

Applied Thermodynamics for Process Modeling

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Introduction

The process industries spend an estimated \$500 billion annually worldwide in conceptual design, process engineering, detailed engineering, construction, startup, plant operations, and maintenance for chemical, refining, polymer and power plants.

In order for chemical engineers to successfully execute these process and product studies, they perform process modeling and capture knowledge of the thermodynamic properties and phase behavior of the chemical systems they work with.

Process modeling is a key enabling technology for process development and design, equipment sizing and rating, and process debottlenecking and optimization. More recently, process modeling has enabled offline dynamic simulation for controllability studies, operator training simulators, online model-based process sensors, state-estimation, look-ahead predictors, and online process control and optimization. Success in process modeling is critically dependent upon accurate descriptions of the thermodynamic properties and phase behavior of the concerned chemical systems. A perspective is offered here on applied thermodynamics from an industrial viewpoint.

Industry Uses Thermodynamic Innovations

Industry uses a wide array of thermodynamic innovations: engineering correlations, reference quality models, estimation methods, databanks, and flash algorithms.

- Chemical engineers benefit most from models and correlations that capture the dominant physical and chemical behavior of chemical systems. Engineers use these correlative models within a thermodynamic modeling framework to describe and validate available data and to extrapolate with reasonable confidence outside the range of available data.
- For commonly encountered systems such as water and steam, air, ammonia, and light hydrocarbons, comprehensive experi-

mental data are available and accurate description is essential and feasible. Highly parameterized models are accepted and useful if they represent available data within experimental accuracy. These reference quality models suffer the disadvantage, however, of not easily allowing incorporation of additional components into the system being modeled.

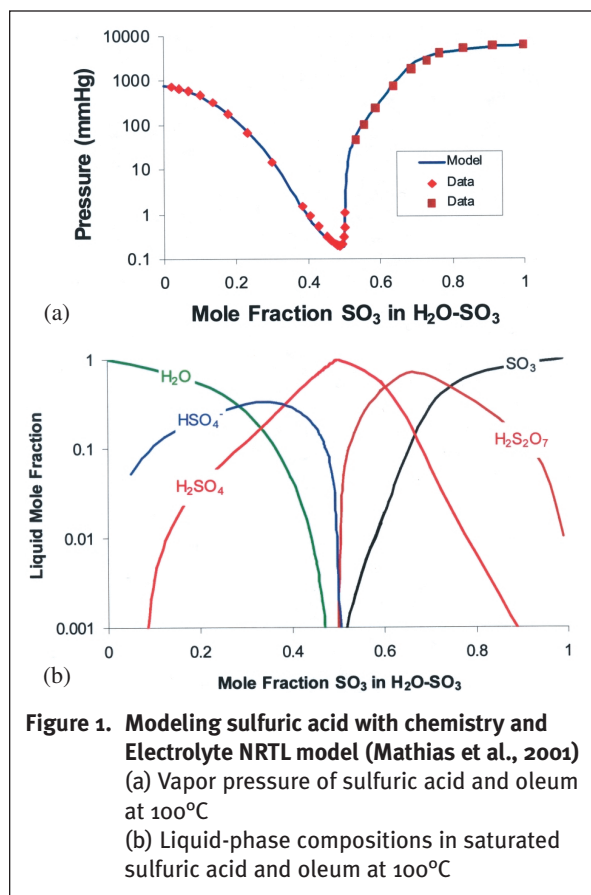


Figure 1. Modeling sulfuric acid with chemistry and Electrolyte NRTL model (Mathias et al., 2001)
 (a) Vapor pressure of sulfuric acid and oleum at 100°C
 (b) Liquid-phase compositions in saturated sulfuric acid and oleum at 100°C

- Engineers frequently lack either experimental data or expertise to develop and validate models. As a result, they often rely on estimation techniques such as group-contribution methods.
- Engineers need databanks that are compilations of validated experimental data and model parameters for pure component and mixture properties. Databanks and correlations of known accuracy play key roles in engineering calculations.
- The value of thermodynamic models is especially evident in “flash” calculations. Robust and computationally efficient flash algorithms for a variety of phase equilibrium and chemical equilibrium conditions are an integral part of the practice of applied thermodynamics.

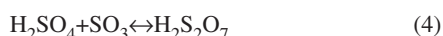
Practicing engineers prefer “simple and intuitive” thermodynamic models that can be applied easily. Models that are constantly being revised, sophisticated theories requiring expert users, models with excessive computational load, or models requiring extensive parameterization (i.e., ternary parameters), have limited industrial applications.

Thermodynamic Modeling Deliver Value in Industrial Practice

Example 1. A number of process licensors and manufacturers are concerned with designing, optimizing, and troubleshooting sulfuric acid plants. Sulfuric acid is the largest volume chemical produced, and certain aspects of it make the development of accurate and reliable process models difficult and challenging. Figure 1a demon-

strates that the vapor pressure of sulfuric acid mixtures varies by more than four orders of magnitude between pure water and pure oleum (pure SO_3).

Mathias et al. (2001) used a solution chemistry model together with the electrolyte NRTL activity coefficient model (Chen et al., 1982) to develop an accurate thermodynamic model for the entire range of sulfuric acid mixtures - from pure water to concentrated sulfuric acid to pure oleum (pure SO_3). The chemistry model, which is a practical representation for the ionization and complexation that occurs in the sulfuric acid system, is as follows



Reactions 1 and 2 describe the ionizations that occur in strongly acidic solutions. Concentrated sulfuric acid tends to dissociate into water and sulfur trioxide described by Reaction 3. Reaction 4 captures the formation of $\text{H}_2\text{S}_2\text{O}_7$ in oleum mixtures. Figure 1b presents the liquid-phase concentrations of the various species in sulfuric acid mixtures.

The complete model provides a phenomenologically correct and accurate description of the thermodynamic properties (vapor-liquid equilibrium, as well as properties such as heat of mixing and heat capacity) of this system over the entire range of concentrations. This model enables improvements in plant design, plant troubleshooting, and, in the future, will be used for online information systems and process control.

Example 2. The polyolefin industry is concerned with liquid-liquid and vapor-liquid fractionation of polyethylene downstream from polymerization reactors (Cheluget et al., 2001). In polyolefin solution polymerization processes (see Figures 2a and 2b), ethylene is polymerized in a solvent medium such as cyclohexane. Downstream of the reactor, the process stream is heated and discharged through pressure letdown in a vapor-liquid flash. Prior to the letdown, the heating process sometimes results in the process stream exceeding its lower critical solution temperature (LCST), with the subsequent formation of two liquid-like phases between which the polymer is fractionated. Above the critical temperature of the solvent, one of these phases is a supercritical phase. This phenomenon may result in undesirable plant operation consequences, as one of the phases usually contains a high concentration of polymer with high viscosity.

In the vapor-liquid flash separator, most of the unreacted ethylene, other residual co-monomers, such as 1-butene and 1-octene, as well as a significant portion of the solvent, leave as vapor. The liquid stream from this unit contains polymer and solvent, with small amounts of residual monomer and co-monomer. Depending on the process conditions, low molecular weight oligomers of the polymer product may leave with the gaseous stream. This fractionation may or may not be desirable as it impacts on product end-use properties such as melt index. Therefore, it is important for process engineers to identify the degree of fractionation at given temperatures and pressures.

Using the PC-SAFT (Gross and Sadowski, 2001) equation of state (EOS) and a computationally efficient polymer flash algorithm, Cheluget et al. (2001) demonstrated how to model the polymer phase behavior including polymer fractionation during phase separation. They characterized the complex molecular weight distribution of polyethylene using hundreds of discrete polymer components each with a unique degree of polymerization. Due to the

homologous nature of these polymer components, they share the same segment-specific EOS parameters. Cheluget et al. (2001) performed rigorous phase equilibrium calculations to investigate the effects of temperature, pressure, and feed composition on polymer fractionation. The model helps process engineers identify conditions causing phase separation and the resulting fractionation of polymers in the co-existing phases.

Thermodynamic Models in Industry

Significant investment is required to apply a model to solve a specific industrial problem. Once a model is successfully used for the simulation or design of a plant or a process, the model becomes a corporate asset, and it is integrated into company business processes. Models often remain in use as long as the plant or the process is in service or until the perceived advantages of a new

model justify the substantial investment needed to upgrade to a new model. Industry rarely updates or re-invents its thermodynamic models with newer and better thermodynamic correlations unless a clear advantage is evident.

Engineers would like one “universal” model for all chemical systems. While no such “universal” model exists, the process industries have converged to a small set of proven models, each for a special class of chemical systems. Table 1 lists some choice models used in the process industries today.

Each successful model raises the bar for the introduction of new models. It often takes a long time—up to 10 years or more—for a new model to be conceived, developed, applied, and finally accepted by industry. The speed of acceptance of a new model depends

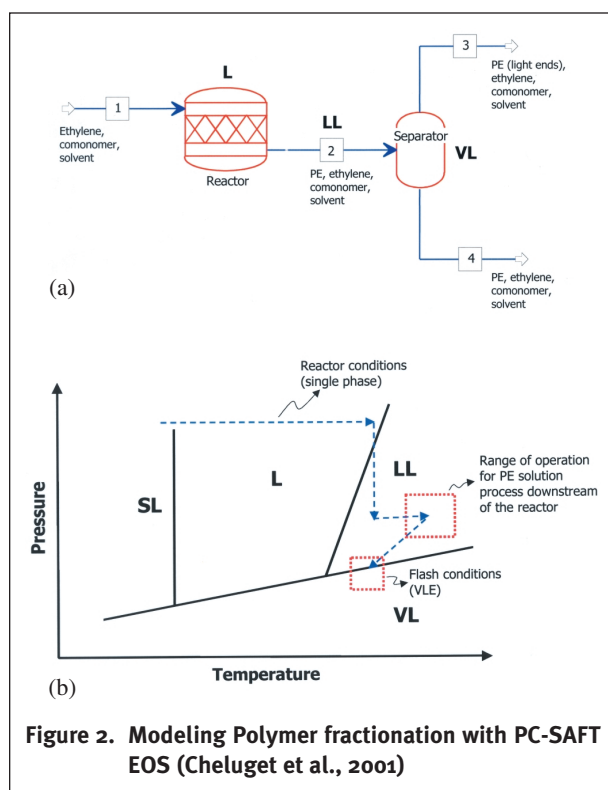


Figure 2. Modeling Polymer fractionation with PC-SAFT EOS (Cheluget et al., 2001)

on the potential value for industry and on the effort made by innovators to go to market and work with industry. Education of end users is a key requirement as more and more chemical engineers pride themselves on being generalists rather than specialists. User-oriented and commercially supported software tools help overcome some barriers and accelerate the acceptance process.

Past Accomplishments

Applied thermodynamics has had a long and successful history of technological innovation. Figure 3 presents some notable concepts and models that contributed to the practice of applied thermodynamics in process modeling. In this article we provide references primarily for publications after 1990; for additional references, see textbooks like Tester and Modell (1997), Prausnitz et al. (1999a), and Poling et al. (2001).

The van der Waals (vdW) equation-of-state (EOS) was introduced in 1877. Clever parameterizations by Redlich and Kwong (1949), Soave (1972), and Peng and Robinson (1976) significantly improved EOS of the vdW type by biasing the model to represent vapor pressure (at the expense of the PVT representation). This approach continues to provide value, particularly in the gas-processing and petroleum industries. Mathias (1983)

carried this idea further to represent the vapor pressure of polar fluids.

Extensions of the vdW-type EOS to nonideal mixtures followed soon after. This involves using mixing and combining rules to describe composition and temperature dependency of EOS mixture parameters. Huron and Vidal (1979) introduced an innovative mixing rule that combined the local composition concept of activity coefficient models with vdW equations of state, and this idea generated a flurry of research activities. Wong and Sandler (1992) ensured that their mixing rule followed the quadratic composition dependence of the second virial coefficient. The predictive SRK (PSRK) EOS further combined the vdW model, the local composition con-

cept, and the group contribution method to yield a successful correlative and predictive EOS (Holderbaum and Gmehling, 1991).

More theoretical equations of state started with the virial equation of Meyer in 1901. The development of an accurate hard-sphere EOS (e.g., the Carnahan-Starling model, 1969) has formed the basis of highly accurate models, such as the BACK model of Chen and Kreglewski (1977), for correlating properties of nonpolar fluids. The perturbed-hard-chain model (Donohue and Prausnitz, 1978) provided the first statistical mechanical basis for treating large molecules, such as polymers. More recently, a number of equations of state have been developed from statistical mechanical perturbation theories based on hard-sphere chain models, including SAFT (Chapman et al., 1989; Müller and Gubbins, 2001), PHSC (Song et al., 1994), and PC-SAFT (Gross and Sadowski, 2001).

Most reference quality equations of state can be traced to the virial model augmented with empiricism and application of sophisticated data fitting. Beattie and Bridgman developed the first multiparameter equation of state in 1927. This was followed by the BWR (Benedict et al., 1940) and MBWR (Jacobsen et al., 1973) models, with the latter producing highly accurate equations of state for many pure fluids. Schmidt and Wagner (1985) demonstrated the effectiveness

Chemical Systems	Primary Choice Models of Today	Secondary Choice Models	Problem Areas
Air Separation	Peng-Robinson, Soave-Redlich-Kwong	Corresponding States	
Gas Processing	Peng-Robinson, Soave-Redlich-Kwong	BWRS	
Gas Treating	Kent-Eisenberg, Electrolyte NRTL		Data, Parameters, Models for mixed amines
Petroleum Refining	BK10, Chao-Seader, Grayson-Streed, Peng-Robinson, Soave-Redlich-Kwong, Lee-Kessler-Plöcker		Heavy crude characterization
Petrochemicals—VLE	Peng-Robinson, Soave-Redlich-Kwong, PSRK	NRTL, UNIQUAC, UNIFAC	Data, Parameters
Petrochemicals—LLE	NRTL, UNIQUAC		Data, Parameters, Models for VLLE systems
Chemicals	NRTL, UNIQUAC, PSRK	UNIFAC	Data, Parameters
Electrolytes	Electrolyte NRTL, Zemaitis	Pitzer	Data, Parameters, Databanks, Models for polyelectrolytes
Oligomers	Polymer NRTL	UNIQUAC, UNIFAC	Pure component fugacity, Databanks
Polymers	Polymer NRTL, PC-SAFT	Sanchez-Lacombe, SAFT, UNIFAC-FV	Data, Parameters, Databanks, Flash algorithms, Models for polar polymers, block copolymers
Steam	NBS/NRC		
Environmental	UNIFAC+Henry's Law		Data
Pharma/Biological	None		Data, Databanks, Models

of optimizing the form of the equation of state through statistical search techniques by developing a reference quality model for oxygen. This technique has been adopted for several fluids and, for example, produced the most recent "Steam Tables" (Wagner and Kruse, 1998).

Activity coefficient models first appeared in the pioneering work of Margules in 1890 and Van Laar in 1910. They identified the idea of liquid-phase nonideality, and its representation by phenomenologically plausible algebraic functions that have the correct limiting behavior. Wilson (1964) contributed the all-important "local composition" concept that enabled correlation of nonideal

While experiment and theory has led to past innovations, we expect simulation to become an increasingly important tool for the development of applied thermodynamic models. Simulation (or computational molecular science) has now developed to the point where it can be useful for quantitative predictions. As stated in the *Technology Roadmap for Computational Chemistry* (1999), “among other applications, it supplies quantitative estimates of engineering parameters such as heats of formation and heats of reaction, entropies and heat capacities, reaction rate constants, and transport properties like viscosity and thermal conductivity that are needed to construct macroscale models of complete chemical processes.” More recently, efforts by chemical engineers have advanced techniques for the prediction of phase equilibrium.

The difference between simulation and experiment has been succinctly stated by Laesecke and van der Gulik (2002). Simulations provide insight into the behavior of a model system in a given thermodynamic state for specified interactions (electronic wave function and/or force fields used to approximate the real interactions). Experimental measurements, on the other hand, confine the sample into a thermodynamic state, and the interaction rules are inferred from the observed macroscopic response of the sample. Simulation helps us understand what we know, while experiment may reveal what we do not yet know.

Models are also being developed based on quantum mechanics, but they do not require the enormous computational burden of molecular dynamics or Monte Carlo simulations. An example is the COSMO-RS method mentioned earlier. Another approach has been to use molecular orbital *ab initio* calculations to compute interaction energies between pairs of molecules in a molecular cluster (Sum and Sandler, 1999), which is then used as the energy parameters in the Wilson and UNIQUAC models and to predict phase equilibrium. In another approach, Lin and Sandler (1999) equated the γ^∞ expressions from both quantum chemical continuum solvation models and UNIQUAC to relate the UNIQUAC binary interaction parameters to the charging free energies determined from *ab initio* calculations.

Simulation is being used to complement experimental measurements. Siepmann et al. (1993) performed a simulation study that discriminated between two experimental methods that gave different results for the variation of the mass-based critical density of n-alkanes with carbon number. McCabe et al. (2001) used simulation results to discriminate between two sets of published correlations for the viscosity of perfluorobutane. Simulation is especially valuable when trying to extrapolate known results into regions where experimentation is not easily accomplished, such as extremely high or low pressures and temperatures, fluids in pores, etc. It is notable that the *Journal of Chemical & Engineering Data* now accepts articles containing results solely obtained from molecular simulation (March, 2001).

Simulation is increasingly being used to develop and validate applied thermodynamic models. Murad and Powles (1993) used simulation to replicate Pfeffer's 1877 experiment on osmosis in semipermeable membranes and to justify van't Hoff's model. Chen et al. (1999) used simulation results from Paritosh and Murad (1996) to support their model for ionic hydration.

Some Unsolved Problems and New Challenges

“Chemical engineering thermodynamics should be application oriented and research in chemical engineering thermodynamics should be concerned with new applications” (Prausnitz, 1999b).

We urge applied thermodynamicists to be entrepreneurs, who understand how they can create value, and continue to look for new opportunities.

Many unsolved problems await further development of applied thermodynamics; some are listed in Table 1. They are primarily related to more experimental data and model parameters. In a number of cases, better models are clearly needed.

While applied thermodynamicists have been quite successful in modeling highly nonideal systems with activity coefficient models such as NRTL and UNIQUAC, these models do not always yield reliable results when extrapolated from binary systems to ternary or multicomponent systems, especially for liquid-liquid equilibrium. We need models that provide higher confidence levels when we extrapolate beyond binary systems. Also, while we can identify a set of activity coefficient model parameters for VLE and another set for LLE, we often fail to find one set that allows us to model VLLE systems adequately.

Group-contribution estimation methods yield satisfactory results for various pure component properties and mixture properties for systems containing small organic molecules typically encountered in the petrochemical industry. However, the applicability of current group contribution methods is very limited. For example, applications of such methods to systems with ions, isomers, chiral compounds, multimoiety compounds, surfactants, oligomers, and polymers are far from adequate.

While thermodynamically consistent models have been developed and applied for wide varieties of aqueous electrolyte systems, we still do not have enough experience or understanding about mixed solvent electrolytes. Furthermore, there is still a strong need to develop and compile model parameters for important electrolyte systems such as mixed amines, mixed acids, caustic, brines, etc.

There are successful thermodynamic models for chemicals, polymers, and electrolytes. However, what is the engineer to do when required to model systems with all of the above systems present? There are many industrial systems where chemicals, polymers, electrolytes, and surfactants occur together, for example, in emulsion polymerization. Another example is consumer products, such as shampoo. Phase separation modeling remains a key challenge for the producers of consumer products.

Additional polymer characteristics need to be addressed to improve polymer process modeling. These characteristics include mixed polymers and polymer microstructures such as block copolymers or alternating copolymers, polymer crystallinity, polymer branching frequency, and copolymer composition distribution. For example, the use of bivariate (such as molecular weight and chemical composition) and multivariate distributions is becoming more prevalent in industry, and thermodynamic models need to be able to deal with such detailed characterizations.

To capture the value of thermodynamic innovations, efficient and reliable flash algorithms are needed for high-pressure systems, systems with multiple phases such as vapor-water-monomer-polymer equilibrium for emulsion systems, systems with surface agents that form interfaces, systems with multiple liquids and solid precipitation, VLLE polymer systems with a molecular weight distribution, polymer systems with molecular weight and chemical composition bivariate distribution, polymer systems with local mesoscopic structure (microdomains), or even biological systems encountered in cellular molecular processes.

Although a number of established thermophysical property databanks exist for systems with hydrocarbons and small mole-

cules, they only supply verified correlations for a very small fraction of the compounds found in *Chemical Abstracts*, etc. Unfilled needs remain for critically evaluated databanks for systems with complex molecules such as electrolytes (elemental and organic), isomers, surfactants, segments, oligomers, and polymers. These needs become particularly acute as we expand our modeling efforts beyond basic petrochemicals.

How do we take advantage of molecular simulation in the development of engineering correlations and estimation methods? Should we use simulation to generate simulated "data" and then identify model parameters for engineering calculations from the simulated "data?" Could simulation-based group contribution models offer higher accuracy for wider varieties of chemicals than existing group contribution models do? Can simulation help bridge the gap between process modeling and the lack of experimental data in areas such as electrolyte thermodynamics or transport properties for polymer solutions? A few innovators have suggested ways to use results of molecular simulation to advance development of engineering correlations and parameterize estimation methods. We need more such work.

There are frontier areas such as biotechnology and bioprocesses in which applied thermodynamics should be important, but so far these have had little impact. Biopolymers include polar polymers with segments derived from various forms of amino acids and sugar molecules. Some of the amino acids may be ionized, and some biopolymers can form local secondary structures such as an α -helix or a β -sheet. These local structures are the basis for the formation of tertiary and quaternary structures. Practical models for aqueous systems containing such polymers and other polyelectrolytes need to be developed. Protein precipitation plays an important role in downstream processing in biotechnology. Engineers need models of selective protein precipitation to improve enzyme recovery efficiency. Can we extend our existing thermodynamic models to describe protein solubility that depends on pH, ionic strength, electrolyte composition, protein composition, surface hydrophobicity, surface charge distribution, etc?

The cell is a sophisticated chemical manufacturing facility in which there are numerous chemicals and reaction pathways in various subcellular units. We can anticipate that the modeling technology that has been so successful for the process industries will be extended to biological processes. Cells contain various chemicals such as glucose, fatty acids, glycerol, lactate, ATP, phospholipids, phospholipid bilayer, proteins, genes, mRNA, tRNA, rRNA, etc. Will thermodynamicists take on this challenge to help understand and model cellular molecular processes?

Concluding Remarks

Applied thermodynamics has been a key enabling technology for process modeling. The progress of applied thermodynamics has benefited from insights arising from experimental measurements, theory, and, most recently, computational chemistry. Thermodynamic innovations have yielded models that provide accurate descriptions of the properties and phase behavior of chemical systems in the process industries. Applied thermodynamics will continue to provide value to chemical engineering by focusing on the needs of practicing engineers, while drawing on advances in experiment, theory, and simulation.

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