THERMODYNAMIC PROPERTIES AND MODELS FOR ENGINEERING APPLICATIONS

Georgios M. Kontogeorgis
Technical University of Denmark

Keywords: Thermodynamic models, phase equilibria, cubic equations of state, activity coefficient models, mixing rules, association models, CPA, SAFT, biotechnology, colloids and interfaces, electrolytes, chemical reactions

Contents

Summary

This chapter highlights the important thermodynamic models available to-date for engineering applications, especially those related to petroleum, chemical, material (including polymer), and pharmaceutical industries as well as biotechnology. While thermodynamic models can be used for calculating a wide range of properties, it is especially phase behavior that is emphasized in this work. First, the basic models (cubic equations of state and activity coefficient models) are presented with special emphasis on the solubility parameters, local composition and group contribution concepts. This section is completed with an application of thermodynamics in assessing the fate of persistent chemicals and their distribution in environmental ecosystems. Advanced mixing rules for the cubic equations of state and the association models based on perturbation theory especially the SAFT and CPA equations of state are discussed next. Some results are also shown for aqueous and multicomponent systems. Finally, four challenging areas and applications are presented; models for electrolytes, thermodynamics in biotechnology and for colloids and interfaces as well as in conjunction to chemical reactions. In all areas, case studies and examples are presented. The chapter closes with an outlook to the future.

1. Introduction – Importance of Thermodynamic Properties

The foundations of thermodynamics are its laws, which are the soundest theory, never so far revised. These laws provide a unique framework for describing physicochemical phenomena. However, despite their incredible beauty, these laws cannot take us very far without thermophysical/thermodynamic data.

Thermodynamic and transport property data are crucial in the oil & gas industries e.g. for flow assurance and oil recovery, in the chemical industries e.g. for the design of separation processes, in the pharmaceutical and polymer industries e.g. for solvent selection and emission control but also in the environmental science e.g. for the estimation of the distribution of chemical in various ecosystems and recently also in biotechnology e.g. the origin of many diseases is traced to aggregation of proteins and several protein separations also require thermodynamic data.

Many separation processes in chemical and biochemical engineering as well as in petroleum industries depend on phase equilibrium data. Depending on the application and compounds involved, different types of data are needed e.g. vapor-liquid equilibrium (VLE) for many distillations, liquid-liquid equilibrium (LLE) for liquid extractions and solid-liquid equilibrium (SLE) for crystallization. Accurate design of separation processes requires good phase equilibrium data. Prausnitz et al. (1999) mention that, in many cases, more than 40% of the cost of the design is related to the separation units.

Many researchers have tried to develop universal or semi-universal thermodynamic models which could be used for any type of compound, mixture and condition but this has not as yet been possible, as illustrated by the many available thermodynamic models. All the existing thermodynamic models are approximate, while most of them are empirical or semi-empirical. This is a picture far different from a universal thermodynamic theory.

Some of the most characteristic models will be briefly presented in this chapter. Commercial process simulators also offer many model choices, in some cases accompanied by "decision trees" for selecting the most appropriate ones, as shown by Carlson (1996). The reason why so many models are available/needed is because of the :

- Huge number of very diverse compounds and mixtures: hydrocarbons/oil, alcohols, water, polymers, electrolytes, biochemicals, proteins, enzymes,... - in all possible combinations !
- Almost infinite number of conditions (concentration, temperature, pressure) and phases in equilibrium (VLE, LLE, VLLE, SLE, SGE,..), but also due to
- Different needs in many applications e.g. do we need a detailed design (phase diagram) or a qualitative analysis (yes/no answer) and how fast is the answer needed?
- Experimental data are difficult to obtain for all these diverse systems and conditions

Fortunately, there are some "general" concepts or model categories which have wide applicability. These are:

- The cubic equations of state

- The corresponding states principle
- Regular solutions theory and solubility parameters
- The local composition concept and corresponding models (including the advanced mixing rules for equations of state based on these local composition type models)
- The group contribution concept
- The free-volume effect (especially for polymer solutions)
- The association theories

All these models and concepts will be addressed in this work.

-
-
-

Bibliography

A. George, Y. Chiang, B. Guo, A. Arabshahi, Z. Cai, W.W. Wilson (1994). Second Virial Coefficient as Predictor in Protein Crystal Growth *Acta Cryst*. D50, 361 [The concept of osmotic virial coefficients in crystallization]

A. Klamt (1995). Conductor-like screening model for real solvents – a new approach to the quantitative calculation of solvation phenomena. *J. Phys. Chem., 99(7)*, 2224-2235.
A. Klamt, G. Schuurmann (1993). COSMO – A new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient *J. Chem. Soc. Perkin Trans.*, *2(5)*, 799-805.. [Two articles from Dr. Klamt, the developer of the famous COSMO-RS model]

A.Bondi (1968) *Physical Properties of Molecular Crystals, Liquid and Glasses*. John Wiley and Sons, 1968. [An excellent now out of print book on properties of gases, liquids and solids]

A.M. Klibanov (2001). Improving enzymes by using them in organic solvents . *Nature*, *409(6817)*, 241-246. [Thermodynamic in Bio-catalysis]

Aa. Fredenslund, R. Jones, J.M. Prausnitz (1975) Group-contribution estimation of activity coefficients in non-ideal liquid mixtures. *AIChE J., 21*, 1086. [The first article where the UNIFAC model is presented]

B.E. Poling, J.M. Prausnitz, J.P. O'Connell, (2001). *The properties of gases and liquids* (5^{th} edition). McGraw-Hill.

C. Boukouvalas, N. Spiliotis, P. Coutsikos, N. Tzouvaras, D.P. Tassios (1994) Prediction of vapor-liquid equilibrium with the LCVM model – A linear combination of the Vidal and Michelsen Mixing Rules coupled with the original UNIFAC and the t-mPR equation of state. *Fluid Phase Equilibria*, *92*, 75 [The first article on the LCVM model]

C. K. Hall (2008). Thermodynamic and kinetic origins of Alzheimer's and related diseases: a chemical engineer's perspective . *AIChE J.*, 54(8), 1956-1962. [Thermodynamic concepts in understanding the cataract disease]

C. Tsonopoulos, J.L. Heidman, (1986). High-pressure vapor-liquid equilibria with cubic equations of state. *Fluid Phase Equilibria*, *29*, 391-414. [The opinion of oil industry for cubic equations of state. Old but still of interest!]

C.C.Chen, P.M.Mathias (2002), Applied Thermodynamics for Process Modeling *AIChE J.*,*48*, 194. [Article from researchers from ASPEN on industrial needs]

C.J. van Oss, D.R. Absolom, A.W. Neumann (1980). Applications of net repulsive van der Waals forces between different particles, macromolecules or biological cells in liquids. *Colloids and Interfaces, 1(1),* 45-56. [Two articles illustrating the van Oss et al. Acid-base theory in interfacial science and some applications]

C.J. van Oss, M.K. Chaudhury, R.J. Good (1987), Monopolar Surfaces *Advances in Colloid and Interface Science*

C.M. Hansen (2000). *Hansen Solubility Parameters. A User's Handbook*. CRC Press. [An excellent book summarizing tables and applications of the Hansen solubility parameters]

D. Mackay, (1991). *Multimedia Environmental Models: The Fugacity Approach.* Lewis Publishers Inc. [Famous book illustrating a novel approach for environmental assessment using thermodynamic concepts]

D.P. Tassios, (1993) *Applied Chemical Engineering Thermodynamics*, Springer-Verlag, [Textbook in applied thermodynamics, with special chapters on cubic EoS and statistical thermodynamics]

D.S. Abrams, J.M. Prausnitz (1975). Statistical thermodynamics of liquid mixtures-new expression for excess Gibbs energy of partly or completely miscible systems. *AIChE J., 21(1),* 116. [The first article of the UNIQUAC model]

D.S.H. Wong, S.I. Sandler, (1992). A theoretically correct mixing rule for cubic equations of state *AIChE J., 38(5)*, 671. [One of the first articles of the Wong-Sandler mixing rules for cubic EoS]

D-Y. Peng, D.B. Robinson, (1976) New two-constant equation of state *Ind. Eng. Chem. Fundam., 15(1),* 59. [the first article on the famous Peng-Robinson equation of state]

E. Hendriks (2001),Applied Thermodynamics in Industry, A pragmatic approach. *Fluid Phase Equilibria, 311*, 83. [Recent article presenting needs and applications of thermodynamic models to the petroleum industry]

E. Hendriks, G.M. Kontogeorgis, R. Dohrn, J-C. de Hemptinne, I.G. Economou, L.F. Zilnik, V. Vesovic (2010), Industrial Requirements for Thermodynamics and Transport Properties. *Ind. Eng. Chem. Res.*, *49*, 11131. [Article presenting the results from a recent investigation on industrial needs for thermodynamic models based on questionnaires sent to industries; investigation carried out from EFCE working party on thermodynamic and transport properties]

E. McCafferty, (2002). Acid-base effects in polymer adhesion at metal surfaces, *J. Adhesion Sci. Technol., 16(3),* 239-255 [Article illustrating exciting applications of the acid-base theory to adhesion studies]

E.A. Carlson (1996) Don't gamble with physical properties for simulations. *Chem. Eng. Progress*, *October*, 35-46. [An article from ASPEN on industrial needs]

E.A. Macedo, (2005). Solubility of amino acids, sugars, and proteins . *Pure Appl. Chem., 77(3)*, 559-568. [Review on models for amino acid solutions]

E.C. Voutsas, Stamatis, F. Kolisis, D.P. Tassios (2002). Solvent effects on equilibrium position and initial rate of lipase-catalyzed esterification reactions in organic solvents: Experimental results and prediction capabilities *Biocatalysis and Biotransformation*, *20(2),* 101-109. [UNIFAC applied to enzyme-catalyzed reactions]

G. Soave, (1972). Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.*, 1197. [the first article on the famous Soave-Redlich-Kwong equation of state]

G. Wilson, (1964). Vapor-Liquid Equilibrium XI. A New Expression for the Excess Free Energy of Mixing, J. American. *J. Am. Chem. Soc.*, *86*, 127. [The first article of the Wilson equation]

G.M. Kontogeorgis, Aa. Fredenslund, D.P. Tassios (1993), A Simple Activity Coefficient Model for the Prediction of Solvent Activities in Polymer Solutions. *Ind. Eng. Chem. Res., 32,* 362. [The first article of the Entropic-FV model for polymer solutions]

G.M. Kontogeorgis, E. Voutsas, I. Yakoumis, D.P. Tassios, (1996). An equation of state for associating fluids. *Ind. Eng. Chem. Res., 35,* 4310.[The first article of the CPA equation of state]

G.M. Kontogeorgis, G.K. Folas (2010), *Thermodynamic models for industrial applications. From Classical and advanced mixing rules to association theories.* John Wiley and Sons. [Recent book on thermodynamic models for industrial applications, emphasis on SAFT and CPA type approaches]

G.M. Kontogeorgis, Ph. Coutsikos (2012). Thirty years with EoS/GE models – what have we learned? *Ind.*

Eng. Chem. Res., 51(11), 4119-4142. [Recent article reviewing the capabilities and limitations of the EoS/GE mixing rules]

H. Cheng, G.M. Kontogeorgis, E.H. Stenb (2002), Prediction of micelle formation for aqueous polyoxyethylene alcohol solutions with the UNIFAC model. *Ind. Eng. Chem. Res.*, *41(5)*, 892-898. [UNIFAC applications to CMC of surfactant solutions]

H. Renon, J.M. Prausnitz, (1968). Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures *AIChE J.*, *14(1)*, 135. [The first article of the NRTL model]

I. Tsivintzelis, I.G. Economou, G.M. Kontogeorgis, (2009). Modeling the solid-liquid equilibrium in pharmaceutical-solvent mixtures: systems with complex hydrogen bonding behavior. *AIChE J.*,*55(3)*, 756-770.

I. Tsivintzelis, I.G. Economou, G.M. Kontogeorgis, (2009). Modeling the phase behavior in mixtures of pharmaceuticals with liquid and supercritical solvents. *J. Phys. Chem. B*, *113*, 6446-6458. [Two articles on a new model, the NRHB EoS, for pharmaceuticals]

J. Abildskov, J.P. O'Connell (2005). Prediction of solubilities of complex medium-sized chemicals. Solutes in pure solvents, mixed solvents and cosolvent mixtures . Symposium on Computer-Aided Process Engineering-15, 20A and 20B Book Series: COMPUTER-AIDED CHEMICAL ENGINEERING, Volume: 20a-20b Pages: 217-222 Published: 2005. Editor(s): Puigjaner L; Espuna A [Application of simple models to pharmaceuticals]

J. Ahlers, J. Gmehling (2001) Development of an universal group contribution equation of state I. Prediction of liquid densities for pure compounds with a volume translated Peng-Robinson equation of state. *Fluid Phase Equilibria*, *191*, 177. [A new advanced mixing rule for cubic EoS, which is expected to have great impact in the future]

J. Gross, G. Sadowski (2001). Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res., 40(4)*, 1244-1260. [The first article where the PC-SAFT model is presented]

J.M. Prausnitz, (1996), . Molecular thermodynamics: Opportunities and responsibilities. *Fluid Phase Equilibria, 116*, 12-26.

J.M. Prausnitz, (1999). Thermodynamics and the other chemical engineering sciences: old models for new chemical products and processes *Fluid Phase Equilibria, 158-160*, 95-111.

J.M. Prausnitz, (2003) Molecular thermodynamics for some applications in biotechnology. *J. Chem. Thermodyn., 35*, 21-39.

J.M. Prausnitz, L. Foose, (2007) Three frontiers in the thermodynamics of protein solutions. *Pure Appl. Chem., 79*, 1435-1444.

J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo (1999). *Molecular Thermodynamics of Fluid-Phase Equilibria* (3rd edition). Prentice Hall Int. [Two excellent "classic" books by Prausnitz and co-workers on thermodynamic models and theories. A must in the field – both of them!]

J.M. Woll, T.A. Hatton (1989). A simple phenomenological thermodynamic model for protein partitioning in reversed micellar systems. *Bioprocess Engineering*, *4(5)*, 193-199. [Interesting article on the concept of partition coefficient in biotechnology using micelles]

J.M.Prausnitz, Th.Buck, Aa.Fredenslund, E. Hala, (1983). Panel discussion. 1. Current trends in research and development.´ *Fluid Phase Equilibria*, *14*, 403-408.

J.R. Svendsen, G.M. Kontogeorgis, S. Kiil, C. Weinell, , M. Grønlund,(2007). Adhesion between coating layers based on epoxy and silicon. *Journal of Colloid and Interface Science*, *316*, 678-686. [Application of the acid-base theory and other concepts on an industrial adhesion problem]

L.F. Cameretti, G. Sadowski (2008). Modeling of aqueous amino acid and polypeptide solutions with PC-SAPT. *Chemical Engineering and Processing, 47(6)*, 1018-1025. [Application of the PC-SAFT model to amino-acids]

M.J. Huron, J. Vidal (1979), New mixing rules in simple equations of state for representing vapor-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilibria, 3*, 255. [The original article of the Huron-Vidal model]

M.L. Michelsen, J.M. Mollerup, (2004, 2007). *Thermodynamic models: Fundamentals & Computational Aspects*. Tie-Line Publications, 2007 (2nd edition). [Excellent book by two pioneers on computational aspects for thermodynamic models. A "must" for anyone who wishes to program thermodynamic models]

M. Prausnitz, (1989)- Biotechnology: A new frontier for molecular thermodynamics. *Fluid Phase Equilibria*, 53, 439-451.[Six articles from prof. Prausnitz, one of the greatest scientists in applied thermodynamics. The articles handle needs and developments in thermodynamic modeling, as well as applications to biotechnology]

M.S. Wertheim, (1984). Fluids with highly directional attractive forces. 1, Statistical thermodynamics. *J. Stat. Phys., 35(1-2)*, 19-34.

M.S. Wertheim, (1984). Fluids with highly directional attractive forces. 2. Thermodynamic perturbation theory and integral equations. *J. Stat. Phys., 35(1-2)*, 35-47.

M.S. Wertheim, (1986). Fluids with highly directional attractive forces. 3. Multiple attraction sites *J. Stat. Phys., 42(3-4)*, 459-476.

M.S. Wertheim, (1986). Fluids with highly directional attractive forces. 4. Equilibrium polymerization. *J. Stat. Phys., 42(3-4)*, 477-492. [The four "classical" now articles of Wertheim which are considered the beginning/inspiration in the development of SAFT. They are hard to read and require knowledge of graph theory]

M.V. Flores, E.C. Voutsas, N. Spiliotis, G.M. Eccleston, G. Bell, D.P. Tassios (2001). Critical micelle concentrations of nonionic surfactants in organic solvents: Approximate prediction with UNIFAC *J. Colloid and Interface Science, 240(1)*, 277-283. [Application of UNIFAC models to CMC of surfactants]

N. von Solms, M.L. Michelsen G.M. Kontogeorgis (2003), Computational and Physical Performance of a modified PC-SAFT Equation of State for highly asymmetric and associating mixtures, *42*, 1098-1105. [The sPC-SAFT equation of state, a modification of the PC-SAFT model]

P. Kolar, J-W. Shen, A. Tsuboi, T. Ishikawam, T. (2002). Solvent selection for pharmaceuticals, *Fluid Phase Equilibria*, *194-197*, 771-782. [Article from Mitsubishi chemicals scientists on thermodynamic models for pharmaceutical applications]

P. Thorlaksen, J. Abildskov, G.M. Kontogeorgis, (2003). Prediction of gas solubilities in elastomeric polymers for the design of thermopane windows, *Fluid Phase Equilibria*, *211*, 17-33. [A simple model for gas solubilities in polymers]

P.J. Halling (1990). Solvent selection for biocatalysis in mainly organic systems – predictions of effects of equilibrium position. *Biotechnology and Bioengineering, 35(7)*, 691-701. [Thermodynamics in Bio-catalysis]

R.S. King, H.W. Blanch, J.M. Prausnitz (1988), Molecular thermodynamics of aqueous 2-phase systems for bioseparations. *AIChE J., 34(10)*, 1585-1594. [A simple but successful approach for modeling aqueous two-phase systems for protein separation]

S. Dahl, M.L. Michelsen (1990), High-pressure vapor-liquid equilibrium with a UNIFAC-based equation of state *AIChE J., 36(12)*, 1829. [The first article where the MHV1 and MHV2 models are presented]

S. Ruppert, S.I. Sandler, A.M Lenhoff, (2001). Correlation between the osmotic second virial coefficient and the solubility of proteins *Biotechnol. Prog., 17(1)*, 182-187. [The osmotic virial coefficient in correlating protein solubility]

S. Zeck (1991),. Thermodynamics in process development in the chemical industry - importance, benefits, current state and future development. *Fluid Phase Equilib.* , *70*, 125-140. [Thermodynamic needs of the chemical industry. An article earlier than 1990 – still of great interest today]

S.I. Sandler, (1999). Unusual chemical thermodynamics *J. Chem. Thermodynamics*, *31*, 3. [Thermodynamic concepts in assessing the fate of chemicals in environment]

S.S. Dey, J.M. Prausnitz (2011). Opportunities for Chemical Engineering Thermodynamics in Biotechnology: Some Examples *Ind. Eng. Chem. Res., 50*, 3. [Many exciting applications of thermodynamics to biotechnology]

T. Oishi, J.M. Prausnitz, (1978). Estimation of solvent activities in polymer solutions using a group-contribution method. *Ind. Eng. Chem. Process Des. Dev., 17(3)*, 333-339. [The article of the UNIFAC-FV model for polymers]

Th. Lindvig, M.L. Michelsen, G.M. Kontogeorgis, (2002). A Flory-Huggins model based on the Hansen solubility parameters *Fluid Phase Equilibria,203*, 247-260. [Work presenting the combination of Flory-Huggins to Hansen solubility parameters]

Tihic, G.M. Kontogeorgis, N. von Solms, M.L. Michelsen, L. Constantinou, (2008). A predictive group-contribution simplified PC-SAFT equation of state: application to polymer systems. *Ind. Eng. hem. Res., 47*, 5092-5101. [A group-contribution PC-SAFT model]

U. von Stockar; L.A.M van der Wielen (2003), Process integration in biochemical engineering. *Adv. In Biochemical Eng / Biotechnology, 80*, 1. [Needs and applications of thermodynamics in biotechnology]

U. Weidlich, J. Gmehling, (1987). A modified UNIFAC model. 1. Prediction of VLE, HE and gamma-infinity. *Ind. Eng. Chem. Res., 26*, 1372. [The "Dortmund" version of the UNIFAC model]

W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz (1990). New reference equation of state for associating liquids. *Ind. Eng. Chem. Res., 29(8)*, 1709-1721.. [C.C. Chen, Y. Song (2004). Solubility modeling with a nonrandom two-liquid segment activity coefficient model. *Ind. Eng. Chem. Res., 43(26)*, 8354-8362. [The NRTL-SAC model from ASPEN for pharmaceuticals]

Biographical Sketch

Georgios M. Kontogeorgis received a M.Sc. degree in Chemical Engineering (1991) from the Technical University of Athens, Greece and a PhD (1995) from the Technical University of Denmark (DTU). He is since 1999 employed at DTU as faculty member of the Department of Chemical and Biochemical Engineering, first as associate professor and then as full professor in Applied Thermodynamics since 2011. His research and teaching interests are in the fields of applied thermodynamics, environmental engineering, colloids, interfaces and product design as well as biotechnology. He is the coordinator of the DTU M.Sc. education in "Advanced and Applied chemistry". He has supervised/is supervising over 25 PhD students and post-doctoral researchers. He is the author of over 150 peer-review articles in international journals and over 200 conference contributions. He is also the author of several chapters in books and of three books, the most recent one, together with Dr. G.Folas, on thermodynamic models for industrial applications (published in 2010 by Wiley). He has received several awards for his research including the Empirikion Award (Greece) and the Dana Lim award (Denmark). He is currently member of the editorial board of Fluid Phase Equilibria (and several other journals) and also member of the Danish Research Council of Technology and Production Sciences. Professor Kontogeorgis serves/has served as evaluator in research councils in 6 different countries, EU and over 30 scientific journals. He is the vice-chairman of the EFCE (European Federation of Chemical Engineering) – Working party in "Thermodynamics and Transport Phenomena" (http: / / www . wp – ttp . dk /, http : / / www . wp - ttp. d k / ExecutiveBoard . html) and a member of the international steering committee of ESAT (European Symposium of Applied Thermodynamics).