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Life, data, and everything*

Marco A. Satyro

Virtual Materials Group, Inc., The Calgary Centre for Innovative Technology,
830 Campus Place NW, Calgary, Alberta T2N 1N4, Canada

Abstract: The use of thermodynamics for the solution of chemical and process engineering problems is determined by a blend of science, engineering, art, and grit. Although chemical engineering thermodynamics benefits from an ever-increasing body of basic scientific knowledge, the solution of real problems still depends very much on the knowledge of individuals, their creativity, and their determination to recommend solutions. The essence of success is determined by a combination of two apparently simple components—physical property data and how they are used.

Keywords: thermodynamics; phase equilibria; fluid characterization; equations of state; fluid properties.

INTRODUCTION

Scientists should always strive toward precision and accuracy in what they do. This in turn drives them to express themselves in a certain precise and accurate way, which is the style to be used for good technical writing. However, life is usually complicated and messy, information is incomplete, and there are no absolute answers. All that can be done is to provide the best answers possible, based on the information at hand. In this paper, I describe different ways in which incomplete data and models are used to do process engineering.

An important lesson to learn is that numbers coming from a theoretical calculation or a handbook or a database are not just numbers, but they have an intrinsic personality and they represent something that exists in the real world, something that may be messy, imprecise, but real.

The following example is a good illustration of this. For a certain reactor model, the numerical solution of the model equations would not converge, although the model and model parameters had been checked many times and everything seemed satisfactory. The data and the model are shown in Fig. 1. During the modeling, the fitting program had been adjusted until the error between the model and data was zero. All of the 24 heat capacity values, copied from a handbook, were reproduced within machine precision, thanks to a 24-coefficient polynomial. Thus, this was a "perfect" model from a mathematical point of view, but a totally inadequate model from a physical perspective. It was such a bad model that, when second-order derivatives were required, all that was left amounted to numerical noise.

The equation solver could never work because the Jacobian matrix would say one thing and the Hessian something else. The important lesson from this is that starting from the numerical model and treating the thermodynamic model using mathematics without thinking through the physics related to it leads to a large set of equations, while what is underneath the equations may be complete nonsense. Therefore, those who are in the modeling business must be able to see beyond the façade of partial differential equations and look at the core thermodynamic modeling that is actually being used. Doing any-

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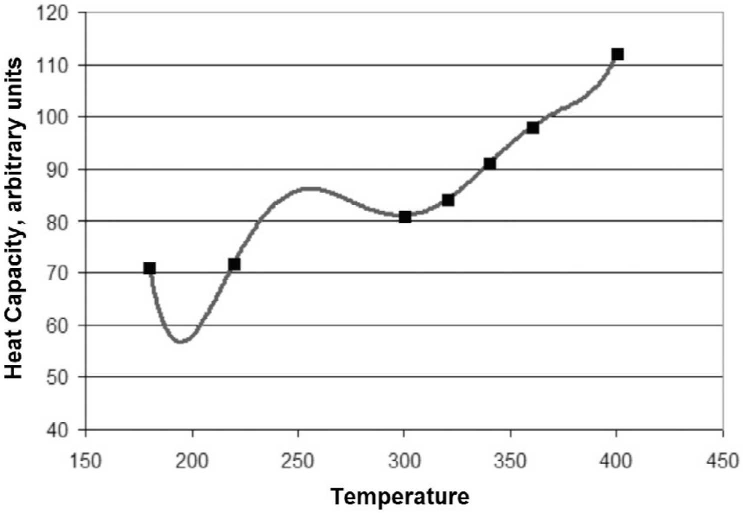

Fig. 1 A mathematically perfect—and perfectly useless—fit.

thing less than that is a recipe for waste and frustration. This is a good point to briefly visit some of the most common pitfalls related to data, modeling, and process design.

PURE-COMPONENT DATA

It is unfortunate, but true, that sometimes, simple pure-component data such as vapor pressures are incorrect in simulator databases or incorrectly entered in the software by users. When combined with automated data regression tools, the error can go unnoticed for a long time. It is common for this error to manifest itself at later stages in a project when recovery systems are designed, or even worse, as process problems that crop up at plant start up. Sometimes the effects are not as dramatic as shown in Fig. 2, but no less irritating.

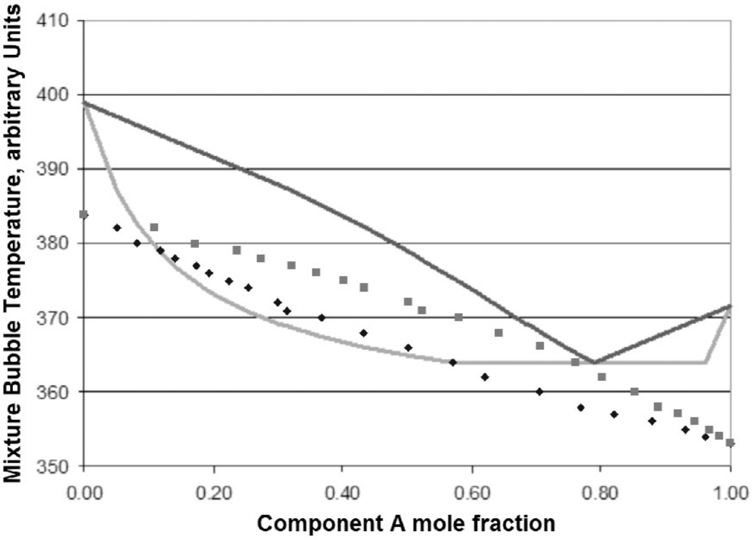

Fig. 2 A mixture model gone AWOL. The mixture is nearly ideal, but the model was created using incorrect pure-component vapor pressures.

BAD DATA

Sometimes the experimental data are just bad, sometimes they are reported incorrectly in journals, and sometimes it is both of the above. A common problem that arises with some binary vapor–liquid equilibrium data is that they are reported using reversed component indexes. To compound the problem, it is unusual to find reasonable reports on data uncertainty in the scientific literature (reproducibility seems to have assumed the place in accuracy more times than we would like to acknowledge). However, this situation is getting better with the availability of NIST's Guided Data Capture software and its suggested use by major journals.

BAD EXTRAPOLATION

Applied thermodynamics as used by the majority of chemical engineers is a semiempirical science at best since the models are in their vast majority semiempirical. Therefore, extrapolations are usually based on rather flimsy science and care should be exercised and time spent in actually understanding the assumptions and data behind the models.

INCOMPLETE DATA

It is undeniable that the energy industry is going to be an important part of our lives for a very long time. With the exhaustion of light oil supplies, we will need to process heavier and heavier stocks. In order to do this, we need to better understand the feed stocks we are trying to process, how they change upon mixing with solvents and how they change when thermally processed. This used to be done using distillation curves, but at this juncture new techniques—experimental and mathematical—are needed.

UNRELIABLE METHODS

Again related to heavy oil processing, it is common to use simplified methods to gather vapor–liquid equilibrium data from oil feed stocks, such as chromatographic or simulated distillation. These methods provide some data that invariably have to be converted into true boiling point data. Unfortunately, the conversion methods are based on reasonably light oils and are notorious for generating unphysical distillation curves with maxima or minima or physically impossible boiling temperatures.

OVERLY COMPLICATED MODELS

There is a degree of truth to the saying that just because something exists it does not mean it should be used. With the advent of computers, the complexity of thermodynamic models naturally increased, in particular with respect to mixing rules for equations of state. Some of these mixing rules are very flexible, with many adjustable parameters. How they behave when computing derived properties is sometimes unknown, and surprises such as unrealistic excess volumes and heat capacities are to be expected. It is worth remembering that a simple model well understood is more valuable than a complex model poorly understood.

Over the years, there have been many instances of bad practice. For example, some systems have been modeled using binary data that were regressed using incorrect pure-component vapor pressures, Fig. 2. There are many examples of models based on binary data where component A was labeled as B and vice-versa in the technical literature (it is often assumed that if it is published it is true, if it comes from an electronic database it is blessed, if it comes from a process simulator it is real), or nearly ideal mixtures modeled using 8-parameter mixing rules. On other occasions, nearly ideal nonreactive mixtures have been modeled using associating equations of state, or used simulators that violated the mass balance, flash systems have been used that would split pure water at 25 °C into two liquid phases, and distillation curve methods have been recommended that predict distillation temperatures below the absolute zero. There are, of course, many other examples of lack of understanding of the basic technology. The challenge for us is to do a better job at training students and young engineers to actually appreciate the reality—or lack thereof—behind the numbers coming from a computer.

Let us consider some *good* problems. Since our economy is truly not at equilibrium, periodically we are presented with challenges that, if properly addressed, promise fortune and glory. In North America, the current goal is cheap—or at least available—energy from hydrocarbon sources. From a supply point of view, there is no lack of carbon and hydrocarbon sources in North America. For example, Alberta's currently known recoverable reserves in the form of tar sands and bitumen are in the order of 180 billion barrels, or in another words, the current Canadian reserves could fulfill the current world oil needs for approximately 25 years. These reserves represent an enormous amount of wealth, political influence, and a significant economical stabilization factor for North America. There is only one catch—we have to get this oil out of the sand and clay. This is messy, costly, and requires engineering on an enormous scale. The amount of material mined is enormous, the requirements of water and energy are incredible, and opportunities for optimization loom everywhere. After all, this should be a simple problem since bitumen has been with us for some 6000 years:

> *Make thee an ark of gopher wood; rooms shalt thou make in the ark, and shalt pitch it within and without with pitch.* Genesis 6:14

In reality, heavy oils and bitumens are complex mixtures full of surprises. The first task is to characterize this material for the simulation of material and energy balances related to the design or optimization of processing facilities. The modeling of complex hydrocarbon mixtures is usually accomplished by measuring the so-called distillation curve, in essence, a batch distillation using a very high reflux. If the reflux is very high, then only a little bit of material is distilled as time passes, and the collected distillate sample corresponds to a material with components distilling between a certain temperature interval*. If you take this process to a differential limit then, in theory, it would be possible to describe a complex mixture by the different components that boil at specific temperatures. In practice, we lump together many components in each sample of collected distillate. With a bit of care, a reasonable description of complex hydrocarbon mixtures can be constructed quickly and reliably. This is the core of computer models used to represent refineries. Unfortunately, a basic problem crops up when we start to model heavy oils. It is found that at around 340 °C, oils start to crack** and the distillation curve that is measured does not correspond to the material we are interested in, but rather it corresponds to a material that is being thermally decomposed.

The obvious way to overcome this problem is to conduct the distillation under vacuum, and then to relate the vacuum boiling points with the boiling point that the material would have at normal pressure. From such measurements, distillation curves have been reported at ambient pressures up to about 550 °C, which is, experimentally, about the highest temperature that can be reached using distillation. With chromatographic methods such as high-temperature simulated distillation, it is possible to go up to 700 °C (albeit the validity of such methods is dependent on proper calibration and interpretation of results for fluids that present a significant amount of aromatics, and is subject to significant uncertainty). Thus, a point is reached where distillation-based technology cannot help to define the fluid, and a new approach is needed to solve the problem. It is now common for us to be asked to model processes where the 550 °C point is in the vicinity of 40 to 50 % of the material being distilled. In another words, we are asked to model the fluid-phase behavior of materials where more than 50 % of the sample *is unknown* as suggested in Fig. 3.

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*Note that even if we could perform experiments at the differential limit it would still be impossible to distinguish between components that boil at approximately the same temperature. Fortunately, for normal refinery modeling this is not an issue.

**Paraffin-based oils crack at lower temperatures than aromatic-based oils.

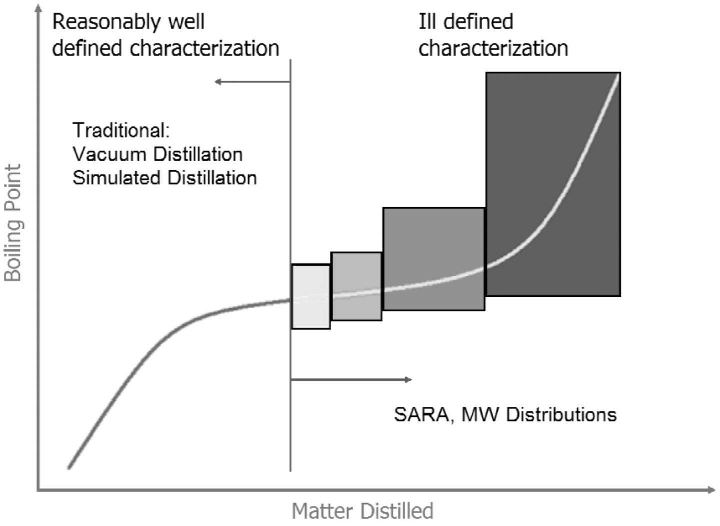

Fig. 3 Processing heavy oils—the right part of the distillation curve represents material that cannot be distilled. Many times we have to create fluid models for process simulation where more than 50 % of the material is not known.

The reason for emphasizing the need to estimate normal boiling points for these heavy fractions is that hydrocarbon process simulation hinges on the usage of generalized correlations for the modeling of vapor pressures (and therefore volatilities) and other properties such as viscosities and thermal conductivities. Thus, with the knowledge of a distillation curve and a liquid density curve (which is easy to measure), the molecular weight of oil fractions can be estimated, and with a normal boiling point, standard liquid density, and molecular weight for each fraction, it is possible to calculate all the other missing properties required for the development of a rather complete thermodynamic model for the prediction of the fluid critical properties, acentric factor, and viscosity, as well as interaction parameters between oil fractions and important inorganic compounds such as hydrogen sulfide, carbon dioxide, and hydrogen.

The reason why Soave modifications of the Redlich–Kwong equation of state and related equations such as Peng–Robinson have become so popular is that, by using a modest amount of data from an oil characterization assay, a reasonably accurate model can be created for a complex hydrocarbon fluid. This in turn provides a good platform for the solution of the material and energy balance equations used to describe a refinery, and in the end we have a quick and inexpensive solution to important industrial problems.

A different way of characterizing the chemistry of heavy hydrocarbon fluids without the use of distillation-based methods is being explored by Yarranton's group at the University of Calgary. The basic idea is simple. If bitumen is subjected to extraction using different solvents, different types of material will separate from the oil matrix, and by studying the different extracts an idea is gained of what makes up the heavy fractions. This type of analysis known as SARA (saturates, aromatics, resin, and asphaltene) analysis provides a promising starting point for characterization where problems related to material decomposition are important, and at least a few density and molecular weight points can be collected to help us characterize bitumens.

If specialized correlations can be created that relate molecular weight and liquid density to equivalent boiling points of heavy hydrocarbons, then a few points of the distillation curve can be estimated and finally the entire fluid can be characterized, based on sensible physical chemical information.

This path is certainly not as straightforward as we would like. Extraction assays take considerable technical skill for reliable results; they are lengthy and also somewhat ambiguous since (in a similar way to distillation curves) the boundaries of material extracted using different solvents are not sharp but rather overlap, hence there is a limited amount of definition to be obtained from this technique. Other experimental challenges range from the processing of very viscous fluids to the presence of finely dispersed inorganic materials such as clays. Following careful measurements and results interpretation, Yarranton's group is continuously working on the transference of this knowledge into useful technology for process calculations. This careful, painstaking work shows its value when used to model thermodynamic equilibrium of bitumens when contacted with hydrocarbon solvents [1]. The results are slowly making headway into process simulations.

Even if characterization methods like the one just described were widely available, surprises lurk, even with the simplest properties of bitumen. In many cases, bitumen is mixed with minerals and the problem is to find ways of getting it out of the reservoir rock. This can be done by heating (such as steam-assisted gravity drainage or SAGD), or using a solvent such as naphtha. With regard to the solvent process, there are a couple of basic questions that need to be answered when designing facilities, namely, what is the density of the fluid which is being processed and does the temperature go up or down when fluids are mixed? In terms of the facilities that are processing thousands of tons of material per hour, these questions translate into large capital investment and energy costs.

It might be supposed that these questions could be answered quickly and reliably, especially given a few more points on the distillation curve and a better characterization of the heavy end. John Shaw from the University of Alberta set out to answer this question by measuring the excess volumes of mixtures of heavy residues and paraffins used to simulate industrial naphtha. John also did something unusual in the way the measurements were performed [2]. Since bitumen is processed in different ways depending on how it is extracted, but blended when fed to the upgrading facility, excess volumes of heavy residue and paraffin were measured with the mixtures produced in different ways as shown in Fig. 4. Some mixtures were produced at a certain temperature and then heated to a desired temperature. Other mixtures were first heated and then mixed and moved to the desired temperature.

From a conventional thermodynamic perspective, the measured excess volumes should be identical within some measurement error. After all, with sufficient care and patience, the systems should get pretty close to thermodynamic equilibrium and therefore the measurement of physical properties should be independent of the path of measurement. However, not only are the results *different* depending on how the mixtures are prepared, they are qualitative *opposite* to one another. A definitive interpretation for these results is not yet available, but a couple of ideas come to mind. The first is that some kind of polymorphism may happen depending on the thermal history of the material, akin to the protein folding of complex molecules that results in a shape change, and therefore the volumetric behavior is different. A second thought is that the approach to equilibrium is so slow that even after several days no significant changes can be detected in the laboratory and much longer equilibration times are necessary.

If this is the case, given the residence times of these materials in the plant would suggest that experiments should be tailored to the way the plant is run because the mixing process is kinetically controlled. This is in fact what is really important for simulations, that is *the way* the process is conducted. This is not an alien concept when dealing with slow chemical reactions, but in this case, we are perhaps considering an entry in a physical property handbook where, in order to make the measured properties relevant we have to specify that this is the excess volume for this bitumen and this solvent mimicking the thermal history of a certain processing technology. This may be a necessary step for the design of processing plants, but it does underline some significant lack of basic knowledge of what we are processing, even at this very basic level.

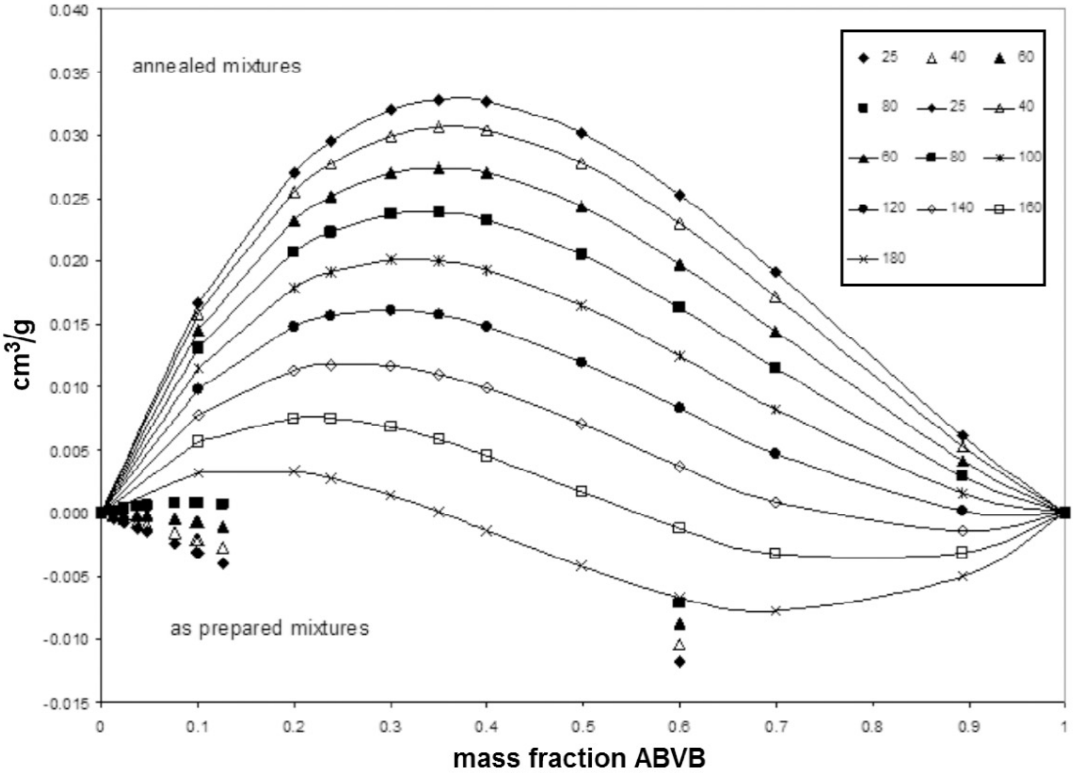

Fig. 4 Different excess volumes are measured depending on how the heavy oil and solvent sample was prepared [2].

Another interesting question that arises with problems related to the characterization of complex materials is that, if these materials *could* be characterized well, do we have sound theoretical models, and do we understand these models well enough to create useful simulations that can be used for actual economic decisions? It is well known that cubic equations of state have been refined to the extreme for the creation of reliable refinery and gas plant models. Cubics are quite attractive from a mathematical perspective, and some rather clever and elegant modifications have been proposed over the years. That said, the modifications related to cubics are usually concentrated on bettering their performance for thermodynamic equilibrium calculations. How they do when they are used to estimate excess volumes, even for a simple mixture of *n*-hexane and *n*-dodecane where all components are well characterized, is shown in Fig. 5. These are the moments where we realize that this type of equation of state is very useful for technical calculations, but as in any model that needs to be buttressed using experimental data for the calculation of accurate results, the theory is weak and good results in one area do not translate into good results in another area.

Realistically, the majority of process simulation calculations done today are based on slight modifications of the van der Waals equation of state, and as van der Waals himself knew, the theoretical base of his equation of state—and as classical physics go, you are hard pressed to come up with something more elegant as suggested in Fig. 6—is weak. Thus, this weak theoretical model is "fixed up" with lots of data, clever data fitting, and empirical generalizations to get accurate answers for a given class of problems. The usage of cubics as the de facto model for the hydrocarbon processing industry is a testament to the brilliance of men such as van der Waals and van Laar. That said, we are using 19th-century technology, and it would be a sad state of affairs if we did not have something better to show at the beginning of the 21st century.

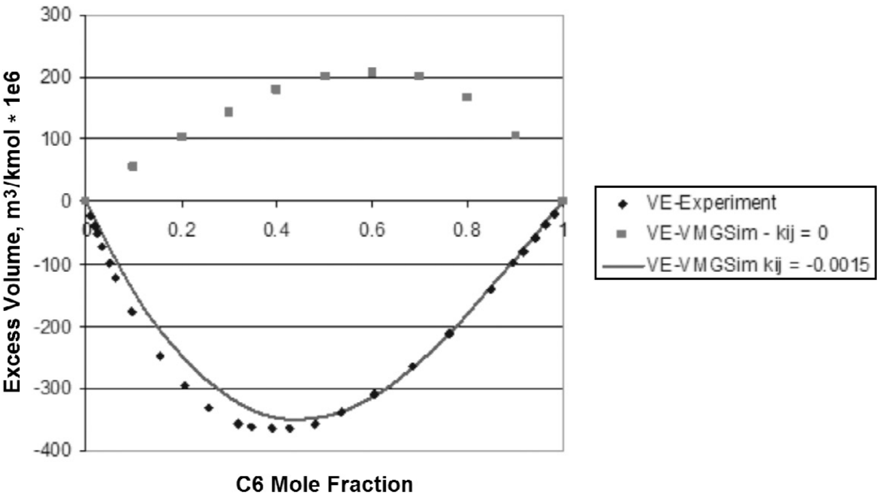

Fig. 5 Note the wrong qualitative behavior for excess volume prediction for a mixture of *n*-hexane and *n*-dodecane using a cubic equation of state unless interaction parameters are used.

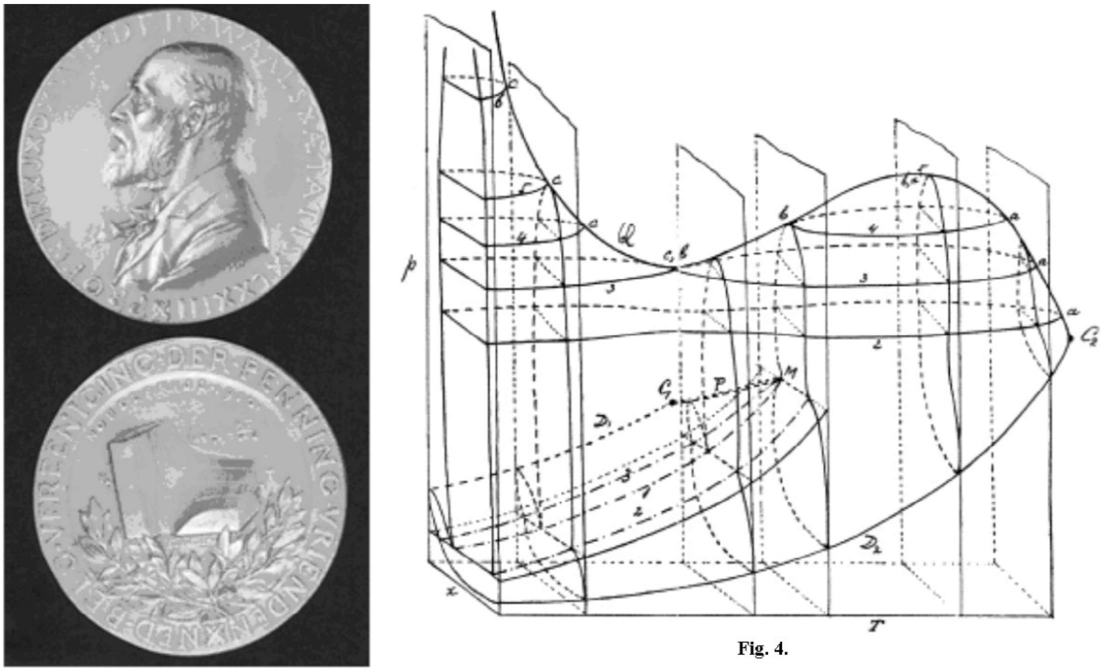

Fig. 6 A testament to practical genius—van der Waals Nobel medal (note the equation and PVT surface)—and van Laar phase diagram for ethane and ethanol (<http://www.knaw.nl/waals/laar.html>).

It is interesting to see that much of the work done by van der Waals and his group was largely ignored between 1914 and 1975. During this period, the lattice theories of fluids came and went following the work done by Prigogine [3] and Guggenheim [4] which was put to use in chemical engineering by Wilson [5] and Prausnitz [6–8]. Equations based on lattice theories are great for predicting the behavior of certain classes of fluids such as hydrocarbons and polymers when removed from critical conditions, as demonstrated by Hildebrand [9] and Scatchard [10] using regular solution theory, and the extension designed to capture entropic effects for polymer solutions from Huggins [11] and Flory [12].

Gibbs free energy equations derived from lattice theories also found wide usage in chemical engineering, and every chemical engineer worth his or her salt will recognize acronyms such as NRTL, UNIQUAC, and UNIFAC. Although some work had been done on the use of theoretical models to come up with binary interaction parameters for lattice-based equations, they remain mainly correlative tools. These models are certainly useful, especially for the simulation of chemical processing at modest pressures, but inadequate for the modeling of fluids at high pressure.

Luckily, two apparently disjointed threads continued to develop. One was motivated by the engineering need for designing equipment for hydrocarbon processing at high pressures and exemplified by the work of Kay [13], Sage [14], Lacey [15], and Katz [16] during the 1940s and 1950s. This work provided useful and extensive data describing the behavior of hydrocarbon mixtures as well as the mixtures of hydrocarbon and water. Significant rationalization of the usage of this data, using a modernized version of the corresponding states theory put forth by van der Waals, was completed by Leland in the 1960s [17]. The second thread is theoretical and starts with the framework for hard-sphere fluids put forth by Kirkwood [18] and the subsequent numerical simulation work done by Alder [19], Wainright [20], and others. The rigorous description of this simple fluid of hard spheres using numerical experiments allowed, in turn, the creation of rigorous reference repulsive contributions for the crafting of theoretically based equations of state, as shown by Percus [21], Yevick [22], Werteheim [23], and Rushbrooke [24]. Also from the theoretical side, Kac [25] showed that the van der Waals equation of state can be rigorously derived using a simple potential for a system of one-dimensional hard rods. The stage was set for the interpretation of the physical picture described by the modest van der Waals equation of state using perturbation theory and a springboard for the methodical construction of new equations of state where more and more physical flavor can be added to the model by adding further contributions to the perturbation term.

Consequently, Chapman and coworkers [26] proposed a model where the Helmholtz energy of a fluid is modeled using a rational perturbation expansion where the terms have a clear physical interpretation. This work was put forth in the form of the statistical association fluid theory (SAFT), and in its various shapes and forms it is now the de facto model for complex mixtures of fluids such as solvents and polymers, eq. 1.

$$A = A^{0} + r\left(A_i^{\mathrm{HS}} + A_i^{\mathrm{Disp}}\right) + A^{\mathrm{chain}} + A^{\mathrm{assoc}} \tag{1}$$

The technical details embedded in eq. 1 are a bit on the complicated side, but that does not detract from the beauty of such an equation. Equation 1 expresses the Helmholtz energy of a fluid by an ideal gas contribution (A^0) and then, in an attempt to add a more realistic representation of the sizes and energies found in the geometry of an actual molecule, the molecule is modeled as a summation of "r" segments, each represented by a hard sphere and a potential energy term [$r(A_i^{\mathrm{HS}} + A_i^{\mathrm{Disp}})$]. This gives the basic structure of the van der Waals equation of state, which was explored in different ways by Longuet–Higgins [27] and Widom [28] in the 1960s. The perturbed hard-chain theory (PCHT) and its variants were explored in the 1970s and 1980s by Beret [29], Donohue [30], Sandler [31], and Prausnitz [32]. SAFT also includes the necessary term for the formation of chains, and it is intrinsically able to model large molecules such as polymers and proteins (A^{chain}). Finally, SAFT also includes a term to model chemical association (A^{assoc}), therefore it has an explicit term to model strong intermolecular forces. Each term has parameters with a clear physical meaning, and thanks to its theoretical clarity, these terms are frequently amenable to generalization. SAFT can often provide reasonable semiquantitative predictions for mixtures for which no experimental data is available, and surprisingly good predictions for complex vapor–liquid equilibrium behavior without the need of adjustable binary parameters, Fig. 7.

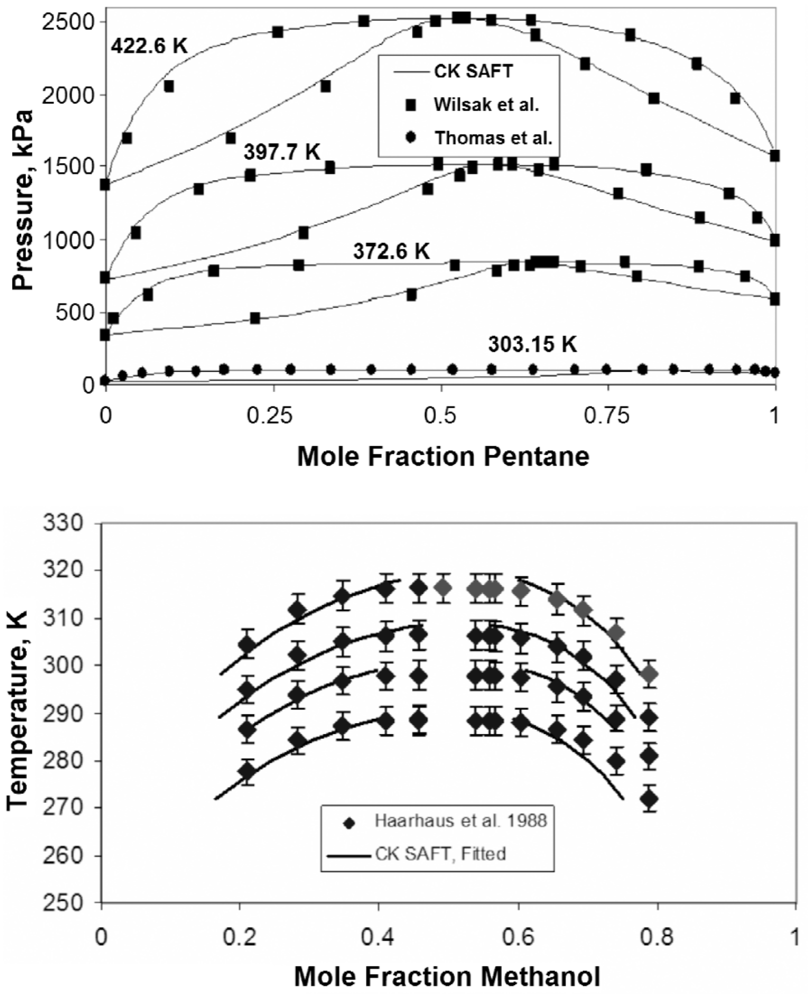

Fig. 7 Modeling of methanol and *n*-pentane vapor–liquid and liquid–liquid equilibrium using the SAFT equation of state. Experimental data from [41–43].

Perhaps the most beautiful closure one can get on the universal appeal of classical thermodynamics is the fact that the SAFT equation of state is simply obtained from the differentiation of the Helmholtz energy with respect to volume, eq. 2.

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,X} \tag{2}$$

The boundary condition expressed by eq. 2 is completely general and does not depend on the internal details of any specific mathematical theory used to model the Helmholtz energy. This is the power of generalization provided by classical thermodynamics. At the same time, useful results from an engineering perspective depend on the details of the mathematical theory used to model the Helmholtz energy and this is the realm of molecular thermodynamics where theory and data are combined to create models that are in turn plugged into the formal machinery of classical thermodynamics as suggested by eq. 2 where useful numbers are computed.

The creation and *acceptance* by engineers of more theoretically based methods is creating a quiet revolution in the field. Computational chemistry developments now allow the creation of detailed molecular models on a desktop. The information from these models can then be parceled into molecular pure-component parameters present in equations of state such as SAFT, resulting in reasonable fluid models that can be constructed quickly and cheaply. In addition, the usage of quantum-mechanical-based models such as COSMO [33] permit the calculation of reasonable excess properties from pure-component parameters only, and in theory a reasonable *facsimile* of Nature can be created. The data, in the form of detailed chemical structures, can be incorporated into an engineering model as pure-component, as well as regressed, interaction parameters for the description of mixture behavior.

Naturally, complete reliance on estimated behavior for all kinds of systems should never happen until the time we have a truly rigorous fluid's theory. That said, I believe we should strive to perform experiments that shed new light on problems and not in areas wherein we already have a good theory and database of experimental confirmation.

It would be rather pleasant if we could concentrate on writing models and then simply rely on a computer to provide a quick and easy solution to the model. However, we should not underestimate the amount of creativity, time, effort, and dogged determination that is required for the creation and maintenance of a reliable flash calculation system.

Athough Gibbs [34] gave us the formal structure of thermodynamic equilibrium in the late 19th century, these equations have yet to be solved. There are many types of flash calculations that can be done in a reliable manner, but problems still happen, sometimes from snags deep inside fluid models such as empirical correlations or numerical problems related to the solution of sets of nonlinear equations, or problems related to how to start the numerical solution. The problem is compounded when flash calculations are to be performed for systems with many components with highly dissimilar molecular characteristics under extreme pressures and temperatures.

These types of problems are frequently encountered in the polymer processing industry, and VLXE is one of the few companies in the world providing this type of service. Led by Torben Laursen, VLXE's technology is used to solve some tough problems related to polymer modeling, including the tracing of complex multiphase diagrams as shown in Figs. 8 and 9, and the calculation of less dramatic properties than VLE or LLE but just as important such as enthalpies, entropies, and densities, which are necessary for the calculation of reliable material and energy balances

Complex materials often require more complex equations of state to model system behavior. In addition to mathematical complexity, these types of materials also require the calculation of different physical properties such as cloud points, complicated phase diagram tracing, and a careful match of mixture critical points as shown in Fig. 10. These calculations are closely related to flash calculations.

As an illustration of how well model and model solutions are inextricably connected when creating robust computer models, we set out to model the behavior of aqueous solutions of amines in contact with acid gases. These systems exhibit significant non-idealities due to the polar nature of the components, high processing pressures, and more importantly the acid–base reactions that happen in liquid phase. It took approximately 12 months to create the thermodynamic model for this. This became really useful when the necessary numerical calculations were developed for fast and reliable flash calculations. From that point on, the science was converted into a technology to be used by process engineers, such as creating reliable distillation tower initialization through the development of convergence routines and extensive model validation. This intensive interplay between modeling, mathematics, and engineering is at the core of the development of robust commercial scientific software.

The talent necessary to bridge mathematical sophistication and the day-to-day litany of problems that involve the usage of computer models in real-life simulation is rare, and it is heartwarming to see that a new generation of engineers and scientists are up to the challenge of not only creating new models, but also making sure that they can be reliably used, thus making a most significant impact in the hands of process engineers.

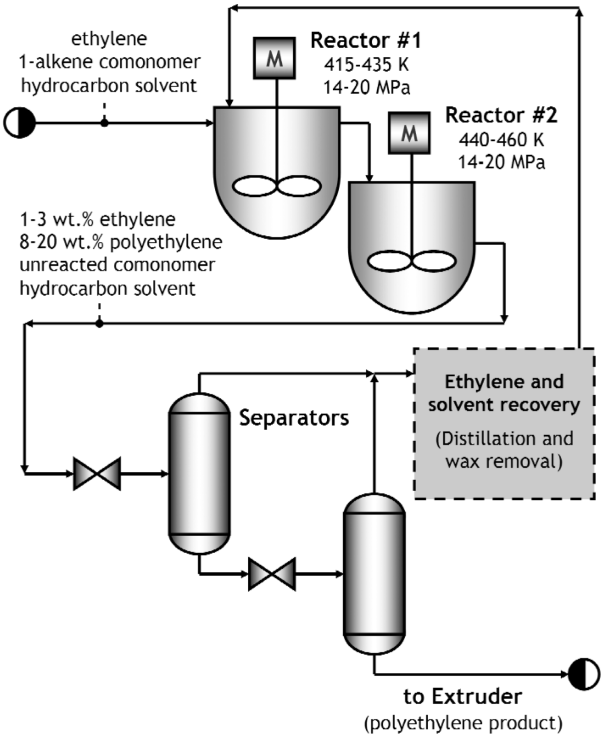

Fig. 8 Processing of complex materials—polyethylene production and solvent recovery [39].

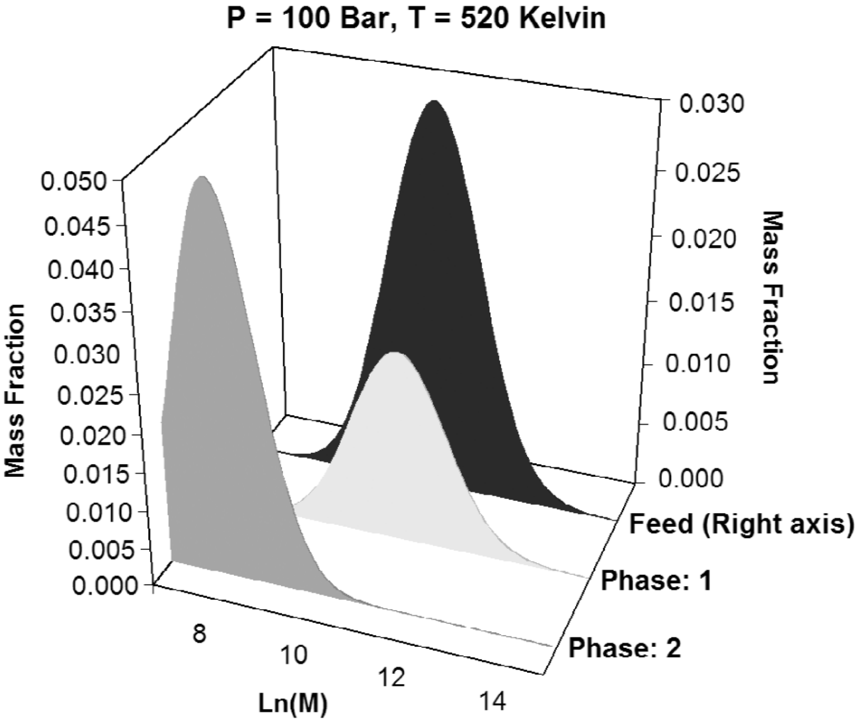

Fig. 9 Flash calculations for complex mixtures—polyethylene VLE at 10 000 kPa and 520 K [40].

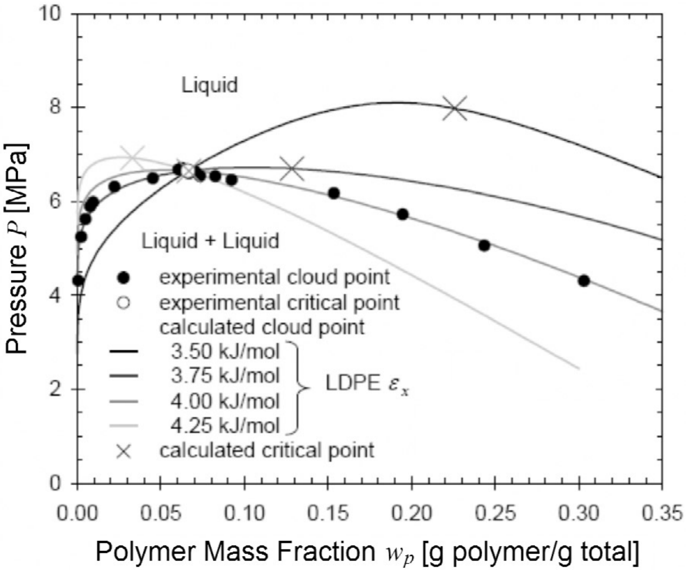

Fig. 10 Simultaneous fitting of cloud and critical points in polymer mixtures [39].

In this interplay between theory and data, we should mention the important contribution by the Thermodynamics Research Center (TRC, formerly at Texas A&M University and now at the National Institute of Standards and Technology in Boulder, Colorado) with their “red books” data collection [35]. More recently, there have been three very significant accomplishments at TRC. First, there was the creation of ThermoML [36], now the IUPAC standard for electronic dissemination of thermodynamic and physical property data. For anyone creating software dependent on physical properties, the availability of a standard for thermodynamic data is invaluable. Next, there is the Guided Data Capture (GDC) [37] software, which is freely distributed. More and more technical journals now accept newly measured data using GDC. This provides a significant reduction in the submission of wrong and inconsistent data, and hence produces a higher level of quality for data for use in process design. Last but not least, TRC is now on the second release of its Thermo Data Engine (TDE) [38]. TDE is in essence a virtual laboratory that can create complete pure-component and, soon, mixture data, based on all the experimental data available in SOURCE and complemented by recommended estimation methods.

We have not yet reached the point where fluid-phase thermodynamics, and flash calculation technology, is advanced enough that we can consider it an appliance. But there are a few specific aspects of it where we are very close. At Virtual Materials, the embedding of this technology in other applications is becoming a reality. For example, flash calculations and phase diagram tracing on-line are now routinely used to warn plant operators of potentially dangerous operating conditions when compressing sour gases, as shown in Fig. 11, avoiding liquid dropping in retrograde conditions, or creating *ersatz* sensors to provide operators with physical properties that cannot be measured, or telling refinery operators the best way to operate units for changing feed stocks [39].

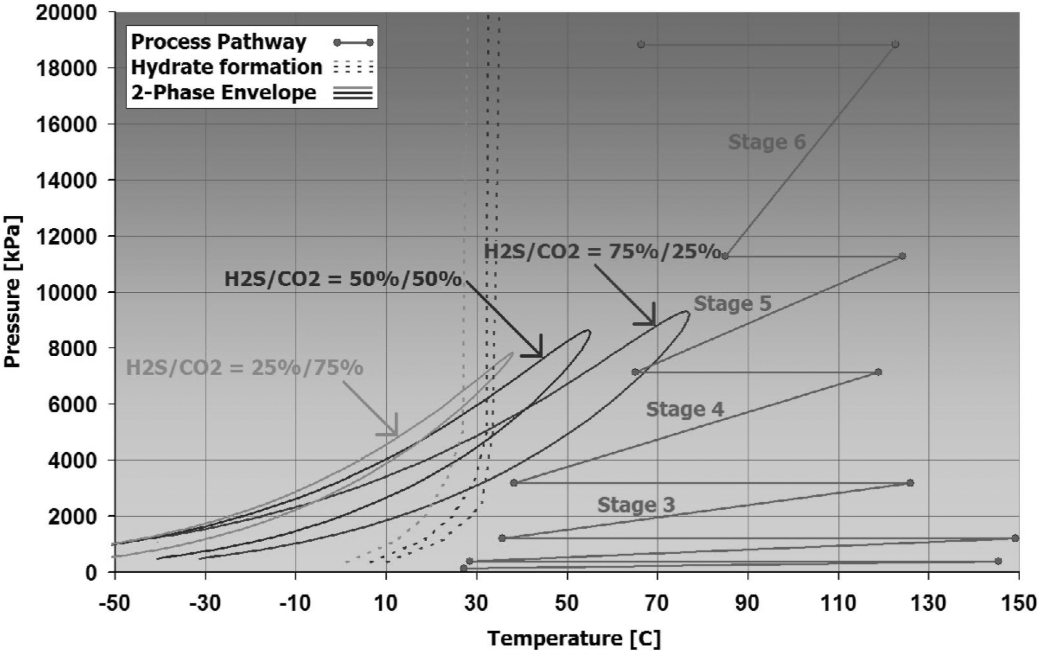

Fig. 11 Thermodynamics used to create appliances—on-line sour gas compression train advisory panel [38].

CONCLUSION

In conclusion, the first and second laws should always be the basis for the development of models for tackling apparently intractable problems in thermodynamics, making full use of the painstaking accumulation of rational knowledge and most reliable experimental data.

REFERENCES

1. H. Alboudwarej, K. Akbarzedeh, J. Beck, W. Y. Svrcek, H. W. Yarranton. *AIChE J.* **49**, 2948 (2003).
2. Y. Maham, X. Zhang, P. Zabeti, J. Goodkey, M. Allain, J. M. Shaw. Presentation at the 7th International Conference on Petroleum Phase Behavior and Fouling, Asheville, NC, 25–29 June 2006.
3. I. Prigogine, R. Defay. *Chemical Thermodynamics*, Longmans Green, London (1954).
4. E. A. Guggenheim. *Proc. Roy. Soc. A* **148**, 304 (1935).
5. G. M. Wilson. *J. Am. Chem. Soc.* **86**, 127 (1964).
6. H. Renon, J. M. Prausnitz. *AIChE J.* **15**, 785 (1969).
7. D. S. Abrams, J. M. Prausnitz. *AIChE J.* **21**, 116 (1975).
8. A. Fredenslund, J. Gmehling, P. Rasmussen. *Vapour-Liquid Equilibrium Using UNIFAC*, Elsevier, Amsterdam (1977).
9. J. H. Hildebrand, R. L. Scott. *The Solubility of Non Electrolytes*, Reinhold, New York (1950).
10. G. Scatchard. *Chem. Rev.* **8**, 321 (1931).
11. M. L. Huggins. *J. Chem. Phys.* **9**, 440 (1941).
12. P. J. Flory. *J. Chem. Phys.* **9**, 660 (1941).
13. W. B. Kay. *Ind. Eng. Chem.* **30**, 459 (1938).
14. B. H. Sage, W. N. Lacey. API Research Project 37.

15. B. H. Sage, W. N. Lacey. Monograph on API Research Project 37 - *Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen*, American Petroleum Institute, New York (1950).
16. D. L. Katz, F. Kurata. *Ind. Eng. Chem.* **32**, 317 (1940).
17. T. W. Leland. *AIChE J.* **12**, 1227 (1966).
18. J. G. Kirkwood. *J. Chem. Phys.* **3**, 300 (1935).
19. B. J. Alder. *J. Chem. Phys.* **40**, 2724 (1964).
20. B. J. Alder, T. E. Wainwright. *Phys. Rev.* **127**, 359 (1962).
21. H. L. Frisch, J. L. Lebowitz (Eds.). *The Equilibrium Theory of Classical Fluids*, Benjamin, New York (1964).
22. J. K. Percus, G. J. Yevick. *Phys. Rev*. **110**, 1 (1958).
23. M. S. Werteheim. *Phys. Rev. Lett.* **10**, 321 (1963).
24. G. S. Rushbrooke. *J. Chem. Phys*. **38**, 1262 (1963).
25. M. Kac. *Phys. Fluids* **2**, 8 (1959).
26. W. G. Chapman, K. E. Gubbins, G. Jackson, M. Radosz. *Ind. Eng. Chem. Res.* **29**, 1709 (1990).
27. H. C. Longuet-Higgins, B. Widom. *Mol. Phys.* **8**, 549 (1964).
28. B. Widom. *J. Chem. Phys.* **39**, 2808 (1963).
29. S. Beret, J. M. Praunitz. *AIChE J.* **21**, 21 (1975).
30. M. D. Donohue, J. M. Prausnitz. *AIChE J.* **24**, 849 (1978).
31. S. I. Sandler. *Fluid Phase Equilibr.* **19**, 235 (1985).
32. S. I. Sandler, K. H. Lee, H. Kim. In *Equations of State: Theories and Applications*, K. C. Chao, R. L. Robinson Jr. (Eds.), pp. 180–200, ACS Symposium Series No. 300, American Chemical Society, Washington, DC (1986).
33. A. Klamt. *COSMO-RS: from Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, Elsevier, Amsterdam (2005).
34. J. W. Gibbs. *The Scientific Papers of J. Willard Gibbs, Vol. 1: Thermodynamics*, Ox Bow Press, Woodbridge, CT (1993).
35. <http://trc.nist.gov/trctables.html>.
36. <http://trc.nist.gov/ThermoML.html>.
37. <http://trc.nist.gov/GDC.htmlTDE>.
38. J. R. Sitter, G. Hay, L. Neumeister. *Hydrocarbon Engineering*, February (2006).
39. R. Krenz. Ph.D. thesis, The University of Calgary (2005).
40. T. Laursen. Personal communication (2006).
41. R. A. Wilsak, S. W. Campbell, G. Thodos. *Fluid Phase Equilibr.* **33**, 157 (1987).
42. S. Thomas, V. Bhethanabotla, S. W. Campbell. *J. Chem. Eng. Data* **36**, 374 (1991).
43. U. Haarhaus, G. M. Schneider. *J. Chem. Thermodyn.* **20**, 1121 (1988).