applications

## From Classical and Advanced Mixing Rules to Association Theories

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*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.*

# Contents

# 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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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:<br>$AAD\,\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{x_{\exp,i}-x_{calc,i}}{x_{\exp,i}}\right)\cdot 100$<br>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:<br>$\Delta P\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{P_{exp,i}-P_{calc,i}}{P_{exp,i}}\right)\cdot 100$<br>in bubble point pressure $P$ of component $i$ |
| $\Delta y$ | average absolute percentage deviation:<br>$\Delta y = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(y_{exp,i}-y_{calc,i}\right)$<br>in the vapor phase mole fraction of component $i$ |
| $\Delta\rho\%$ | average absolute percentage deviation:<br>$\Delta\rho\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{\rho_{exp,i}-\rho_{calc,i}}{\rho_{exp,i}}\right)\cdot 100$<br>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, $6.626 \times 10^{-34}$ 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 |