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Thermophysical Properties: What Have We Learned Recently, and What Do We Still Need to Know?[1]

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Some recent developments in the areas of measurement, prediction, and correlation of thermophysical properties and phase behavior are reviewed. However, important problems remain, and some of these are not being addressed. Here a number of thermophysical properties problem areas are identified based on the prejudices of the author and a small survey of friends and colleagues in industry and academia. Many of the problems arise as result of changes in industrial emphasis, for example, from chemicals to materials and pharmaceuticals, changes in federal or local regulations permitting lower air and water emissions, changes in technology, and an interest in determining the fate of chemicals in the environment. Some of the research needs, both experimental and theoretical, to deal with these problems are discussed.

KEY WORDS: data needs; models; modeling needs; phase behavior; thermodynamic properties; thermophysical properties; transport properties.

1. INTRODUCTION

This paper provides me with an opportunity to discuss my views on the recent progress in a range of areas of thermophysical properties and to present my thoughts on needs for further research. I should point out that my background is chemical engineering, and my industrial contacts are largely with the chemical, petrochemical, and oil industries. Consequently, the views I express are those of an academic chemical engineer, and not of a basic scientist. Therefore, the thermophysical properties needs and accomplishments I identify are more related to industrial trends than to

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more basic scientific research. Also, since this is a paper, not a book, I can discuss only some of the important progress made in recent years. Therefore, I apologize in advance for any and all omissions.

Before discussing the specific accomplishments in the areas of thermophysical properties in recent years and some remaining needs, I want to indicate what I view to be several general trends.

2. MAJOR TRENDS

The first is that industrial needs drive the funding of thermophysical properties research, both those obtained directly from industry on a very short time scale and those provided by federal agencies over a somewhat longer time scale, which are increasingly more mission oriented.

The second trend is that industrial needs have changed. For many years the needs of the chemical, petrochemical, and petroleum industries set the agenda for some of the thermophysical properties research. These industries are now considered to be quite mature, and indeed many companies have undergone a partial metamorphosis to become materials companies, or at least polymers companies, rather than chemical companies in the traditional sense. Therefore, one important need is for data and prediction techniques for the thermophysical properties of materials, especially polymers, polymer blends, block copolymers, high-performance plastics, liquid crystal polymers, micellar solutions, surfactants, etc. To the companies involved, these needs are more important than obtaining higher accuracy information on traditional chemicals.

Another important trend is the need for thermophysical properties information related to the protection of our environment, the distribution of man-made chemicals in the environment, and their accumulation in our bodies. To meet increasingly more stringent environmental regulations, the chemical process industry needs data and estimation methods for the properties of substances at high dilution in water, for Henry's law coefficients, and for octanol–water partition coefficients, among others. These data are needed not merely for the more efficient design of processes, the usual role for thermophysical properties, but for designing or operating a process to meet environmental standards and for risk assessment. In this case, the question is not of the economic efficiency of a chemical process, but whether the process or chemical plant can be operated at all in the face of strict environmental regulation.

Other important needs for phase behavior and thermophysical properties information include for biological materials and pharmaceuticals, for complex fluids including surfactants and micellar fluids, and for other, at least to us, nontraditional areas in which technology is developing rapidly.

Again, I want to stress that information on such systems is more highly valued than additional, more accurate thermophysical properties data for the traditional chemicals that have maintained our interest for so long.

I now move on to my thoughts on some useful recent advances in thermophysical properties research, and a collection of remaining problems. These two parts are not distinct, since in the discussion of the recent advances I also indicate areas for further research. I do want to stress that while the words used here are my own, the ideas behind them have been shaped by the views of friends and colleagues in industry and academia based on the results of an informal survey I conducted. I have distilled some general themes from the written responses to this survey, as well as adding my own, admittedly quite biased views.

3. AREAS IN WHICH SIGNIFICANT PROGRESS HAS BEEN MADE

3.1. The Availability and Ease of Use of Thermodynamic Models in Process Simulators

One of the striking developments in the chemical industry in recent decades has been the evolution of process simulation. This has made it possible to optimize rapidly process designs based on economics or, more recently, for minimum emissions, for safety, or to satisfy other criteria. While in the past each chemical company developed and maintained its own process simulator, the industry is now dominated by a few software companies that have the personnel to put successful new thermodynamic models, enlarged databases, and improved computational algorithms in the hands of the design engineer rapidly. The positive impact of this is that engineers now have the latest computational tools and databases at their disposal. The downside is that the nonspecialist is confronted with a large number of models, and may not be able to choose between them intelligently. Further, few process simulation programs give the engineer any idea of the adequacy of the physical properties models he has chosen for the process under consideration, the completeness of the database from which the model parameters have been obtained, or the sensitivity of the final design to these considerations. Also, the process simulation software is now sufficiently robust that the program may generate answers, albeit incorrect or suboptimal ones, even with a poor choice for the thermodynamic models. This may not be apparent to the engineer, since after all, the results were produced by the computer. Unfortunately, this is an example of GIGO, garbage in, gospel out.

For the design engineer, modern process simulation software is a godsend, though it is a mixed blessing to those of us in the thermophysical properties business. Such programs move what we develop, data and models, rapidly from the research laboratory into the hands of the engineer. However, since these programs also insulate the design engineer from any lack of thermophysical properties data or the inadequacy of the thermodynamic models, they make the justification of our work more difficult. Indeed, among some engineers and management there is the perception that there is little need to measure new data or to develop new thermophysical models; the black box computer model will generate all the information needed. I sense the same feeling in the governmental funding agencies. Therefore, unless we can relate our work in thermophysical properties to environmental problems, to biotechnology, to electronic materials, or to other high-technology areas, we in academia may find it increasingly difficult to obtain continued funding of our research. Also, many of the thermophysical properties research specialist jobs in companies have disappeared as more reliance is placed on externally produced computer software rather than each company maintaining its own in-house process simulator.

In contrast to this rather negative general perception of the importance of thermophysical properties are the results of a survey [1] done by the commercial firm, Simulation Sciences, Inc., of the areas in which the users of their chemical process simulation software have the most difficulty. Their results showed that by far the largest user-identified problem is with thermophysical properties methods and data, which accounted for more than half of all responses. My interpretation is that this difficulty with thermophysical properties actually falls into two categories. The first is choosing which thermophysical properties model is appropriate for the mixture and conditions under consideration. For example, in the area of vapor–liquid equilibrium, current process simulators provide a bewildering choice of activity coefficient and equation-of-state models that can be properly chosen only by a specialist or an experienced engineer. One method of ameliorating this problem is by the development of more robust thermophysical properties models so that a larger range of components and conditions can be described with a single model. The recent combination of activity coefficient models and equations of state, which I discuss later, is one example of this. A goal of future research should be the development of globally applicable thermophysical models to replace many of the specialized models currently in use.

The second difficulty that process engineers encounter is having the necessary experimental data to determine the parameters in their thermophysical properties models, for example, the binary interaction parameters in equations of state or in activity coefficient models. To some extent this problem is being resolved by the development of comprehensive data banks. Though many such databases could be mentioned, the DECHEMA Chemical Data Series [2] is probably the most extensive for fluid phase behavior. These data banks, especially those that are easily computer-accessible, have greatly simplified the life of many engineers and have made file cabinets full of thermophysical properties information obsolete.

While referring to data banks, I cannot help but bring up an issue that I have raised several times in the past. Standardization has had an important positive effect on the modern industrial world. For years I have been appealing, unsuccessfully, to academic and industrial engineers and the database compilers to agree upon a standard or reference set of pure fluids and mixtures and the relevant data that would be used to test thermophysical models. Presently, the developer of a new model uses any set of data he or she accumulates that shows the success of their model, while leaving the user to discover its failures. Consequently, each potential user, company, or software house must individually test each model. This redundancy of effort would be eliminated by the use of an agreed upon standard set of test fluids, mixtures, and properties that the developer of any new model would be expected to use and would allow possible users quickly to discern the range of applicability of any new model.

3.2. Mixture Group Contribution Methods

Experimental measurements are very time-consuming and expensive. Further, experimental data are not likely to be available at exactly the temperature, pressure, or composition range of interest. Therefore, it is desirable to have methods for making predictions of the thermodynamic properties and phase behavior of any mixture. In this regard my colleagues in industry feel that the development of mixture group contribution methods, such as the UNIFAC [3, 4], ASOG [5], and TOM [6] methods, have been one of the most important developments in applied thermodynamics in recent decades. Of these, UNIFAC is the best developed in terms of its range of applicability and the largest database used in obtaining its parameters. UNIFAC is the most commonly used mixture group method, distantly followed by ASOG and TOM.

Since the UNIFAC method has now been in use for almost two decades, its capabilities for the reasonably accurate prediction of low-pressure vapor–liquid equilibria of many systems are known, as are is some of its deficiencies. One of these deficiencies is the inability to differentiate between isomers. Another is its inability to account for proximity effects, that is, the change in behavior of one functional group due to the presence of an adjacent strongly polar functional group on the same molecule [7]. A third is the inability to predict correctly the phase behavior of small molecules containing strongly electronegative atoms such as partially chlorinated and fluorinated C_1 and C_2 hydrocarbons (the HCFCs and HFCs). This last problem has become evident in the search for mixture and especially azeotropic mixture replacements for the ozone-depleting refrigerants currently in use. For the experimentalist, a positive result of this failure of group contribution methods has been the recognition that experimental measurements are still necessary and has led to extensive experimental work at university and industrial laboratories around the world.

Another area in which experimental measurements are needed is for the completion of the UNIFAC (and other mixture group contribution) interaction tables. The recent listing of Hansen et al. [4] shows that UNIFAC parameters have been determined from available, thermodynamically consistent vapor–liquid equilibrium data for only about half of the group–group interactions. From their list one can identify mixtures whose vapor–liquid equilibrium behavior should be measured to determine missing group–group interaction parameters. It is not surprising to discover from such an analysis that many difficult mixtures will need to be measured to complete the parameter matrix.

Vapor–liquid equilibrium measurements done over decades and assembled in the Dortmund Data Bank [8] have been used to develop the current UNIFAC parameter matrix. It is instructive to examine the worldwide rate of generation of experimental vapor–liquid equilibrium data. Professor Gmehling and his collaborators have analyzed the sources of data in their data bank and found a rapid increase in the measurement of vapor–liquid equilibrium between 1950 and 1970, followed by a decrease in the number of systems studied in the most recent decade. The success of mixture group contribution methods is frequently cited as one of the reasons for the decrease in measurement activities.

The UNIFAC method has been much improved over the years. For example, the modified UNIFAC method results in more accurate predictions of infinite dilution activity coefficients, heats of mixing, and vapor–liquid equilibria over a range of temperatures. In addition, UNIFAC has been expanded also to treat polymer solutions and, most recently, electrolyte solutions. It is the only mixture group contribution model that has been extended in this fashion. Before leaving this subject, it is of interest to note that there is also a need for heat of mixing data to improve mixture group contribution methods. Professor Gmehling, again analyzing the data in the Dortmund Data Bank, has found that many of the heat of mixing data were obtained near 25°C, and more than 90% of all available heat of mixing data are within the limited temperature range of 0 to 50°C. Data are needed over a much wider temperature range.

3.3. Computer Simulation

The most important recent development in molecular-level computer simulation, which includes molecular dynamics and Monte Carlo simulation, has been the Gibbs ensemble [9, 10] and other methods that allow the direct calculation of vapor–liquid equilibrium. Additional applications of these methods have included the study of liquid–liquid equilibria, gas–gas equilibria, polymers, and polymer solutions, the self-assembly of surfactant solutions, the denaturation of proteins, and other interesting phenomena. However, computer simulation cannot yet be used for quantitative predictions, largely because of uncertainties in the intermolecular potential function and, perhaps equally important, the neglect of pairwise nonadditivity of the interaction energy that we do not know how to correct. Many examples that one finds in the literature of the quantitative "prediction" of properties by computer simulation result only after significant adjustment of potential parameters. Consequently, what sometimes appears to be a prediction by computer simulation is perhaps better described as sophisticated correlation. At present, there are very few cases in which we can use computer simulation for the accurate *a priori* prediction of the properties of pure fluids or mixtures.

Molecular-level computer simulation has been useful in a number of ways. Perhaps most important is in testing statistical mechanical theories. Since statistical mechanics provides a theoretical basis for thermodynamic fluid properties modeling, a goal has been to derive activity coefficient models, equations of state, and transport properties directly from statistical mechanics with a minimum of assumptions. In fact, progress has been slow, with the most useful thermodynamic models arising from the introduction of many simplifying, and sometimes ad hoc, assumptions into statistical mechanical theory. Molecular computer simulation has been most useful in testing these assumptions. This is because, within the constraints of computer simulation, we obtain essentially exact results for the thermodynamic properties of the model potential we have simulated. Therefore, we can test the underlying basis of a theory or model against simulation data. However, since the model potentials used are so simple and neglect nonadditivity, there are numerous examples of models that describe simulation data well but are not as good as the empirical equations of state and activity coefficient models in common use for correlating experimental data of real fluids and mixtures.

Computer simulation has also proved very useful for answering "what if" questions, and especially for assessing the role of different types of intermolecular forces on thermodynamic properties. That is, one can determine the effect on thermodynamic and transport properties of, for example, dipolar or quadrupolar forces by doing simulations for a model potential without such forces, and then again with these forces. Because of the simplicity of the potentials used, while none of the results might quantitatively describe a real fluid, the difference between the two sets of simulations would indicate the direction and likely magnitude of the change in fluid properties due to the change in the intermolecular potential model. Such procedures have been used to study bulk fluid properties, the adsorption of gases on surfaces, and crystal structures, to name just a few. Another application has been to test mixture local composition models and, especially, compositional enhancements in mixtures involving supercritical fluids.

An important long-term result of such molecular simulation studies could be to allow us to design molecules or mixtures to meet properties specifications as is increasingly being done in medicinal chemistry, and to be able to predict more accurately the properties of molecules from only their structure. Software companies such as Molecular Simulations, Inc., and Biosym already market programs that allow the prediction of a variety of properties of molecules from only their chemical structure.

Simulations are also being used to carry out experiments that cannot be done in the laboratory, for example, studying rapid nucleation behavior, the behavior of molecules in very narrow pores, and transport properties in high-gradient fields. An important and useful engineering application of molecular-level simulations in recent years has been as an extrapolation tool. Here one uses simulation to tune the parameters in the intermolecular potential function to available experimental data and then uses simulation to compute the behavior at experimentally difficult conditions such as at very high temperature and/or pressure. Such information can then be used directly or to produce a set of both experimental and simulation data that are then fit with empirical or semitheoretical models for use by scientists and engineers [11]. While extrapolation is always fraught with uncertainty, simulation that relies on fitting the intermolecular potential function and then doing exact statistical mechanics on the computer may be more satisfactory than using an inexact macroscopic model of the thermodynamic property of interest. Such simulation-based extrapolations have been used, for example, to study molten salts, high-temperature electrolyte solutions of geophysical interest, and the supercritical behavior of mixtures containing light components.

There are also several useful thermodynamic models that have arisen based on statistical mechanical theory and computer simulation. A recent example is the statistical association fluid theory or SAFT equation of state [12, 13], which, though not yet widely accepted, explicitly contains terms relating to the formation of chains and molecular association such as hydrogen bonding. This equation has been used for the study of long-chain molecules, polymers, and mixtures with associating components.

3.4. Computational Chemistry

An area that has been developing rapidly, both in its underlying theoretical basis, range of use, and availability on supercomputers and in the user-friendliness of the software available, is computational quantum chemistry. This computational tool is only just beginning to be used by engineers. One area of application has been in identifying pathways, transition states, and activation energies in reaction chemistry. Another has been in computing potential energies of interaction between atoms and molecules that can then be used in computer simulations. We have used *ab initio* molecular orbital calculations to develop a well-founded basis for

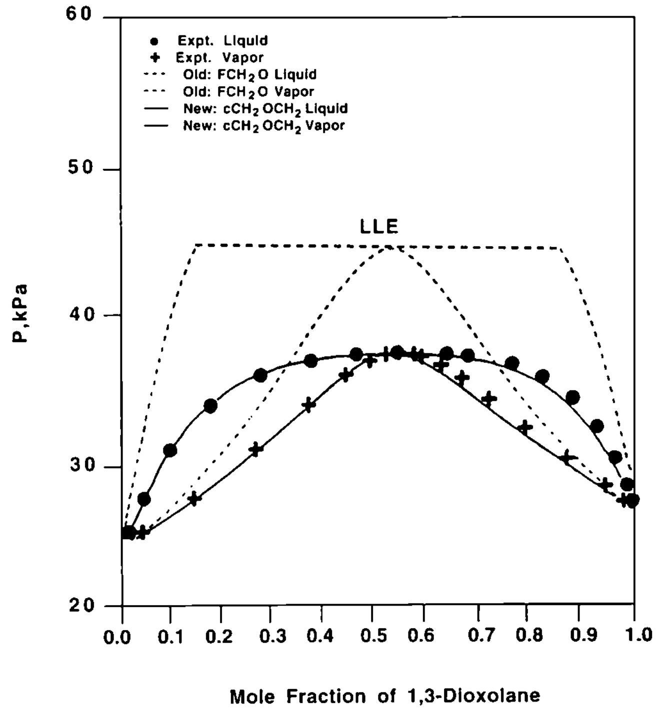

Fig. 1. The vapor–liquid equilibrium of the 1,3-dioxolane + cyclohexane mixture at 313.15 K. The points are experimental data. The dashed lines are the UNIFAC predictions with the empirically defined groups, and the solid lines result from the UNIFAC model with groups chosen based on quantum mechanics calculations of Wu and Sandler [15].

identifying functional groups in group contribution methods [14, 15] such as UNIFAC. The basis for the identification of functional groups is that their electrostatic charge should be independent of the molecule in which the group appears.

One example of the utility of this method is that we show in Fig. 1 how using theoretically based, rather than empirically chosen, functional groups leads to more accurate UNIFAC predictions with the same number of adjustable parameters [15]. Such quantum chemistry calculations have also shown that current group contribution methods will not be successful in dealing with small molecule hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) because the strong electronegativity of the Cl and F atoms result in very different charge distributions from molecule to molecule. Also, problems will arise for fluids with several hydrogen-bonding sites, since there we found that hydrogen-bond energies between the functional groups depend on the proximity of other hydrogen-bonding sites on the same molecule. This is a violation of the group contribution principle that depends on the assumption that a group always behaves in the same manner independent of the molecule on which it is located. We are currently using *ab initio* molecular orbital calculations to compute hydrogen bonding strengths in the hope that we will be able to develop a hybrid group contribution–molecular orbital prediction method for these difficult systems.

3.5. Combination of Equations of State and Activity Coefficient Models

Traditionally equations of state have been used to describe mixtures that do not have large excess free energies of mixing, such as mixtures of hydrocarbons or hydrocarbons and inorganic gases. The advantage of the use of equations of state is that predictions for the phase behavior of mixtures, together with their density and enthalpy, can be made with a single model over large ranges of temperature and pressure with few adjustable parameters. Excess free energy or activity coefficient models, on the other hand, can be used for the phase behavior description of mixtures with large excess free energies of mixing. However, these models require several temperature-dependent parameters and the identification of standard states, which can be a problem with supercritical components. Even when this is done, we do not get any information on phase densities, and may not get any information on the excess enthalpy and entropy of mixing unless measurements are carried out over a range of temperatures.

A number of my industrial colleagues have identified the very recent introduction of mixing rules that allow equations of state to be used with highly nonideal mixtures as one of the important developments of recent years. These mixing rules allow equations of state to describe the phase behavior and thermodynamic properties of mixtures containing very polar compounds, hydrogen-bonding compounds, etc., over large ranges of temperature and pressure with relatively few parameters. The two most successful examples of these are the Wong–Sandler [16–18] and the modified Huron–Vidal MHV2 [19, 20] mixing rules. I briefly discuss the first of these, which has a simpler basis, and for the obvious reason that I know it better.

To illustrate the basis for these mixing rules, I use the simple van der Waals equation of state

$$P=\frac{RT}{v-b}-\frac{a}{v^2} \tag{1}$$

The usual way to extend this equation to mixtures is to use the van der Waals one-fluid mixing rules

$$a_m=\sum_i\sum_j x_ix_ja_{ij} \qquad \text{and} \qquad b_m=\sum_i\sum_j x_ix_jb_{ij} \tag{2}$$

with the combining rules

$$a_{ij}=\sqrt{a_{ii}a_{jj}}(1-k_{ij}) \qquad \text{and} \qquad b_{ij}=\tfrac{1}{2}(b_{ii}+b_{jj}) \tag{3}$$

This mixing rule satisfies the known boundary condition of the quadratic composition dependence of the second virial coefficient

$$B(x_i,T)=\sum_i\sum_j x_ix_jB_{ij}(T)$$

$$\text{since for a cubic equation of state} \quad B_{ii}=b_{ii}-\frac{a_{ii}}{RT} \tag{4}$$

However, this mixing rule constrains two functions, a and b, to satisfy this single boundary condition; the resulting mixture equation of state cannot describe very nonideal mixtures.

The idea of Wong and Sandler is that the choice of the two parameters in a cubic equation of state for mixtures provides two degrees of freedom. They used these two degrees of freedom to ensure that (i) the composition dependence of the mixture equation of state is correct at low density, that is, that the second virial coefficient should be quadratic in mole fraction;

and (ii) at liquid densities the equation of state behaves like any of the common activity coefficient models the user specifies. Thus instead of using Eqs. (2)–(4), to satisfy the first condition, they used the following equation based on Eq. (4) as one part of their mixing rule

$$\left(b-\frac{a}{RT}\right)_m=\sum_i\sum_j x_ix_j\left(b-\frac{a}{RT}\right)_{ij} \tag{5}$$

This ensures that the quadratic composition dependence of the second virial coefficient is satisfied, though it does not specify either a_m or b_m separately. As the second boundary condition they required that

$$\begin{aligned} A^{\mathrm{EX}}_{\mathrm{EOS}}(T, P\to\infty, x_i) &= A^{\mathrm{EX}}_{\gamma}(T, P\to\infty, x_i) \\ &= A^{\mathrm{EX}}_{\gamma}(T, \text{low } P, x_i) = G^{\mathrm{EX}}_{\gamma}(T, \text{low } P, x_i) \end{aligned} \tag{6}$$

Here the first equality requires that at high density the excess Helmholtz free energy of mixing calculated from an equation of state $A^{\mathrm{EX}}_{\mathrm{EOS}}$ should equal that from an activity coefficient model A^{EX}_{γ}, while the remaining two equalities are based on the fact that at liquid densities the excess Helmholtz free energy is essentially independent of pressure and, at low pressures, is equal to the excess Gibbs free energy of mixing.

The combination of Eqs. (5) and (6) results in the following new mixing rules for the a and b parameters:

$$\frac{a_m}{RT}=Q\frac{D}{1-D} \quad \text{and} \quad b_m=\frac{Q}{1-D} \tag{7}$$

with

$$Q=\sum_i\sum_j x_ix_j\left(b-\frac{a}{RT}\right)_{ij} \quad \text{and} \quad D=\sum_i x_i\frac{a_{ii}}{b_{ii}RT}+\frac{G^{\mathrm{EX}}(x_i)}{RT} \tag{8}$$

The combining rule that can be used with this mixing rule is

$$b_{ij}-\frac{a_{ij}}{RT}=\frac{1}{2}(b_{ii}+b_{jj})-\frac{\sqrt{a_{ii}a_{jj}}}{RT}(1-k_{ij}) \tag{9}$$

The combination of Eqs. (7), (8), and (9) leads to an equation of state model that can describe mixtures of any degree of nonideality over large ranges of temperature and pressure.

This mixing rule has been tested in a number of applications and there are several interesting observations. First is that mixtures of any degree of nonideality can now be described over large ranges of temperature and pressure, including strongly polar and other mixtures that previously were not describable by equations of state. Thus the range of applicability of equations of state has been increased. Second, since the equation of state has an inherent temperature dependence, the binary parameters in the mixing rules are much less temperature dependent, indeed almost temperature independent, than when the same activity coefficient models are used to fit experimental data directly. As a consequence it is now possible to use vapor–liquid equilibrium data obtained at low temperature and pressure to make accurate predictions at much higher temperatures and pressures. Third, when combined with UNIFAC, which can be used only at low pressures, equations of state can now be used to make predictions of vapor–liquid equilibria over large ranges of temperature and pressure in the absence of any experimental data. In this case the accuracy of the method at all conditions is essentially limited only by the accuracy of the UNIFAC method at low pressures.

3.6. Improved Spectroscopic Tools that Supply Molecular-Level Information

The area of thermophysical properties is well past the stage of models being completely empirical. Recent models have been based on molecular ideas, such as local compositions in which the composition around each molecule in a mixture may be different from the bulk composition and include specific interactions such as hydrogen bonding. Computer simulation has provided some insight into the extent of local compositions and molecular-level phenomena that need to be included in our models. However, the information we get from computer simulation is for highly idealized models of fluids, so that the utility of this information for real fluids is limited. On the other hand, molecular-level experimental probes have provided information on the local compositions in real fluid mixtures, but for molecules whose interaction potentials are unknown. These probes include x-ray and neutron diffraction for relatively simple molecules and nuclear magnetic resonance (NMR) chemical shifts, NMR relaxation times, fluorescence lifetimes, and ultraviolet light/visible light spectroscopy for some complicated molecules [21–23]. In this way new insight has been obtained into the extent of local composition phenomena (including in supercritical fluid mixtures), the extent of hydrogen-bonding, and other association phenomena, and it has been possible test the underlying basis of currently used local composition models, such as the NRTL (nonrandom two-liquid) model.

3.7. Critical- and Near-Critical-Region Behavior

One of the traditional problem areas for engineers is the description of fluids in the critical and near-critical regions. Classical equations of state in common use give incorrect behavior in these portions of the phase diagram, though from renormalization group theory and other methods, the limiting behavior in the critical region is known. Over the years there has been numerous attempts to use crossover functions to combine simple classical equations with the known limiting behavior. The recent work by Sengers et al. [24, 25] appears to be the most successful in this regard. This work has shown that, based on good theory, it is possible to obtain a quantitative representation of the complete vapor–liquid binodal curve, including the flatness in the coexistence curve in the critical region and the divergence in the constant volume heat capacity. One result of this work has been to show that density fluctuations affect thermodynamic properties even tens of degrees K and several moles per liter in density away from the fluid critical point.

Current work in this area has been concerned with relatively simple pure fluids (inorganic gases, light hydrocarbons, and refrigerants) and needs to be extended to other fluids of engineering interest. A useful advance would be the development of generalized renormalization and crossover functions so that an extensive data-fitting effort does not have to be carried out for each fluid. A second goal should be to develop a better understanding of the thermodynamic and transport properties near mixture critical points, as this is less well understood than for pure fluids and is important for engineering applications.

A separate problem identified by the engineering respondents to my survey is that of computing critical region behavior (including tricritical points, etc.) once a reasonable therodynamic model has been developed. This is a long-standing problem and the work of Heidemann and Khalil [26] and Heidemann and Michelsen [27], based on an analysis of the Helmholtz free energy function, has been especially useful for engineering calculations.

3.8. Electrolyte Solutions

The thermodynamics of aqueous solutions containing electrolytes is an important area of thermophysical properties measurements and modeling. Of special interest are applications including the hydrological fate and transport of chemicals and heavy metals, water treatment processes, chemical processing in aqueous solutions, geophysical processes, and reactions in salt-containing supercritical water as a method of the hydrothermal processing of coal and pollutants. The latter two are examples of areas that have resulted in an interest in electrolyte solutions at high temperatures and pressures.

Thermodynamic models for electrolyte solutions consist of two components. The first is the calculation of the equilibrium or dissociation constants for the salts involved, and the second is the calculation of the activity coefficients. This last part has traditionally been done by a combination of a long-range term, usually an extension of the Debye–Hückel limiting law, and a term that describes the short-range interactions. In recent years several alternate methods of describing electrolyte solutions have come into use. Perhaps the most successful is the Pitzer equations [28] based on the osmotic virial coefficient expansion. With a sufficient number of terms, this expansion can very accurately fit experimental data to high electrolyte molalities, including molten salts. While this model can provide excellent correlations of experimental data, there are no correlations for the Pitzer coefficients that allow extrapolations outside the range of experimental data used in the correlation or predictions in the absence of experimental data. Further, the Pitzer coefficients, which include some of the speciation within the expansion, vary with ionic strength and temperature. Consequently, the coefficients are not generalizable and will change in value in going from a pure to mixed salt. The equations are also not valid when the fluid is very compressible, such as near the critical point of the solvent.

The model of Helgeson [29] can be used to calculate the equilibrium constants over broad ranges of temperature and pressure, provided the equilibrium constant is known at one temperature. This is especially useful in the geophysical modeling of high-temperature, high-pressure aqueous electrolyte solutions. Both the Pitzer and the Helgeson models, together with older models originated by Bromley and Meissner, have been reviewed recently [30] and incorporated into commercially available software packages such as the ESP (environmental simulation program) of OLI Systems, Inc., and EQ6 of Lawrence Livermore Laboratories. While it is fair to say that progress has been, and continues to be, made in the field of electrolyte solutions, much work also remains to be done.

4. SOME INTERESTING PROBLEM AREAS

4.1. Failure of Empirical Thermophysical Models

One illustration of a shortcoming of almost all phase behavior models is that accurate liquid–liquid equilibrium cannot be predicted with model parameters obtained from correlating vapor–liquid equilibrium data. In fact this is symptomatic of a more general problem. The success of predictive models for excess Gibbs free energies and hence phase behavior, such as UNIFAC, and correlative models such as the Van Laar, NRTL, Wilson, and UNIQUAC models, to name a few, might suggest that we have a real understanding of the behavior of liquid mixtures. While chemical engineers have been quite successful in studying vapor–liquid equilibrium, this is only because the excess Gibbs free energy of mixing g^E is a simpler function of composition than the excess enthalpy of mixing h^E and excess entropy of mixing s^E, to which g^E is related by $g^E = h^E - Ts^E$. This is shown, for example, in the data in Fig. 2, based on the work of Kojima [31]. There are two observations to be made from this figure. The first is that while the excess Gibbs free energy of mixing is a simple, almost-symmetric function of composition, its components h^E and s^E are much more complicated. This suggests the occurrence of molecular-level phenomena that are not captured in the simple excess free energy models we use. Second, we see that g^E, h^E, and s^E are all functions of temperature. When necessary, we account for this by making the parameters in our models empirical functions of temperature, without understanding, or trying to account for, the molecular-level phenomena involved.

Evidence of the failure of our empirical models is that when such a model is fit to one set or type of thermodynamic data, it frequently results in inadequate predictions of other types of data. I have already mentioned that an excess Gibbs free energy model fit to vapor–liquid equilibrium data may not lead to accurate predictions of liquid–liquid equilibria. Gmehling and co-workers [32] have shown that fitting a multiparameter

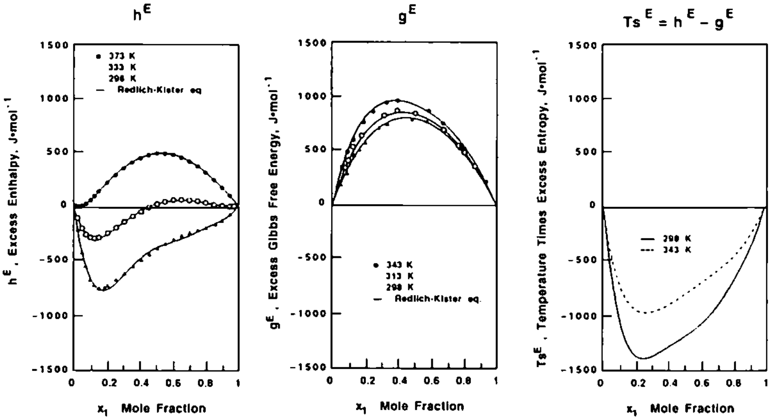

Fig. 2. The excess enthalpy, Gibbs free energy, and entropy of mixing for the ethanol(1) + water(2) system over the temperature range of 298 to 343 K from the calculations of Kojima [31].

excess Gibbs free energy model to only vapor–liquid equilibrium data over a range of temperatures does not lead to accurate predictions for the infinite-dilution activity coefficients, the excess enthalpy or the azeotropic composition as a function of temperature. However, also including the infinite-dilution activity coefficients and the excess enthalpy in the parameter estimation process improves the fit of all these properties. One conclusion is that fitting vapor–liquid equilibrium data, while essential to the design of chemical processes, is not a sufficiently sensitive test of a thermodynamic model, or for determining its parameters, to allow for the prediction of related thermodynamic properties.

Consequently, I return to a comment I made earlier, that what is needed is a global model of the thermodynamic behavior of mixtures that includes the relevant molecular phenomena, such as a continuous transition from physical models of nonideal solutions to chemical association models.

4.2. The Purification and Isolation of Biological Molecules and Pharmaceuticals

Thermophysical properties are of central importance in the chemical industry for the design of purification processes including distillation, liquid extraction, membrane and supercritical separations, etc. Generally separations processes account for a large fraction of the equipment and operating costs of any chemical plant, and the cost of purification increases with decreasing initial composition as is shown in the now famous Sherwood plot [33]. The purification of biological materials and pharmaceuticals represents a special problem in several regards. First, the initial concentration of the substances involved, for example, hormones, viruses, antibiotics, and the products of fermentation processes, may be very low, while a very high-purity product is required. Second, the substances to be recovered are frequently very fragile, so that only a limited range of temperature, pressure, or solvents may be used in the processing, which eliminates traditional separation methods such as distillation and extraction with organic solvents. Finally, the material to be purified may also be poorly characterized.

Two methods used for the purification of biological molecules that rely on thermodynamics and phase behavior are crystallization, in which the biological molecule of interest is made to precipitate from solution using salting-out effects, and extraction in aqueous two-phase polymer systems. In the latter case, dissolving either two appropriately chosen water-soluble, but incompatible polymers in water, or one water-soluble polymer and a salt, produces two aqueous, nondenaturing phases. The biological molecules partition differently between these phases, which is the basis for an extraction process.

The challenge is to describe the partitioning of the biological molecules between the solution and the solid in crystallization, or between the two aqueous phases, and a variety of tools needs to be brought to bear to accomplish this. Both crystallization and aqueous two-phase extraction processes use salts and other electrolytes in aqueous solution, so that a thermodynamic description of electrolytes in aqueous solution is required. Since polymers may be used as the salting-out agent in crystallization, and one or more polymers are present in aqueous two-phase extraction, the thermodynamics of polymer solutions must also be included in the description. Finally, the biological molecules of interest may be sufficiently large to be described best by the methods of colloid science rather than solution thermodynamics. Also, these molecules are usually charged, which is an important factor in their partitioning, and their charge will change with the pH of the solution. Further, since the biological molecules of interest may concentrate at the interface in aqueous two-phase partitioning, an understanding of the properties of interfaces is also needed.

There has been some progress on understanding the behavior of biological molecules in aqueous solutions [34, 35] and at interfaces, but we still do not have a general model that will allow the prediction of the partitioning behavior of biological molecules knowing only their sizes, surface properties, etc.

4.3. The Thermodynamic and Phase Behavior of Structured Fluids

Surfactants and materials that form micellar fluids are a multi-billion-dollar per year commodity used as cleansing agents, in the delivery of herbicides, pesticides, and drugs, in the coatings industry, etc. These materials form structured fluids with very complicated phase behavior as shown in Fig. 3 for the binary mixture of water and a polyethylene glycol ether ($C_{12}E_5$ or penta-ethyleneglycol mono *n*-dodecyl ether) [36]. This mixture has a micellar (L_1) and inverted micellar (L_2) phases, a bilayer phase (L_3), three liquid crystal phases including a viscous isotropic phase V_1, a hexagonal phase H_1, a lamellar phase L_α, and a micellar phase I_1. There is much to be done in understanding the thermodynamics and phase behavior of these mixtures. In fact, my colleagues working in this field regard the phase diagrams for common chemical systems to be quite boring.

4.4. The Thermodynamic Characterization of Large, Polydisperse Species

Chemical species are generally characterized by their formula, structure, critical properties, molecular properties (dipole moment, etc.) and

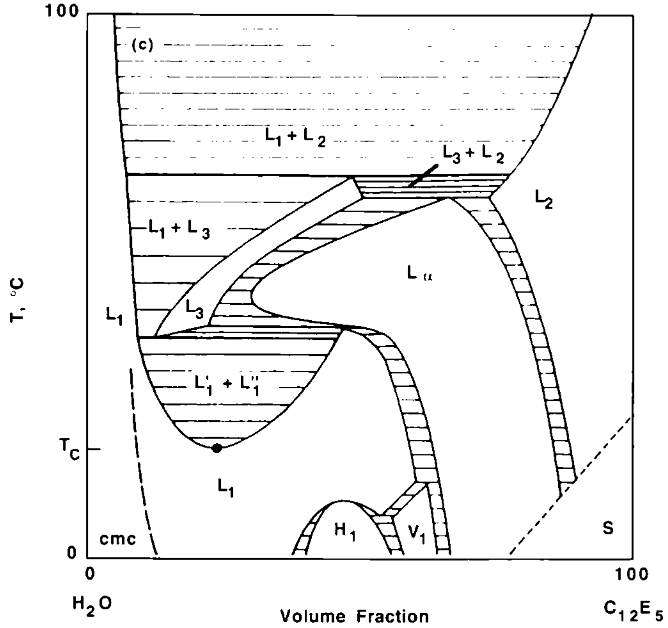

Fig. 3. The phase diagram of the water + penta-ethyleneglycol mono *n*-dodecyl ether ($C_{12}E_5$) showing the variety of lamellar liquid crystal phases that form [36].

the macroscopic properties (density, boiling point, vapor pressure, etc.) However, such information is not available to characterize many materials of engineering interest. An obvious example is the asphaltenes, waxes, and high molecular weight hydrocarbons present in petroleum, which decompose well before their critical temperature is reached, and the residuals from the vacuum distillation of crude oils.

A remaining problem in the fuels industry, according to my survey, is for a better, more scientifically based characterization for petroleum fractions with normal boiling points higher than 800°F. The normal boiling point and specific or API gravity, sometimes with a PONA (paraffin-olefin-naphthene-aromatic) analysis, frequently used in the petroleum industry is insufficient. New analytic tools have now become available to determine the speciation and composition of these heavy ends. For example, high-resolution field ionization mass spectroscopy has been used to identify more than 3000 compounds present in the residues from vacuum distillation of crude oil [37]. The challenge now is to determine how to use this information in refinery processing. Indeed, we have a situation in which the analytical methods have progressed more rapidly than our ability to use the information they generate. Obviously some sort of lumping scheme will be needed when so many components are involved. This might be done by a return to the thermodynamics of continuous mixtures, a subject of great research interest to the thermodynamics community 5 years ago.

5. AREAS FOR ADDITIONAL THERMOPHYSICAL PROPERTIES RESEARCH

Many other areas in which thermophysical properties research is needed were identified in my survey. Some of these are very specific, and others are quite broad. These research needs are listed, without comment or explanation, in the Appendix.

APPENDIX

A.1. Additional Thermodynamic Measurement Needs for the Chemicals, Petrochemicals, and Oil Industries

Properties of mixtures at high dilution for environmental modeling
Henry's coefficients of gas mixtures in solvent mixtures
Phase behavior of strongly associating fluids such as HF
Phase behavior of mercaptans and sulfur compounds in hydrocarbon mixtures
Properties of solids including hydrates, waxes, and asphaltenes and the phase behavior of asphalts and asphaltenes
Phase behavior of hydrocarbons with benzene and aromatic extraction solvents
Enthalpies of water/hydrocarbon systems
Interfacial tension, both static and dynamic

A.2. Additional Thermodynamic Measurement Needs for the Materials-Related Industries

Properties of very dilute mixtures for high-purity chemicals and electronic materials
Phase behavior of micellar and other structured solutions
Phase behavior of surfactant solutions
Phase behavior of water soluble polymers
Phase behavior of gels
Properties and phase behavior of polymers, polymer solutions, copolymers, and polymer blends, including blend miscibility and polymer adhesion
Surface phenomena

A.3. Additional Thermodynamic Modeling Needs for the Chemicals, Petrochemicals, and Oil Industries

Henry's coefficients of gas mixtures in equilibrium with solvent mixtures
Thermodynamics of polyelectrolyte systems
Phase equilibria models for mixtures consisting of salts, acids, or bases
Better predictive capabilities near the critical point of mixtures, including property predictions in the critical and retrograde region
Description of LLE near the plait point (This is a particular problem with distillation columns that exhibit LLE on one or more stages but is not a general problem in liquid extraction, where the mutual solubilities are small.)
Phase behavior of strongly associating fluids such as HF
Interfacial tension, both static and dynamic
Thermodynamic framework for multisolvent electrolyte systems
Estimation methods for the solubility of sparingly soluble organic compounds in water
Accurate calculation of the differential and integral heats of vaporization of mixtures
Accurate calculation of the enthalpies of absorption and adsorption
Models for the adsorption of ions and molecules on the surface of solids in an aqueous environment for the simulation of groundwater contamination
Modeling phase equilibrium in reactive systems
Modeling phase equilibrium of electrolyte solutions that span a large range, i.e., from highly dilute to extremely strong acids, and thus go from completely dissociated to essentially undissociated solutions

A.4. Additional Thermodynamic Modeling Needs for the Materials Industries

Thermodynamics of polyelectrolyte systems
Phase behavior of micellar, surfactant, and other structured solutions
Phase behavior of polymers and polymer solutions, including the influence of pressure on miscibility windows. This includes liquid–liquid equilibrium of systems exhibiting both UCST and LCST, i.e., closed-loop behavior, which is important in increasing the compatibility of polymers
Phase behavior of polymers with solvents and gases, which is important in numerous applications, including the supercritical extraction and expansion (RESS) of polymers
Modeling of polymer/solvent systems over the whole composition range

A.5. Transport Property Measurement Needs

Diffusion coefficients of species in complex mixtures [Most diffusion coefficient measurements are for a single solute in a pure solvent; there are few measurements of diffusion in liquid mixtures.]

Properties of polymers, polymer solutions, copolymers, and polymer blends including gas and solute permeabilities

Transport properties in the critical and near-critical region

A.6. Transport Property Modeling Needs

Models for the diffusion coefficients of species in complex mixtures

Liquid viscosities of petroleum fractions with normal boiling points greater than 800°F, and/or carbon numbers greater than 28. In these cases we need to include a characterization which includes the molecular structure; normal boiling point and specific or API gravity are insufficient

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