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Thermodynamics of Fluid-Phase Equilibria for Standard Chemical Engineering Operations

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Thermodynamics provides one of the scientific cornerstones of chemical engineering. This review considers how thermodynamics is and has been used to provide phase equilibria as required for design of standard chemical engineering processes with emphasis on distillation and other conventional separation operations. While this review does not consider "modern" thermodynamics for high-tech applications, attention is given to 50 years of progress in developing excess-Gibbs-energy models and engineering-oriented equations of state; these developments indicate rising use of molecular physics and statistical mechanics whose application for chemical process design is made possible by increasingly powerful computers. As yet, results from molecular simulations have not had a major influence on thermodynamics for conventional chemical engineering; however, it is likely that molecular simulation methods will become increasingly useful, especially when supported by quantum-mechanical calculations for describing intermolecular forces in complex systems. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 739–761, 2004
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Introduction

Separation of fluid mixtures is one of the cornerstones of chemical engineering. For rational design of a typical separation process (for example, distillation), we require thermodynamic properties of mixtures; in particular, for a system that has two or more phases at some temperature and pressure, we require the equilibrium concentrations of all components in all phases. Thermodynamics provides a tool for meeting that requirement.

For many chemical products (especially commodity chemicals), the cost of separation makes a significant contribution to the total cost of production. Therefore, there is a strong economic incentive to perform separations with optimum efficiency. Thermodynamics can contribute toward that optimization. In this article, we indicate some of the highlights of progress in the thermodynamics of phase equilibria since the *AIChE Journal* began about 50 years ago.

Although it is clear that, in addition to phase equilibria, thermodynamics also provides useful caloric information (enthalpy balances) that affects separation operations, we do not consider that here. Furthermore, we recognize that in recent years, thermodynamic research has given rising attention to product (as opposed to process) design. There is good reason to

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believe that "modern" chemical engineering will be increasingly concerned not with large-scale production of classical (commodity) chemicals, but with new (specialty) materials for application in biotechnology, medicine, pharmaceuticals, electronics, and optics, as well as in the food and personal-care industries. Thermodynamics can contribute to the development of these "new" areas and, indeed, much progress toward that end has been reported in the ever-growing literature. In our short review here, it is not possible to give adequate attention to "new" thermodynamics. This review is essentially confined to progress in thermodynamics for what is often called "traditional" chemical engineering.

Furthermore, during the last 50 years, the literature on applied thermodynamics has grown to vast proportions, even when we limit our attention to phase equilibria. Therefore, this review cannot be comprehensive. Indeed, it is unavoidably selective, reflecting the authors' (right or wrong) opinions and preferences. Space and time are finite, and some subconscious prejudice is always with us. The authors, therefore, apologize to their colleagues whose work is not sufficiently mentioned here or worse, not mentioned at all. Because the editor has necessarily limited the total number of pages available to us, we must, with regret, omit much that may merit inclusion.

Fifty years ago, most chemical engineering thermodynamics was based on representation of experimental data in charts, tables, and correlating equations that had little, if any, theoretical basis. Fifty years ago, most chemical engineering thermodynamics was in what we may call an empirical stage. However, the word "empirical" has several interpretations. When we represent experimental data by a table or diagram (for example, the steam tables or a Mollier diagram), we call such representation empirical. When we fit experimental ideal-gas heat capacities to, say, a quadratic function of temperature, we choose that algebraic function only because it is convenient to do so. However, when, for example, we fit vapor–pressure data as a function of temperature, we inevitably do so by expressing the logarithm of the vapor pressure as a function of the reciprocal absolute temperature. This expression is also empirical but in this case our choice of dependent and independent variables follows from a theoretical basis, viz. the Clausius–Clapeyron equation. Similarly, when for a binary mixture, we represent vapor-liquid equilibrium data with, say, the Margules equation for activity coefficients, we also call that representation empirical, although it has a theoretical foundation, viz. the Gibbs–Duhem equation. We should distinguish between "blind" empiricism, where we fit experimental data to a totally arbitrary mathematical function, and "thermodynamically-grounded" empiricism where data are expressed in terms of a mathematical function suggested by classical thermodynamics.

If now, in addition to thermodynamics, we introduce into our method of representation some more-or-less crude picture of molecular properties, for example, the van der Waals equation of state, we are still in some sense empirical but now we are in another realm of representation that we may call "phenomenological" thermodynamics. The advantage of proceeding from "blind" to "thermodynamically-grounded" to "phenomenological" is not only economy in the number of adjustable parameters but also in rising ability to interpolate and (cautiously) extrapolate limited experimental data to new conditions, where experimental data are unavailable. Because "phenomenological" thermodynamics uses molecular concepts, an alternate

designation is to say "molecular" thermodynamics. The most striking engineering-oriented examples of molecular thermodynamics are provided by numerous useful correlations, based on the theorem of corresponding states or on the concept of group contributions.

In contrast to what we (somewhat carelessly) call "empirical" thermodynamics, we also have "modern theoretical" thermodynamics that uses statistical mechanics and molecular simulations. In this "theoretical" area, we relate macroscopic thermodynamic properties to microscopic characteristics in a more-or-less rigorous manner.

Although "thermodynamically-grounded" thermodynamics was well known fifty years ago, and whereas some correlations based on corresponding states or group contributions have a long history, the last 50 years have provided significant progress in "phenomenological" or "molecular" thermodynamics with numerous applications in chemical process design. During the last 25 years, there has also been much progress in statistical thermodynamics and molecular simulation. However, regrettably, with few exceptions, that progress has not yet seen significant application in engineering design of fluid-phase chemical processes.

For engineering application, applied thermodynamics is primarily a tool for "stretching" experimental data: given some data for limited conditions, thermodynamics provides procedures for generating data at other conditions. However, thermodynamics is not magic. Without some experimental information, it cannot do anything useful. Therefore, for progress in applied thermodynamics, the role of experiment is essential: there is a pervasive need for ever more experimental results. Anyone who "does" thermodynamics is much indebted to those who work in laboratories to obtain thermodynamic properties. It is impossible here to mention even a small fraction of the vast body of new experimental results obtained over a period of fifty years. However, it is necessary here to thank the hundreds of experimentalists who have provided essential contributions to progress in chemical thermodynamics. Particular recognition must go to the laboratories of Grant Wilson (Provo, Utah) and D. Richon (Fontainebleau, France) who have pioneered in obtaining experimental results for " difficult" industrial systems.

A useful compilation of experimental phase-equilibrium data is provided by the multivolume DECHEMA series (Behrens and Eckermann, 1980–1997).

Thermodynamic Properties of Pure Fluids

For common fluids (for example, water, ammonia, light hydrocarbons, carbon dioxide, sulfur dioxide, and some freons) we have detailed thermodynamic data conveniently compiled in tables and charts; the outstanding example of such compilations is the steam table with periodic improvements and extensions (Harvey et al., 1998; Harvey and Parry, 1999).

Although thermodynamic data for less common fluids are often sketchy, a substantial variety of thermodynamic properties for "normal" fluids can be estimated from corresponding-states correlations, especially those based on Pitzer's use of the acentric factor (1955–1958) for extending and much improving classical (van der Waals) corresponding states (Lee and Kesler, 1975). Here " normal" applies to fluids whose nonpolar or slightly polar (but not hydrogen-bonded) molecules are not

necessarily spherical but may be quasi-elliptical. Although the Lee-Kesler tables are useful for numerous fluids, with few exceptions, correlations that are linear in the acentric factor cannot be used for strongly polar molecules or for oligomers, or other large molecules whose acentric factors exceed (roughly) 0.4.

Two Procedures for Calculating Phase Equilibria

For calculating fluid-phase equilibria, it is common practice to use either one of two methods. In Method I, we use fugacity coefficients for all components in the vapor phase, and activity coefficients for all components in the liquid phase. In Method II, we use fugacity coefficients for all components in all fluid phases. We find fugacity coefficients from an equation of state (EOS), and activity coefficients from a model for the molar excess Gibbs energy, as discussed in numerous textbooks (for example, Smith et al. 2001; Kyle, 1999; Prausnitz et al., 1999; Sandler, 1999; Tester and Modell, 1997). Each method has some advantages and some disadvantages.

For Method I, for every component i, the essential equation of equilibrium is

$$y_i \phi_i^V P = x_i \gamma_i f_i^0 \tag{1}$$

Here y and x are mole fractions in the vapor and the liquid, respectively; P is the total pressure; ϕ^V is the vapor-phase fugacity coefficient, and γ is the liquid-phase activity coefficient. Liquid-phase reference fugacity f^0 is typically the pure-liquid vapor pressure at system temperature with (usually small) corrections for pure-fluid vapor-phase nonideality, and for the effect of total pressure (Poynting factor).

For liquid–liquid equilibria, where the same standard state is used in all phases, we have

$$(x_i \gamma_i)' = (x_i \gamma_i)'' \tag{2}$$

where "and" refer, respectively, to the two liquid phases.

For Method II, for every component i, the essential equation of equilibrium is

$$y_i \phi_i^V = x_i \phi_i^L \tag{3}$$

for vapor-liquid equilibria or

$$(x_i \phi_i^L)' = (x_i \phi_i^L)'' \tag{4}$$

for liquid–liquid equilibria. Here superscripts V and L refer, respectively, to the vapor phase and liquid phase; while $'$ and $''$ refer, respectively, to the two liquid phases.

Before 1950, Method I was dominant because there was reluctance to use an equation of state for condensed fluids. Although many years before, van der Waals had clearly shown that his (and similar) equations of state are applicable to both gases and liquids, there was little confidence in the ability of such equations to represent the properties of liquids with sufficient accuracy. Furthermore, before computers became readily available, equilibrium calculations were prohibitive if both phases were described by an equation of state. For liquid-
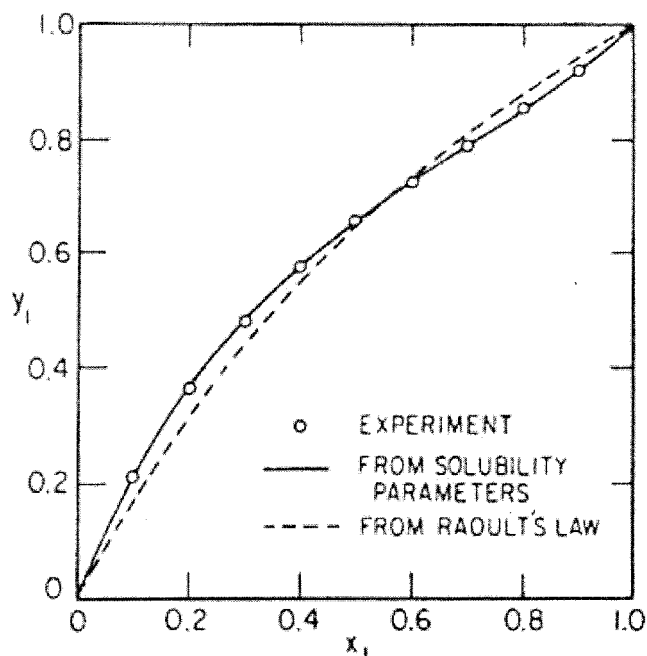
Figure 1. Predicted VLE for C_6H_6(1)/n-C_7H_{16}(2) at 70 °C with the original regular solution theory.

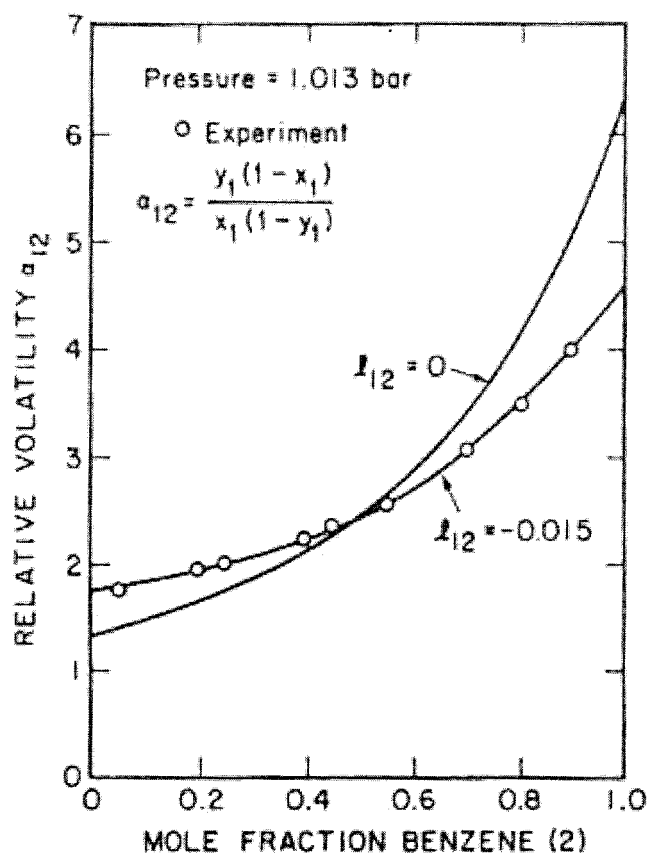Here y is the vapor-phase mole fraction and x is the liquid-phase mole fraction.

phase mixtures, there was a preference to use well established activity-coefficient models (typically the Margules and van Laar equations). However, a pioneering application of Method II was presented by Benedict et al. (1940, 1942) whose Benedict-Webb-Rubin (BWR) equation of state provided the basis for an extensive correlation of high-pressure vapor–liquid equilibria of paraffin mixtures. However, because computers were then in their infancy, the cumbersome BWR equation was not used much. Furthermore, because the BWR equation of state for a mixture (at that time) contained only pure-component (no binary) constants, its accuracy was limited.

Activity-Coefficient Models for Liquid Mixtures of Nonelectrolytes

More than one-hundred years ago, Margules proposed to correlate isothermal binary vapor–liquid equilibria (VLE) with a power series in a liquid-phase mole fraction to represent ln γ_1, where γ_1 is the activity coefficient of component 1. The activity coefficient of component 2, γ_2, is then obtained from the Gibbs–Duhem equation without requiring additional parameters. About 15 years later, van Laar derived equations for ln γ_1 and ln γ_2 based on the original van der Waals equation of state. After introducing a key simplifying assumption for liquids at modest pressures (no volume change upon isothermal mixing), van Laar assumed that the isothermal entropy of mixing at constant volume is equal to that for an ideal solution. Furthermore, upon assuming that the cross coefficient in the van der Waals equation of state a_{12} is given by the geometric mean ($a_{12} = \sqrt{a_{11}a_{22}}$), van Laar obtained expressions for ln γ_1 and ln γ_2 that require only pure component parameters. However, regrettably, agreement with experiment was not good.
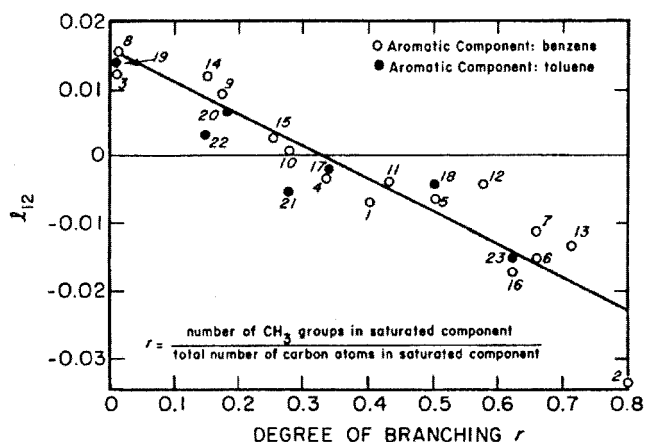
About 1930, Hildebrand and (independently) Scatchard, presented a derivation similar to that of van Laar but, instead of van der Waals constant *a,* they used the concept of cohesive energy density, that is, the energy required to vaporize a liquid per unit liquid volume; the square root of this cohesive energy density is the well-known solubility parameter δ. In the final Hildebrand expressions for ln γ_1 and ln γ_2, the square root of the cohesive energy density appears because of a geometric-mean assumption similar to that used by van Laar. Because of this geometric-mean assumption, the original regular-solution theory is predictive, requiring only pure-component experimental data (vapor pressures, enthalpies of vaporization, and liquid densities). For simple mixtures, Hildebrand's regular-solution theory often gives a good approximation as illustrated in Figure 1.

Results from regular-solution theory did not have appreciable influence in chemical engineering thermodynamics until about 25 years after that theory was published. To make the theory more flexible, the geometric-mean assumption is corrected by introducing a single binary coefficient l_{12} that very much improves agreement with experiment. Figure 2 illustrates how binary parameter l_{12} can significantly increase the accuracy of the regular-solution theory. Numerous efforts have not succeeded in correlating l_{12} in terms of pure-component properties. Such a correlation is possible only for limited situations, as illustrated in Figure 3.

Figure 3. Binary parameter ℓ^{12} for aromatic-saturated hydrocarbon mixtures at 50 °C.

Binary systems shown are: 1. Benzene(2)-Pentane(1); 2. Benzene(2)-Neopentane(1); 3.Benzene(2)-Cyclopentane(1); 4. Benzene(2)-Hexane(1); 5. Benzene(2)-Methylpentane(1); 6. Benzene(2)-2, 2-Dimethylbutane(1); 7. Benzene(2)-2, 3-Dimethylbutane(1); 8. Benzene(2)-Cyclohexane(1); 9. Benzene(2)-Methylcyclopentane(1); 10. Benzene(2)-Heptane(1); 11. Benzene(2)-3-Methylhexane(1); 12. Benzene(2)-2, 4-Dimethylpentane(1);13. Benzene(2)-2, 2, 3-Trimethylbutane(1); 14. Benzene(2)-Methylcyclohexane(1); 15. Benzene(2)-Octane(1); 16. Benzene(2)-2, 2, 4-Trimethylpentane(1); 17. Toluene(2)-Hexane(1); 18. Toluene(2)-3-Methylpentane(1); 19. Toluene(2)-Cyclohexane(1); 20. Toluene(2)- Methylcyclopentane (1); 21. Toluene(2)-Heptane(1); 22. Toluene(2)-Methylcyclohexane(1); 23. Toluene(2)-2, 2, 4-Trimethylpentane(1).

Figure 2. VLE with the regular solution theory with binary parameter ℓ^{12}.

Effect of ℓ^{12} on calculating relative volatility for the 2, 2-dimethylbutane(1)/benzene(2) system.

When the modified regular-solution theory for liquid mixtures was combined with the Redlich–Kwong equation of state for vapor mixtures, it was possible to correlate a large body of VLE data for mixed hydrocarbons, including those at high pressures found in the petroleum and natural-gas industries (Prausnitz et al., 1960). The resulting Chao–Seader correlation (Chao and Seader, 1961) was used extensively in industry until it was replaced by other simpler methods, based on a cubic equation of state applied to all fluid phases.

Until about 1964, most chemical engineering applications of activity coefficients were based on either the Margules or the van Laar equations, although in practice, the two binary coefficients in the van Laar equation were not those based on the van der Waals equation of state, but instead, those obtained from reduction of binary VLE data.

In an influential article, Wohl (1946) showed how activity-coefficient equations can be systematically derived from a phenomenological model where the molar excess Gibbs energy g^E is expressed as a function of liquid-phase composition. Wohl's systematic method had two primary effects: first, it encouraged the development of new models (variations on Margules and van Laar), and second, very important for distillation column design, it showed how binary VLE data can be systematically "scaled up" to predict VLE for ternary (and higher) liquid mixtures with or without requiring any ternary (or higher) VLE data (Severns et al., 1955).

For liquid mixtures containing strongly polar or hydrogen-bonding components, the van Laar equations for activity coefficients are often not satisfactory, especially when applied to multicomponent liquid–liquid equilibria (LLE). For LLE, we

can use the Margules equations but for good agreement with experiment for ternary (and higher) systems, it is often necessary to use many empirical coefficients.

If ternary (and higher) coefficients are omitted, Wohl's method for multicomponent liquid mixtures assumes additivity; for a ternary mixture, g^E is essentially given by the sum $g_{12}^E + g_{13}^E + g_{23}^E$ where the subscripts denote binary mixtures. However, whereas molecular considerations indicate that additivity is (approximately) correct for h^E, the excess molar enthalpy (heat of mixing), there is no physical basis for the additivity of g^E. Wohl's method, in effect, emphasizes the contribution of h^E, while neglecting the contribution of s^E, the molar excess entropy ($g^E = h^E - Ts^E$).

With a fundamentally different method that emphasizes s^E (rather than h^E), Wilson (Wilson, 1964) derived an equation for g^E based on a generalization of Flory's theoretical expression for the entropy of mixing noninteracting spheres and chains of spheres (polymers). To take molecular interactions into account, Wilson used the concept of local composition that, in turn, is based on Guggenheim's quasi-chemical theory for nonrandom mixing, that is, the tendency of molecules in a liquid mixture to show preferences in choosing their immediate neighbors. For example, in a mixture of methanol and hexane, because of hydrogen bonding between two (or more) methanol molecules, a methanol molecule prefers to be near another methanol molecule, rather than near a hexane molecule. However, in a mixture of chloroform and acetone, because of hydrogen bonding between the *CH* group of chloroform and the *C= O* group of acetone, a chloroform molecule prefers to be near an acetone molecule.

With two binary constants per binary mixture, Wilson's equation for g^E is often superior to the older two-constant equations, especially for VLE of mixtures where one (or more) components can hydrogen bond. Unfortunately, however, Wilson's equation cannot be used for binary LLE without one additional binary parameter.

Encouraged by Wilson's use of the local composition concept of 1964, two other models with the same concept were proposed: Renon's nonrandom two-liquid (NRTL) model of 1968, and Abrams' universal quasi-chemical (UNIQUAC) model of 1975. Although the theoretical basis of these local-composition models is not strong, subsequent to their publication, they obtained some support from molecular simulation studies (Hu et al., 1983; Nakanishi and Tanaka, 1983; Phillips and Brennecke, 1993). Although NRTL uses three adjustable parameters per binary, one of these (nonrandomness parameter α_{12}) can often be set *a priori*; a typical value is $\alpha_{12} = 0.3$. Both NRTL and UNIQUAC are readily generalized to multicomponent mixtures without additional parameters, and both may be used for VLE and LLE.

Modifications of the Wilson equation and the NRTL equation have been used to describe phase equilibria in polymer solutions (Heil and Prausnitz, 1966; Chen 1993).

The UNIQUAC equations use only two adjustable binary parameters per binary and, because the configurational part of the excess entropy is based on Flory's expression for mixtures of noninteracting short and long-chain molecules, UNIQUAC is directly applicable to liquid mixtures that contain polymers. Furthermore, because UNIQUAC separates the configurational entropy contribution to g^E from the residual contribution that is primarily because of attractive intermolecular forces whenever
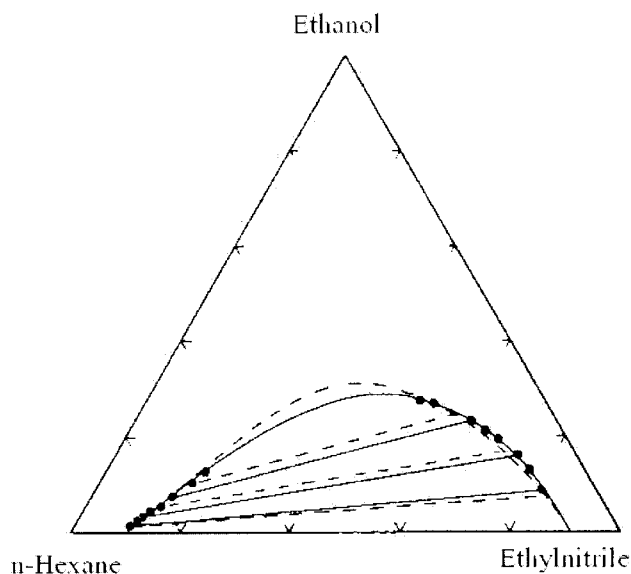
Figure 4. Experimental and calculated ternary LLE for ethanol-ethylnitrile-n-hexane at 40 °C.

Concentrations are in mole fractions. Dashed lines are predictive calculations with parameters obtained from binary systems; points are experimental data, and full lines are observed phase-envelope and experimental tie lines (Nagata and Kawamura, 1979).

the components in the mixture are not identical in size and shape, extension to multicomponent mixtures (like the Wilson model) does not rely on simple additivity of binary excess Gibbs energies.

NRTL and UNIQUAC have been extensively used for about thirty years, largely (but not totally) replacing the equations of Margules, van Laar, and Wilson.

Finally, for liquid mixtures containing strongly interacting molecules (for example, alcohols), some models for g^E are based on chemical equilibria either with or without a contribution from "physical" interactions. Because molecules do not "know" whether they are "doing" physics or chemistry, any division between "physical" and "chemical" interactions is somewhat arbitrary. Nevertheless, when guided by molecular physics, such arbitrary division can be useful for correlation of experimental data.

A "chemical" theory for activity coefficients was first introduced nearly 100 years ago by Dolezalek who claimed that a real mixture is an ideal solution provided that we correctly identify the mixture's molecules. For example, VLE for mixtures of ethanol and heptane can be represented by an ideal-solution calculation when we consider that some ethanol molecules are dimers, or trimers, and so on, as determined by chemical equilibrium constants. Improvement is obtained when, in addition, we allow the various "true" chemical species to interact with each other through "physical" forces as given by an equation of the Margules, van Laar, NRTL or UNIQUAC form. Because such "chemical" theories necessarily require numerous adjustable equilibrium constants, it is customary, in practice, to make simplifying assumptions; a common one is to assume that the equilibrium constant for association (for example, alcohols) is independent of the degree of association. Figure 4 shows calculated and measured liquid–liquid equilib-

ria for the ethanol–ethylnitrile–n–hexane system at 40°C. Calculations for the molar excess Gibbs energy use a chemical-plus-UNIQUAC equation g^E. These calculations use two binary "physical" (UNIQUAC) parameters and two "chemical" parameters (Nagata and Kawamura, 1979). A more detailed "chemical plus physical" model is the ERAS model developed by Heintz and coworkers (Heintz et al., 1986; Letcher et al., 1995); "chemical plus physical" solution theory is frequently used for describing the properties of electrolyte solutions (for example, Lu and Maurer, 1993).

Although "chemical" theories are often successful for binary mixtures, generalization to ternary (and higher) mixtures with more than one associated component is often not possible without introduction of numerous additional adjustable parameters or additional (doubtful) simplifications. However, for some cases, good results are achieved as indicated by Nagata et al. (2000).

Effect of Temperature on VLE and LLE

The effect of temperature presents a fundamental problem in the application of activity-coefficient models because the adjustable binary (or higher) parameters depend on temperature. Although thermodynamics provides exact equations that relate that temperature dependence to either the excess enthalpy or excess entropy of mixing, such equations are of little use because the required enthalpy or entropy data are only rarely available. Fortunately, for VLE calculations, the effect of temperature on activity coefficients is often not large; the primary effect of temperature on VLE comes from the (large) known effect of temperature on pure-component vapor pressures. For VLE, it is common practice either to neglect the effect of temperature on $\ln \gamma_i$ or, as predicted by regular-solution theory, to assume that at constant composition, $\ln \gamma_i$ is proportional to $1/T$. However, for LLE (where pure-component vapor pressures play no role), the effect of temperature is likely to be significant. Regrettably, at present, we do not have any consistently reliable molecular thermodynamic methods for calculating the effect of temperature on LLE.

Solubilities of Gases and Solids

At moderate pressures, the solubility of a gas j in a liquid i is given by Henry's constants H_{ij} that depends on temperature. We have a reasonably large data base for these constants for common gases in a variety of common liquids. However, the major part of that data base is for temperatures near 25 °C; the further we go from 25°C, the smaller the database. For some nonpolar systems, we can estimate Henry's constants with Hildebrand's (Hildebrand et al., 1970) or Shair's correlation (Prausnitz and Shair, 1961) based on solubility parameters. For advanced pressures, we can add a correction to Henry's law using partial molar volumes of the gaseous solutes; these are often not known but for nonpolar systems, we can often estimate them with a correlation (for example, Lyckman et al., 1965; Brelvi and O'Connell, 1972). Some correlations for Henry's constants are based on scaled-particle theory (Pierotti, 1976, Geller et al., 1976) or on assumptions concerning the radial distribution function for a solute molecule completely surrounded by solvent molecules (Hu et al., 1985).

The effect of temperature on gas solubility follows, in part,
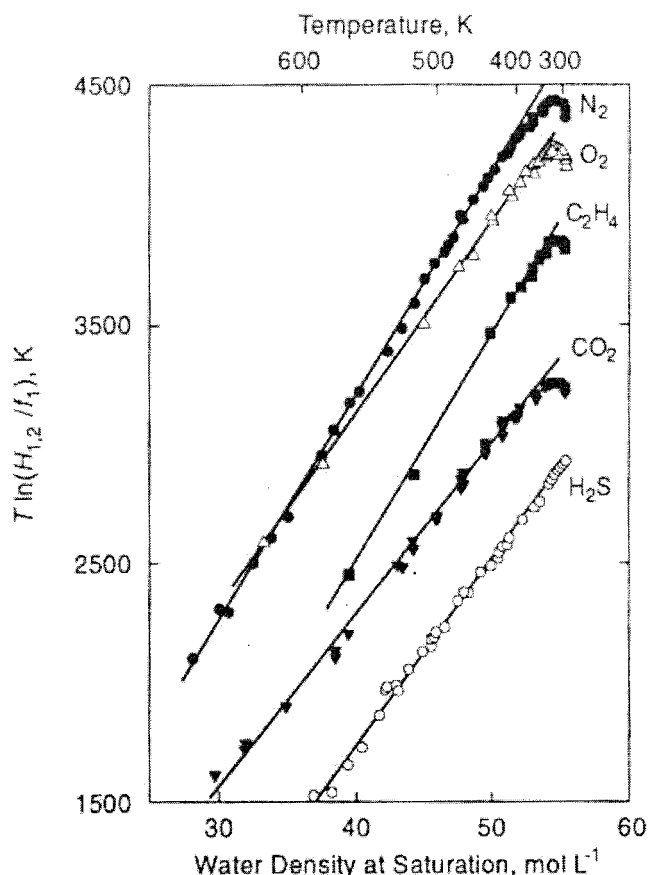
Figure 5. Henry's constant for several gases (2) in water (1) from Japas and Levelt-Sengers (1989).

The line is obtained from a linear equation where ρ is solvent density and parameters A and B are constants for each gas. The solvent's fugacity is f_1.

from the effect of temperature on solvent density. For many cases, solvent density is the dominant influence on Henry's constant. An example is shown in Figure 5 that correlates solubilities of five gases in water over a large temperature range. In Figure 5, f_1 is the fugacity of the solvent.

Some attention has been given to correlating Henry's constant for a gas in a mixed solvent. For simple systems, for a gas j, good approximations can often be made with a volume-fraction average for $\ln H_j$ that requires knowing only H_j for every solvent in the mixture. A better approximation is often obtained by assuming additivity of binary interactions. In that case, for a ternary mixture, we need not only H_j for gas j in both pure solvents but, in addition, some information on interactions in the binary (gasfree) solvent mixture (Campanella et al., 1987; Shulgin and Ruckenstein, 2002).

In nonelectrolyte systems, the solubilities of solids are commonly calculated by referring the solute's activity coefficient to the solute's subcooled liquid. The ratio of the fictitious vapor pressure (or fugacity) of the subcooled liquid to that of the stable solid at the same temperature is found from knowing primarily the solute's melting temperature and enthalpy of fusion, and secondary, from the difference in heat capacities of the solid and subcooled liquid. Correlations of solid solubilities based on such calculations have been presented by numerous
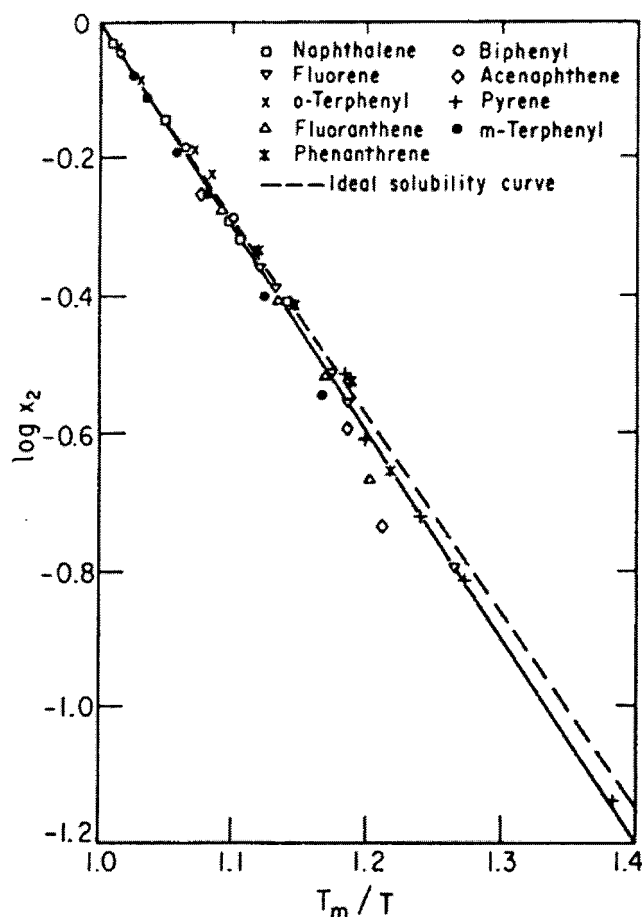
Figure 6. Solubility of aromatic solids in benzene at different temperatures.

The ideal solubility is calculated with the equation:

$$\log x_2 = -\left(\frac{54.4}{2.303R}\right)\left(\frac{T_m}{T} - 1\right)$$

where 54.4 Jmol^{-1} K^{-1} is an average value for the entropy of fusion of solids considered. T_m is the melting temperature, and x_2 is the mole fraction of the solute in the liquid solution.

authors, notably by McLaughlin (McLaughlin and Zainal, 1959, 1960; Choi and Mclaughlin, 1983); an example is shown in Figure 6.

Thermodynamic Properties from Group Contributions

Because desired thermodynamic data are frequently in short supply, many efforts have been made to estimate these properties from known molecular structure. If we divide a molecule into its constituent groups, it then seems reasonable to assume that each group contributes to a particular thermodynamic property, such as the molar volume, or the normal boiling point. For example, Seinfeld and coworkers (Asher et al., 2002) have used group contributions to estimate thermodynamic properties of some oxygen containing liquids and solids that are required for analysis of air-pollution data.

Because corresponding-states-correlation methods are often useful, it is particularly important to estimate the critical tem-

perature and pressure of a pure fluid; as a result, starting in the mid-fifties, the literature is rich in group-contribution methods for estimating critical properties; some of these are summarized in "Properties of Gases and Liquids" by Poling et al. (2001).

It is by no means simple to establish a reliable group-contribution method for pure fluids, however, it is more difficult to establish such a method for fluid mixtures, in particular, for activity coefficients of all components in that mixture. However, for applications in chemical process design, it is useful to have such a correlation because, for many (indeed, most) mixtures, activity-coefficient data are at best sketchy and often nonexistent.

About 75 years ago, Langmuir briefly discussed a possible activity-coefficient correlation based on group contributions. However, Langmuir's idea remained dormant for about 40 years, primarily because the required data base was too small, and because the necessary calculations are too tedious without a computer. Langmuir's idea was revived by Deal and Derr (1969) who presented an early version of their ASOG correlation . To use this correlation, we need temperature-dependent group–group parameters; because Deal and Derr provided only a few of these parameters, the usefulness of ASOG was severely limited. At present, its usefulness is somewhat larger thanks to a monograph (Kojima and Tochigi, 1979) and articles by Tochigi et al. (1990, 1998).

When the UNIQUAC model for activity coefficients is modified toward a group contribution form, it leads to the UNIFAC correlation (Fredenslund et al., 1975), UNIFAC is simpler to use than ASOG because (to a rough approximation) its parameters are independent of temperature. UNIFAC was eagerly picked up by numerous users because the authors of UNIFAC supplied necessary software; a monograph (Fredenslund et al.,
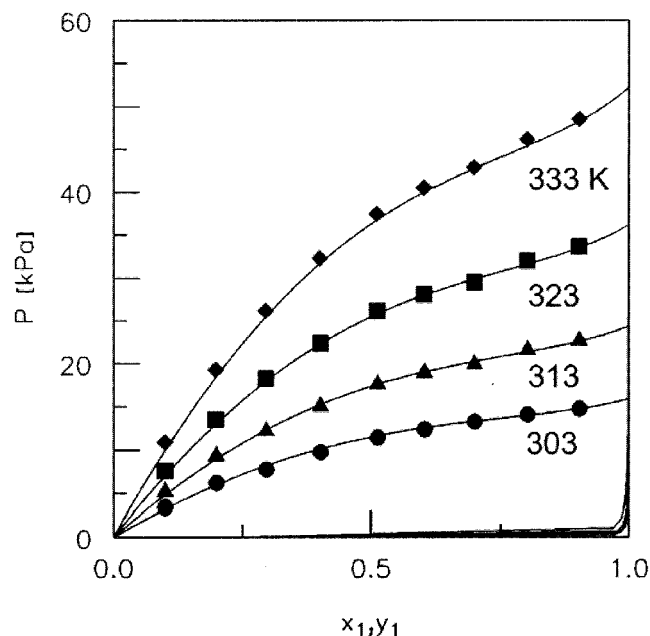
Figure 7. VLE calculations for the benzene(1)-sulfolane(2) system at several temperatures with UNIFAC (Wittig et al., 2003).

In the vapor phase, the mole fraction y_1 is essentially unity for pressures higher than 5 kPa.
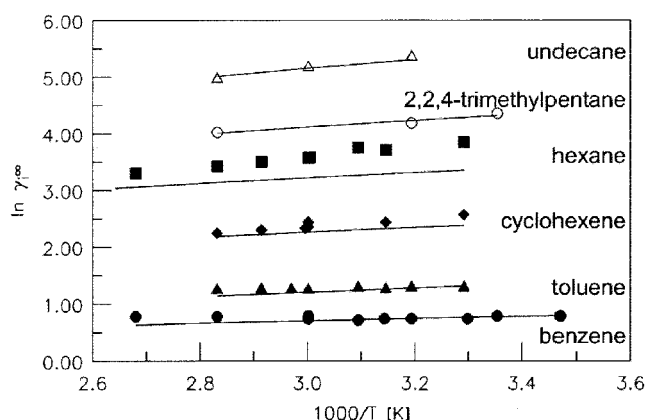
Figure 8. Comparison of activity coefficients at infinite dilution predicted by UNIFAC with experiment for benzene, toluene, cyclohexene, hexane, 2, 2, 4-trimethylpentane and undecane in sulfolane at several temperatures (Wittig et al., 2003).

1977), and a subsequent series of articles provided a large number of group–group interaction parameters (Gmehling et al., 1982; Macedo et al., 1983; Hansen et al., 1991; Fredenslund and Sørensen, 1994; Wittig et al., 2003). UNIFAC is simple to use because it requires no experimental mixture data; as a result, UNIFAC became immensely popular, despite its limitations, especially for dilute solutions. Numerous empirical modifications, primarily by Gmehling and coworkers (including temperature dependence of some UNIFAC parameters) have improved the ability of UNIFAC to predict activity coefficients in binary or multicomponent liquid mixtures of typical subcritical liquids, including hydrocarbons, petrochemicals and water. To illustrate, Figure 7 shows vapor-liquid equilibria for the benzene(1)-sulfolane(2) system at several temperatures with a recent set of UNIFAC parameters from Wittig et al. (2003). Figure 8 compares activity coefficients at infinite dilution, predicted by UNIFAC with experiment.

Oishi's extension of UNIFAC to polymer solutions (Oishi and Prausnitz, 1978) has been modified by others (for example, Holten-Anderson et al., 1987; Goydan et al., 1989). A few efforts have been made to extend UNIFAC to solutions containing electrolytes; especially for dilute solutions, such extensions requires important corrections for the long-range forces between charged particles. Furthermore, such extensions are necessarily limited because the data base is essentially confined to aqueous systems.

Efforts to include supercritical components (for example, hydrogen) have not had much success because UNIFAC is based on a lattice model where each molecule is confined to the immediate vicinity of a lattice position. A lattice model is not suitable for a highly mobile gaseous solute. Furthermore, in UNIFAC, the activity coefficient refers to a standard state fugacity of pure liquid at system temperature. For a supercritical component that fugacity is necessarily hypothetical.

The primary application of UNIFAC is to estimate VLE for multicomponent mixtures of nonelectrolytes for screening and for preliminary design of distillation or absorption operations. Although UNIFAC can often provide good results, like all group-contribution methods, UNIFAC is not always reliable, especially for liquid mixtures where the molecules of one (or more) components have two or more close-by polar groups (for example, ethylene glycol). As indicated later, some recent promising developments with quantum mechanics are directed at reducing this limitation of UNIFAC. Although, UNIFAC provides an attractive method for estimating phase equilibria, it is important to keep in mind that, as yet, there is no substitute for high-quality experimental data.

Because ASOG and UNIFAC parameters are obtained from binary VLE data, predictions from ASOG and UNIFAC are useful only for VLE, not for LLE. In VLE calculations, the primary quantities are pure-component vapor pressures; activity coefficients play only a secondary role. However, in LLE calculations, where activity coefficients are primary, a much higher degree of accuracy is required. UNIFAC correlations for LLE (discussed in Poling et al., 2001) are useful only for semiquantitative predictions. Better results can be achieved when UNIFAC LLE parameters are regressed from (and then applied to) a limited class of mixtures. For example, Hooper et al., (1988) presented a set of UNIFAC LLE parameters for aqueous mixtures, containing hydrocarbons and their derivatives for temperatures between ambient and 200°C.

The DISQUAC group-contribution correlation is useful for estimating enthalpies of liquid mixtures (Kehiaian, 1983, 1985).

A semiempirical class of methods that tries to account for the correlation between close-by polar groups uses descriptors. In these methods, the structure of a molecule is represented by a two-dimensional(2-D) graph, with vertices (atoms) and edges (bonds). The numerical values resulting from the operation of a given descriptor on a graph are related to a physical property, for example, the activity coefficient at infinite dilution (Faulon et al., 2003; He and Zhong, 2003). Because the method has little theoretical basis, the type and the number of descriptors needed is property-dependent, that is, the method is specific for each thermodynamic property. Furthermore, for reliable predictions, any correlation based on descriptors requires a large database.

The SPACE model with solvatochromic parameters for estimating activity coefficients is an extension of regular-solution theory where the cohesive energy density is separated into dispersion forces, dipole forces, and hydrogen bonding. The dipolarity and hydrogen-bond basicity, and acidity parameters were correlated with the activity coefficient database by Hait et al. (1993). Castells et al. (1999) compare different methods (including SPACE) to calculate activity coefficients for dilute systems. A method similar to SPACE is described by Abraham and Platts (2001); their group contribution model is used to calculate solubilities of several pharmaceutical liquids and solids in water at 289 K. A recent method for calculating solubilities of pharmaceuticals is given by Abildskov and O'Connell (2003).

Equations of state (EOS)

In the period 1950–1975, there were two major developments that persuaded chemical engineers to make more use of Method II that is, to use an EOS for fluid-phase (especially VLE) equilibria. First, in the mid-1950s, several authors suggested that successful extension of a pure-component equation

of state to mixtures could be much improved by introducing one binary constant into the (somewhat arbitrary) mixing rules, that relate the constants for a mixture to its composition. For example, in the van der Waals EOS, parameter a for a mixture is written in the form

$$a(mixture) = \sum_i \sum_j z_i z_j a_{ij} \qquad (5)$$

where i and j represent components and z is the mole fraction. When $i = j$, van der Waals constant a_{ij} is that for the pure component. When $i \neq j$, the common procedure is to calculate a_{ij} as the geometric mean corrected by $(1 - k_{ij})$ where k_{ij} is a binary parameter

$$a_{ij} = \sqrt{a_{ii} a_{jj}} \, (1 - k_{ij}) \qquad (6)$$

Parameter k_{ij} is obtained from some experimental data for the $i - j$ binary. It seems strange now, but it was not until about 1955–1960 that the currently ubiquitous k_{12} became a common feature of articles in chemical engineering thermodynamics. It was during that period that lists of k_{12} appeared and that (mostly futile) attempts were made to correlate k_{12} with properties of pure components 1 and 2.

Second, about 1965, there was a growing recognition that because an EOS of the van der Waals form can be used to generate both vapor-phase fugacity coefficients or liquid-phase
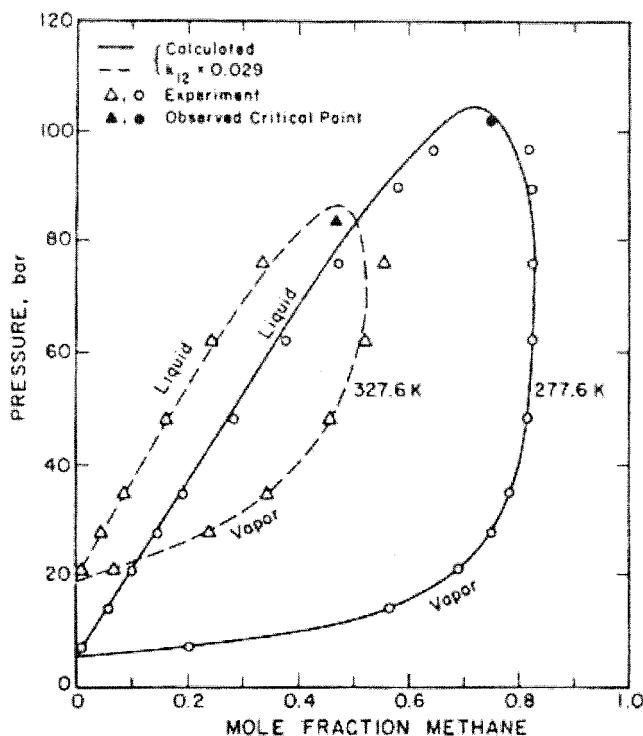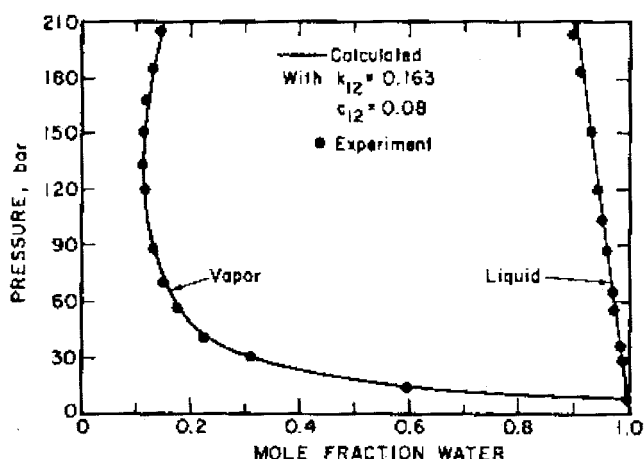
Figure 10. Isothermal pressure-composition phase diagram for water-hydrogen sulfide.

Calculation with the Redlich-Kwong-Soave equation of state (Evelein et al., 1976). Parameters k_{12} and c_{12} were adjusted to give good agreement with experimental data from Selleck et al. (1952).

activity coefficients, it would be attractive to use one EOS for all fluid phases. However, to apply that idea, the pure-component constants in the equation of state must be evaluated to fit what for VLE is the most important quantity, viz. the pure-component vapor pressure. If an EOS can correctly give the vapor pressure of every pure component in the mixture, VLE for a mixture can be calculated, essentially, by interpolation as dictated by mixing rules. When these mixing rules are made sufficiently flexible through one (or sometimes two) adjustable binary parameters, good results for VLE can often be achieved. To illustrate, Figure 9 shows experimental and calculated results for methane-propane. Although k_{12} is very small compared to unity, it nevertheless has a significant effect.

Because methane and propane are simple and similar molecules, a single binary parameter is sufficient to achieve good results. To represent phase equilibria for the much more complex system, water-hydrogen sulfide, Evelein et al. (1976) introduced a second parameter c_{12} in the mixing rule for van der Waals size-parameter b. With two binary parameters, it is possible to achieve good agreement with experiment as shown in Figure 10.

As a result of these happy developments, the literature was soon flooded with proposed EOS where the pure-component constants were fit to pure-component vapor pressure data. In this flood, a favorite target was to modify the Redlich–Kwong (RK) EOS, published in 1949, where the authors had introduced a simple but remarkably effective modification of the density dependence in the van der Waals equation. Because Redlich and Kwong were concerned only with dense gases, not liquids, their particular temperature dependence was dictated by second-virial coefficient (not vapor pressure) data. After about 1972, numerous articles reported modifications of the RK EOS where, for each pure fluid, the characteristic attractive constant a is given as a function of temperature such that good agreement is obtained with experimental vapor-pressure data. The best known modification of the RK EOS is that by Soave (1972) who was one of the first to show that a simple EOS of

Figure 9. Isothermal pressure-composition phase diagram for methane-propane.

Calculation with the Redlich-Kwong-Soave equation of state (Prausnitz et al., 1999). Parameter k_{12} was adjusted to give good agreement with experimental data from Reamer et al. (1950).

the van der Waals form is useful for calculating VLE of a variety of mixtures at both moderate and high pressures.

In 1976, Peng and Robinson (PR) published their modification of the van der Waals EOS (Peng and Robinson, 1976) that, unlike Soave's modification (SRK), introduces a new density dependence in addition to a new temperature dependence into the RK equation. Although Soave's equation and the PR equation necessarily (by design) give good vapor pressures, the PR EOS gives better liquid densities. The PR EOS and the SRK EOS are now the most common "working horses" for calculating high-pressure VLE in the natural-gas, petroleum and petrochemical industries. For application of the PR EOS to mixtures containing polar as well as nonpolar components, a particularly useful correlation is that given by Vera and Stryjek (1986). For mixtures where one (or more) components are well below their normal boiling points, a useful modification is that by Mathias and Copeman (1983).

The van der Waals EOS is a perturbation on a highly oversimplified model for hard spheres; the perturbation is intended to account for attractive forces, although, in effect, it also corrects the oversimplified hard-sphere term. Equations of the van der Waals form can be improved with a more realistic hard-sphere model or by changing the density dependence of the perturbation term or both. Many efforts along these lines have been reported. However, except for the Soave and PR equations, they have not enjoyed much success in chemical process-design calculations essentially for two reasons: first, because for some "improved" EOS, additional constants must be determined from some experimental physical property that may not be readily available, and second, because the calculations are often more tedious if the EOS is not (unlike the PR and Soave EOS) cubic in volume; in that event, iterations are needed to find the fugacity coefficient when temperature, pressure and composition are given. Although standard computers can easily perform such iterations, when very many VLE calculations are required for a particular design, impatient engineers prefer an EOS where calculations are relatively simple and fast.

Because all analytic EOS based on the van der Waals model are poor in the vapor-liquid (VL) critical region, some attempts have been reported to obtain improvement by translation (Peneloux et al., 1982; Mathias et al., 1989), that is, by adding a correction (in the first approximation, a constant) to the volume in the EOS; this correction horizontally moves (translates) the V–L coexistence curve plotted on P–V coordinates. The correction is designed to make the calculated critical coordinates (V_C, T_C, P_C) agree with experiment. This procedure has been used to calculate better saturated liquid volumes, however, because the correction toward that end introduces errors elsewhere in the P–V plane, this excessively empirical translation procedure has only limited application (Valderrama, 2003).

Calculation of VLE in the critical region provides a severe challenge because any attempt to do so along rigorous lines (renormalization group theory) requires numerous approximations and much computer time. Although some efforts have been reported toward better representation of VLE in the critical region (for example, Anisimov and Sengers, 2000; Lue and Prausnitz, 1998; Jiang and Prausnitz, 1999; Kiselev et al., 2001; Kiselev et al., 2002), as yet, they are not sufficiently developed for general engineering use.
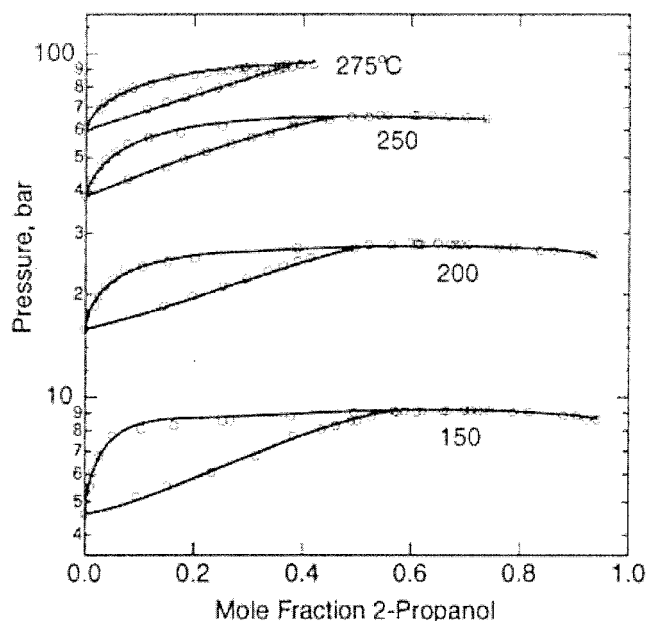
Figure 11. Isothermal pressure-composition phase diagram for 2-propanol/water.

Calculation with the PR EOS as modified by Stryjek and Vera (1986), and Wong-Sandler mixing rules (Wong and Sandler, 1992) with k_{12}=0.326 (Orbey and Sandler, 1998).

Toward further improvement of EOS for VLE, during the 1980's significant attention was given to establish better mixing rules. Because the EOS can be used to find the molar excess Gibbs energy, Vidal (1978, 1983) suggested that experimental data for liquid-mixture activity coefficients be used to determine both mixing rules and binary constants that appear in those rules. The resulting EOS can then be used to generate VLE at temperatures and pressures beyond those used to fix the constants that appear in the mixing rules.

Unfortunately, the procedure suggested by Vidal (and others) leads to a thermodynamic inconsistency because the corresponding mixing rules, in general, do not give the theoretically correct quadratic composition dependence of the second virial coefficient. To avoid this problem, it was suggested that the mixing rules should be modified such that they simultaneously reproduce the activity-coefficient data at high fluid densities, and at low fluid densities, the correct composition dependence of the second virial coefficient. The most successful of these suggestions is the Wong-Sandler (WS) mixing rules (Wong and Sandler, 1992). Subsequent experience with these rules led to a monograph that gives details and pertinent computer programs (Orbey and Sandler, 1998). Figure 11 shows a successful application of WS mixing rules.

In another example, shown in Figure 12, the PR EOS with WS mixing rules was used to calculate LLE. Here, Escobedo-Alvarado and Sandler (1998) used experimental LLE data at low pressure to determine binary parameters in the WS mixing rules. The PR EOS was then used to predict LLE at higher pressures up to 781 *bar*.

The phenomenological basis of a traditional EOS of the van der Waals form is based on molecules that are spherical (or globular). That basis is not appropriate for fluids with chain-like molecules, especially polymers, not only because such
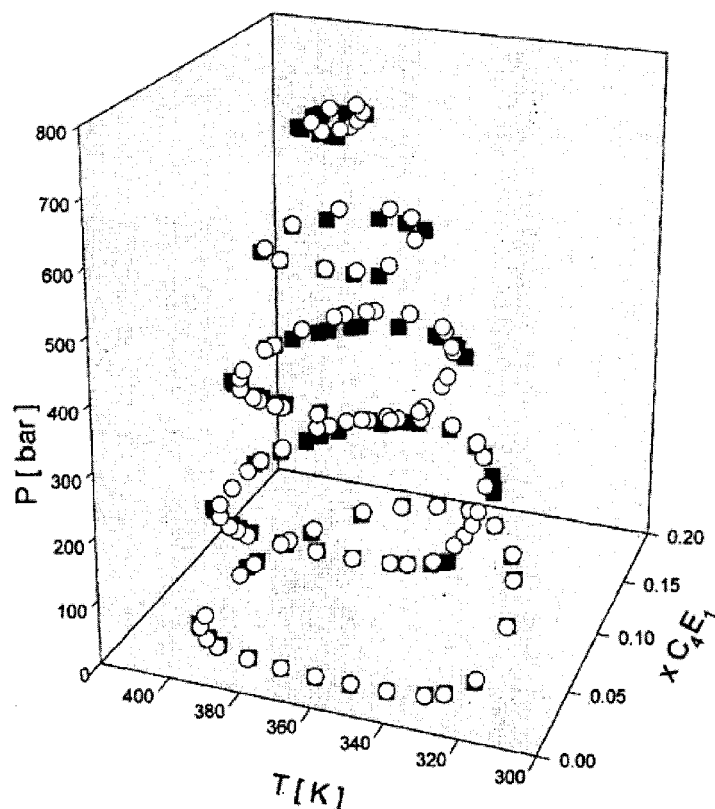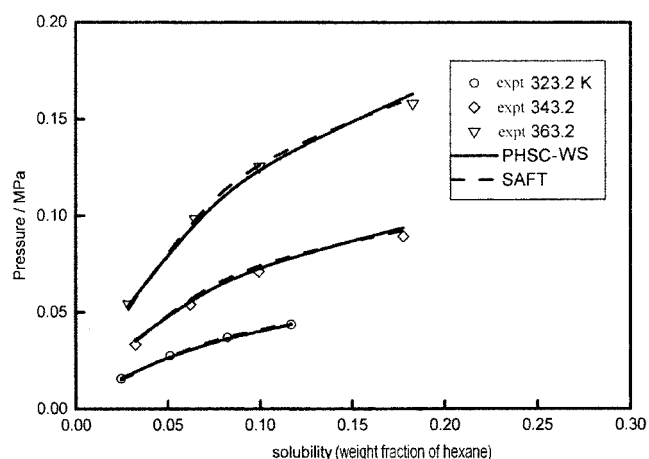
Figure 12. Calculated and experimental LLE for the 2-butoxyethanol (C_4E_1)/water system, with the Peng-Robinson EOS and Wong-Sandler-NRTL mixing rules where x is the mole fraction.

Low-pressure LLE data were used to determine binary parameters in the EOS (Escobedo-Alvarado and Sandler, 1998).

molecules are not spherically symmetric in shape, but also because such molecules (unlike small spheres) exercise rotations, and vibrations that, because they depend on density, must be included in a suitable EOS (Vera and Prausnitz, 1972).

A phenomenological EOS for chain-like molecules

(PHCT = perturbed hard chain theory) was proposed in 1975 (Beret and Prausnitz, 1975) based on Prigogine's theory for liquid polymers (Prigogine, 1957); a particularly simple form of PHCT is the cubic EOS of Sako et al. (1989). In essence, PHCT is similar to the van der Waals model but, unlike that model (in its original form), it allows for contributions from so-called external degrees of freedom (density-dependent rota-


Figure 13. Calculated and experimental hexane (weight-fraction) solubility in a polypropylene copolymer.

Here, expt means experimental data. Calculations with the perturbed-hard-sphere EOS with Wong-Sandler mixing rules or with the SAFT EOS (Feng et al., 2001).
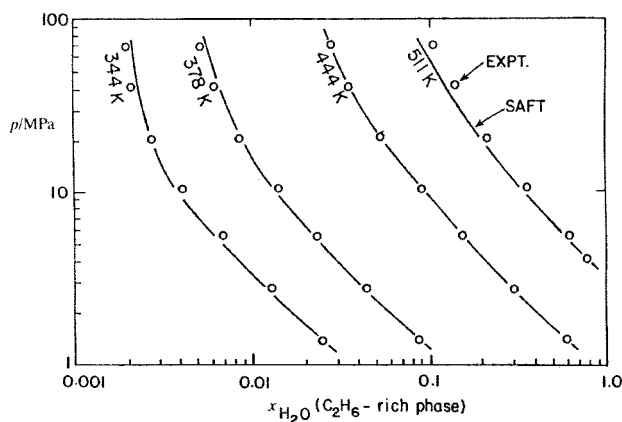
Figure 14. Experimental and calculated (mole-fraction) solubility of water in the ethanerich phase for water-ethane mixtures (Huang and Radosz, 1991, 1993).
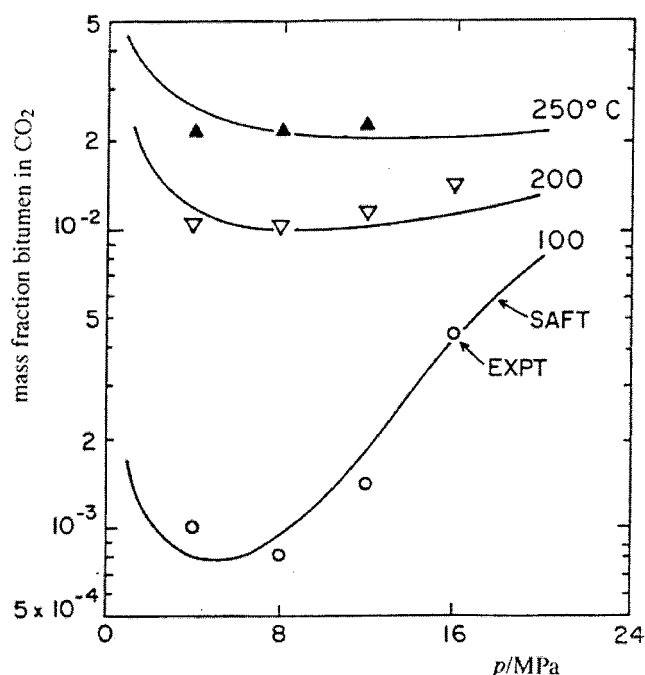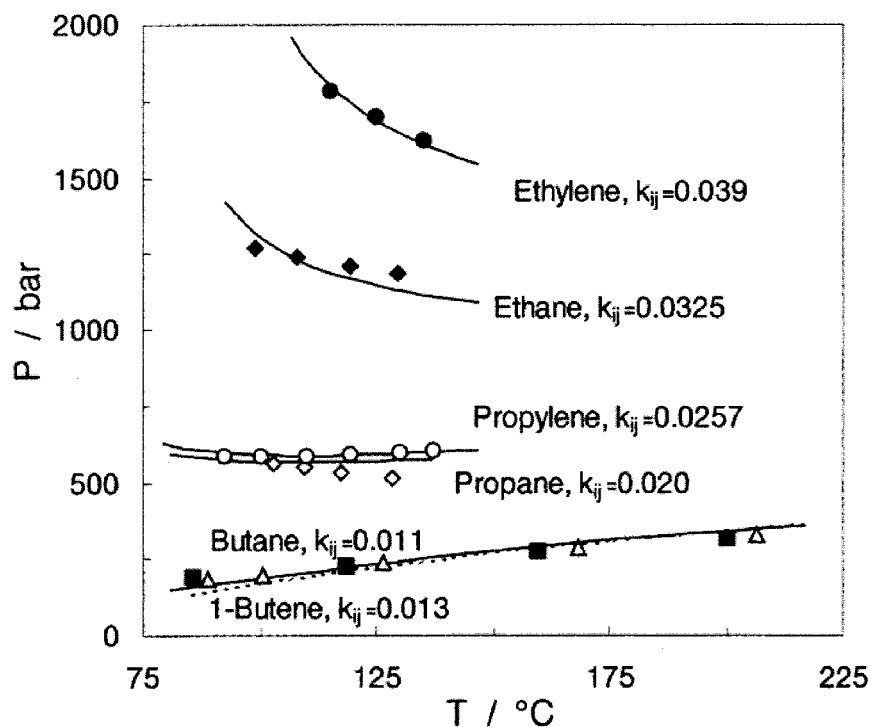
Figure 15. Experimental and calculated solubility of bitumen in compressed carbon dioxide (Huang and Radosz, 1991).

used extensively in representing phase equilibria for vapor-phase polymer-monomer-solvent mixtures at high pressure as used, for example, in the production of polyethylene (Feng et al., 2001), as shown in Figure 13.

When attention is limited to the liquid phase, an EOS by Flory (1965, 1970), Eichinger and Flory (1968), and Patterson (1969) can be used to find the so-called equation-of-state contribution to the excess Gibbs energy of a polymer solution. These contributions that arise because of differences in free volume of the polymer solution's components are neglected in the classical Flory–Huggins lattice theory for polymer solutions. These contribution are essential for explaining the often observed high-temperature lower critical-solution temperature of polymer solutions and polymer blends (Olabisi et al., 1979). An alternative method by Sanchez and Lacombe (1976, 1978) proposed a relatively simple EOS for polymers that is an extension of Flory–Huggins lattice theory. The essential contribution of this equation is the inclusion of holes (empty sites) into the lattice. This inclusion provides the communal entropy at the ideal gas limit. Smirnova and Victorov (2000) give a comprehensive review of EOS based on lattice models.

An elegant theory by Wertheim (1984–1986) has led to SAFT (Chapman et al., 1989 and 1990), a theoretically well-founded EOS for chain-like molecules where SAFT stands for Statistical Association Fluid Theory. Müller and Gubbins (2001) have given a user-friendly review of the derivation and applications of SAFT. To illustrate, Figure 14 shows the application of SAFT to represent properties of a solution containing a strongly associating component, and Figures 15 shows calculated and experimental phase equilibria for a solution containing components with large size difference.

tions and vibrations) in addition to translations to the EOS. An EOS similar to PHCT is the chain-of-rotators EOS (Chien et al., 1983; Kim et al., 1986). Variations of PHCT have been


Figure 16. Comparison of experimental and calculated cloud points with the perturbedchain-SAFT EOS for mixtures of polyethylene and several solvents: ethylene, ethane, propylene, propane, butane, and 1-butene (Gross et al., 2003).
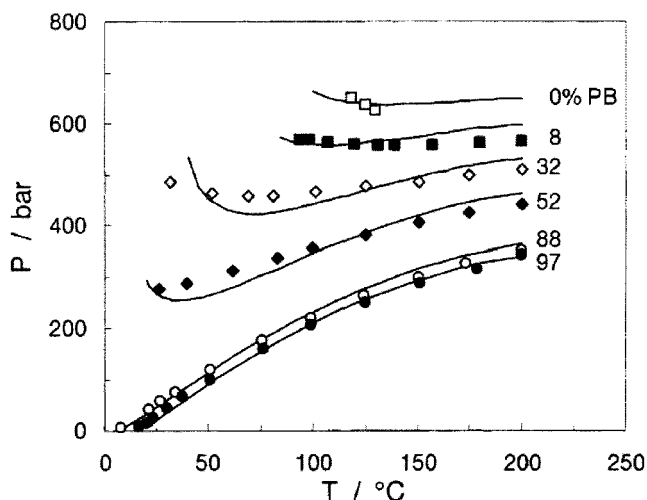
Figure 17. Comparison of experimental and calculated cloud points with the perturbedchain-SAFT EOS for mixtures of poly(ethylene-*co*-1-butene) and propane with varying repeat-unit composition (from 0 to 97 mass %) of 1-butene in the copolymer (Gross et al., 2003).

% PB represents the percentage of 1-butene in the polymer.

On the basis of some clever assumptions concerning the structure of a chain-molecule fluid, Chiew (1990, 1991) has derived an EOS for polymer and polymer-like fluids that, in effect, is similar to SAFT. By considering the next-to-nearest-neighbor cavity correlation function, Hu et al. (1995) obtained a more accurate EOS for hard-sphere chain fluid mixtures in
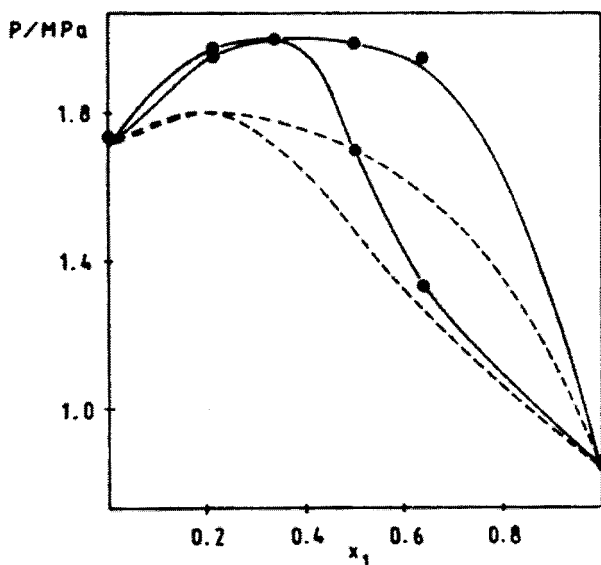
Figure 18. Calculated and experimental VLE for sulfur dioxide (1)-propane (2) at 50 °C.

Full lines are for calculations with an optimized binary interaction parameter (k_{12}), whereas dotted lines are for $k_{12}=0$. Here x is mole fraction, and the points are experimental data.Calculations with the Association-plus-PR EOS of Anderko (1989).
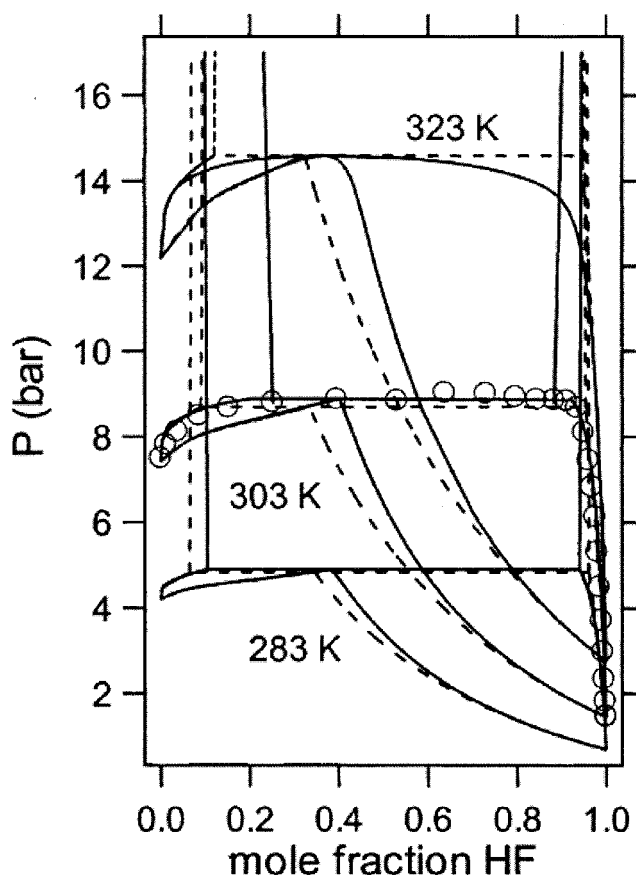

Figure 19. Calculated and experimental *Pxy* diagram for the hydrogen fluoride/refrigerant R12 system.

Lines are for the Association-plus-PR EOS proposed by Visco and Kofke (1999). Solid lines use the van der Waals mixing rules, whereas the dashed lines use the Wong-Sandler mixing rules (Baburao and Visco, 2002).

good agreement with computer simulation data. In other SAFT-related studies, a number of successful efforts have incorporated a more accurate description of the structure and free energy of the monomer reference fluid (Ghonasgi and Chapman, 1994; McCabe et al., 2001, Paredes et al., 2001, Paricaud et al., 2002). For example, Gross and Sadowski (2001) applied second-order Barker-Henderson perturbation theory to a hard-chain reference fluid to improve the SAFT equation of state. To illustrate, Figures 16 and 17 show calculated and experimental phase equilibria for some polymer and copolymer solutions, respectively.

In addition to poor agreement with experiment in the critical region, all currently available EOS for chain-like molecules suffer from one limitation: for long chains, at dilute conditions, the calculated second virial coefficient has an incorrect dependence on chain length. As a result, SAFT (and similar) EOS give unreliable results for the dilute polymer phase when used to calculate fluid–fluid equilibria when the polymer is concentrated in one phase and dilute in the other.

For strongly associating components it is tempting to superimpose a "chemical" theory onto a "physical" EOS. The general procedure for doing so was shown by Heidemann and Prausnitz (1976) who introduced a chemical association equi-
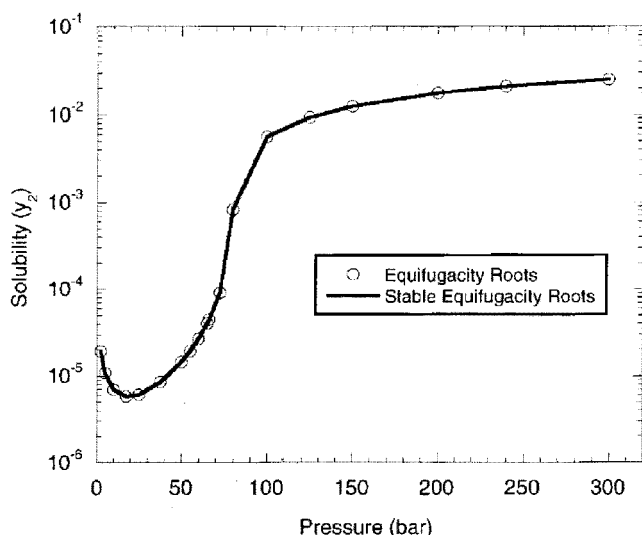
Figure 20. PR EOS calculation of the solubility of biphenyl in CO_2 at 35 °C.

At this temperature, there is only one equifugacity root at each pressure, and that root corresponds to stable solid-fluid equilibrium (Xu et al., 2000). Here y is the mole fraction.

librium constant into the van der Waals EOS. Following some reasonable simplifications, an analytic EOS was derived with two physical interaction constants, van der Waals a and b, and one temperature-dependent equilibrium constant, $K\,(T)$. On the basis of similar ideas, several authors have represented the properties of solutions containing one associating component and one or more normal fluids; an example is shown in Figure 18 by Anderko (1989). Another example for particularly "nasty" mixtures containing hydrogen fluoride is shown in Figure 19.

Equations of state have been used extensively to design supercritical-extraction processes (McHugh and Krukonis, 1994). Because supercritical extraction uses high pressures and because of the large difference in size and shape between solute and solvent, these systems present a variety of phase diagrams. For example, binary mixtures of ethane-linalool and ethane-limonene present double retrograde condensation, as discussed by Raeissi and Peters (2002, 2003). For supercritical-extraction conditions, calculation of phase equilibria with an EOS, and the equifugacity criteria may present multiple roots. The "correct" root should be selected by a global phase-stability method. In a series of articles, Brennecke and Stadtherr (Xu et al., 2000; Maier et al., 2000; Xu et al., 2002) used an EOS to obtain high-pressure solid-fluid equilibria. To illustrate, Figures 20 and 21 show the solubility of biphenyl in CO2 at different pressures calculated with two methods: equifugacity and global optimization. Figure 21 shows that, at 333.15K the equifugacity calculation gives an unstable root at some pressures.

Most supercritical-extraction processes use carbon dioxide as the solvent because of its attractive environmental properties. Because many compounds have very low solubilities in carbon dioxide, even at high pressures, a supercritical-extraction process may require an undesirable high solvent flow rate. To increase solubilities dramatically, it has been suggested to add a surfactant that can form micelles of the extracted compounds in the solvent. However, ordinary surfactants (intended

for oil-water systems) are not effective in dense carbon dioxide. In a significant contribution that shows the importance of chemistry in applied thermodynamics, Beckman (Ghenciu et al., 1998; Sarbu et al., 2000) synthesized entirely new surfactants suitable for micellization in dense carbon dioxide.

Equations of state can be used to describe adsorption of pure gases and their mixtures on solid surfaces. An early discussion was given by Van Ness (1969); a more recent one is by Myers (2002). Here, the parameters of the EOS depend not only on the adsorbate but also on the adsorbent, that is, the solid surface provides an energetic field that affects the forces between the adsorbed molecules.

Equations of state are useful for design of crystallization processes where it is important that the precipitated solids have a narrow size distribution (Chang and Randolph, 1989, 1990), and for calculating hydrate formation in moist natural gases as discussed in the monograph by Sloan (1990).

Equations of state are also useful for describing particle precipitation from liquid solution. For that case, it is convenient to write the EOS in terms of the McMillan–Mayer framework (1945) where the potentially precipitating particles are dissolved in a continuous liquid medium. The pressure is replaced by the osmotic pressure; the density now is not the density of the system but that of the particles in the liquid medium. Although this type of EOS has been used for many years in colloid science, it has received only little attention from chemical engineers in the conventional chemical industries. Ogston (Laurent and Ogston, 1963; Edmond and Ogston, 1968) has used an EOS in the McMillan-Mayer framework to describe dilute solutions of two (or more) polymers, while Wu et al. (1998, 2000) have shown how an EOS of this type can be used to describe precipitation of asphaltenes from heavy petroleum.

Regardless of what EOS is used, perhaps the most important engineering application of an EOS lies in the estimation of
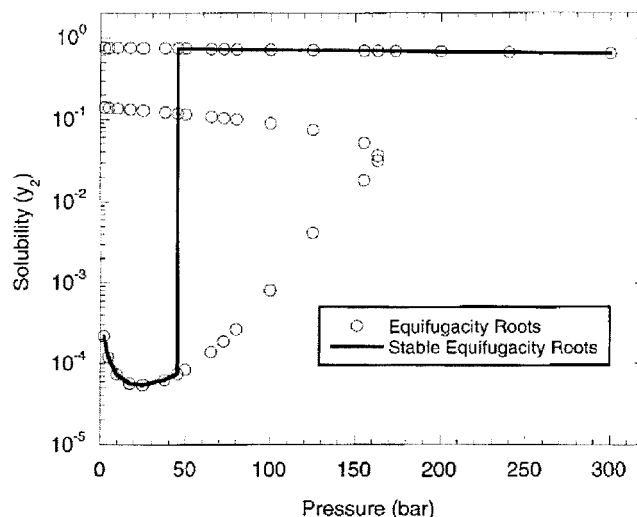
Figure 21. PR EOS calculation of the solubility of biphenyl in CO_2 at 60 °C.

At this temperature, there are multiple equifugacity roots for pressures below 160 bar. At low pressure, the lowest solubility root corresponds to stable equilibrium, but at higher pressure, it is the highest solubility root that is stable. A three-phase line, indicating solid-liquid-vapor coexistence, occurs at about 45.19 bar (Xu et al., 2000). Here y is mole fraction.
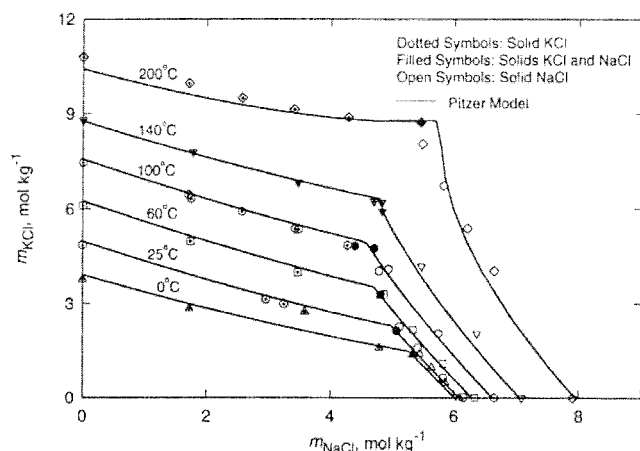
Figure 22. Calculated and experimental solubilities of salts in the ternary system NaCl/KCl/H₂O at several temperatures.

Intersections of isothermal curves represent calculated ternary invariant points where three phases are in equilibrium: pure NaCl solid, pure KCl solid, and aqueous solution containing both salts (from Prausnitz et al., 1999). Here, m = mobility.

multicomponent VLE with only parameters obtained from single-component and binary experimental data (or from correlations based on such data). In an EOS of the van der Waals form, we consider only two-body interactions. Therefore, once we have properly extended that EOS to a binary mixture, no further assumptions are required to achieve extension to ternary (and higher) mixtures. In a mixture, two-body interactions are reflected by mixing rules that are quadratic in composition. If mixing rules use higher-order terms, extension from binary to ternary (and higher) mixtures presents significant theoretical
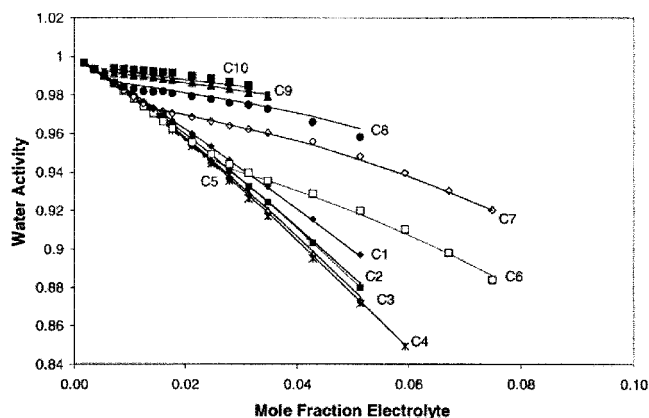
Figure 23. Calculated and experimental water activities at different electrolyte concentrations for various aqueous sodium carboxylates: methanoate (C1), ethanoate (C2), propanoate (C3), butanoate (C4), pentanoate (C5), hexanoate (C6), heptanoate (C7),octanoate (C8), nonanoate (C9), and decanoate (C10).

Calculations with a g^E model that combines NRTL for ionic systems with NRTL for oligomers are able to describe the abrupt change in the water activity at the critical micelle concentration (Chen et al., 2001).
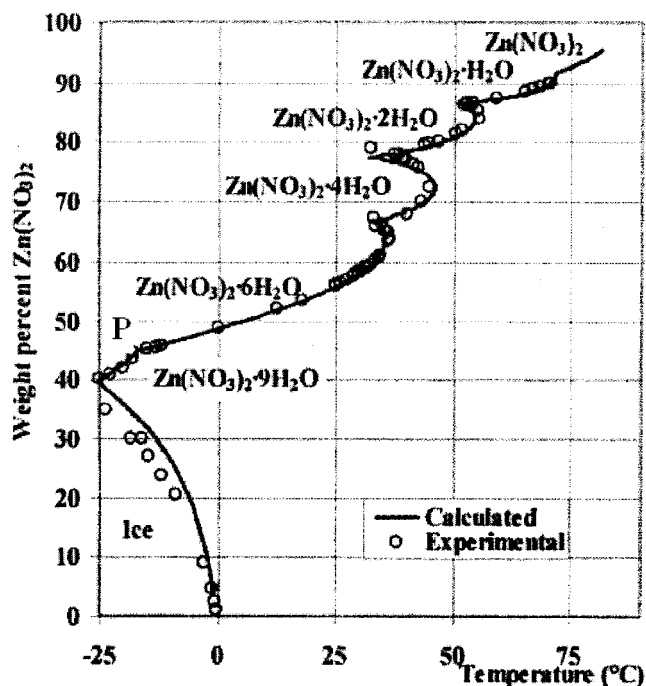
Figure 24. Solubility of Zn(NO₃)₂ in water as a function of temperature.

In addition to the anhydrous salt, five hydrates are formed in the solution containing zinc nitrate: nonahydrate, hexahydrate, tetrahydrate, dihydrate, and monohydrate. Calculations using a g^E model that combines UNIQUAC with the Debye–Huckel theory are able to describe the five eutectic points and one peritectic point (P) of the aqueous Zn(NO₃)₂ system (from Iliuta et al., 2002).

problems as noted by Michelsen and Kistenmacher (1990) and by Mollerup and Michelsen (1992).

Extensive experience in applying an EOS to calculate fluid-phase equilibria has shown that for typical fluid mixtures, the role of details in the EOS itself or in its mixing rules is less important than that of the choice of constants obtained from some experimental source.
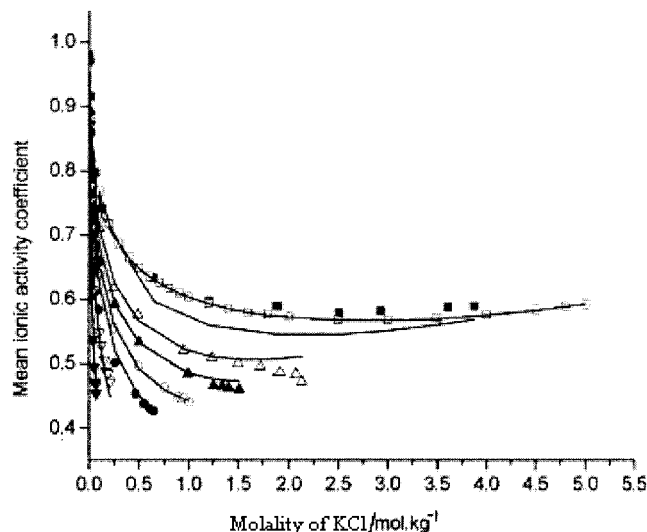
Electrolyte Solutions

Because electrostatic forces between ions are long-range, the physical chemistry of electrolyte solutions is qualitatively different from (and more difficult than) that for solutions of nonelectrolytes. Because electric neutrality must be maintained, the concentrations of cations and anions are not independent. As a result, conventional experimental thermodynamic data for electrolyte solutions do not give the activity of the cation and that of the anion but instead, a mean ionic activity coefficient. Furthermore, because salts are not volatile at ordinary temperatures, mean ionic activity coefficients refer not to the pure electrolyte but to an ideal dilute solution of the electrolyte in the solvent.

For very dilute solutions of strong electrolytes (complete dissociation into ions), we have the Debye–Hückel (DH) theory of 1923; this theory gives the mean ionic activity coefficient arising from electrostatic ion–ion forces in a medium of known dielectric constant. In its rigorous, highly dilute limit, DH theory neglects the finite sizes of the ions and van der
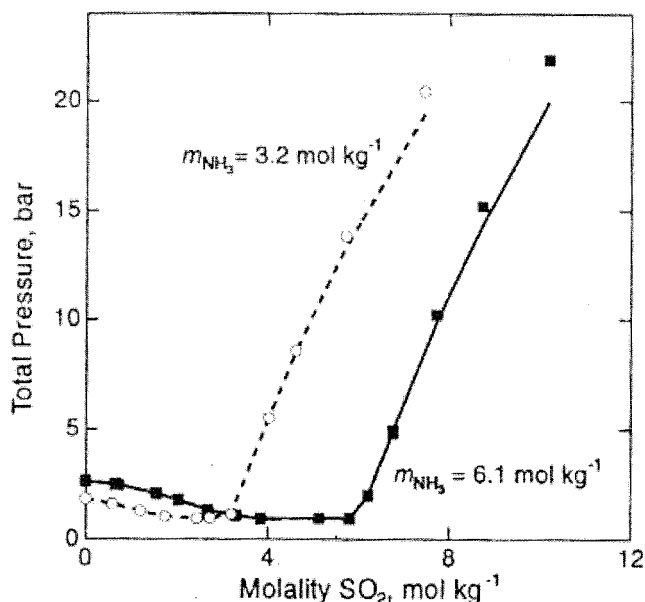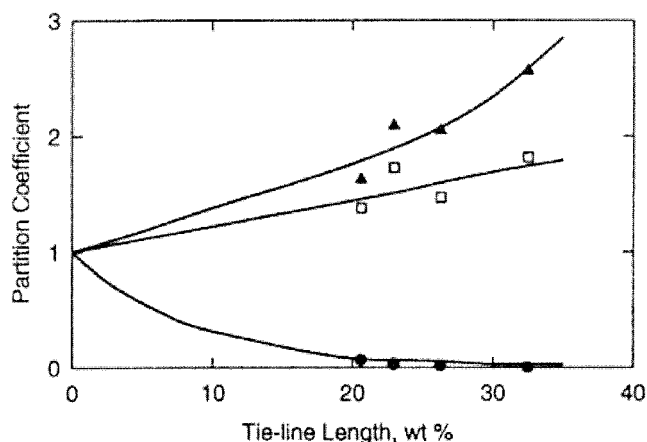
Figure 25. Simultaneous solubilities of NH₃ and SO₂ in water at 100 °C, calculated by Edwards et al. (1978); experimental results are from Rumpf et al. (1993).

Figure 27. Calculated and experimental partition coefficients for three dilute proteins in an aqueous two-phase system containing PEG 3350, dextran T-70, and 50 mM KCl (overall) at pH = 7.5 and 25 °C.

The partition coefficient is defined by the ratio of the protein molalities. Experimental and calculated results are for albumin (circles), chymotrypsin (squares), and lysozyme (triangles) (Haynes et al., 1991).

Waals attractive forces between ions. To describe the thermodynamic properties of concentrated electrolyte solutions, numerous phenomenological extensions of DH theory have been presented. Perhaps the most successful is the one by Pitzer (1973, 1995) which, in effect, expresses the excess Gibbs energy (relative to an ideal dilute solution) as a sum of two parts: the first part is based on a slightly modified DH theory,

Figure 26. Calculated and experimental mean ionic activity coefficients of KCl in mixtures of methanol and water at 25 °C: pure water (□), 90 wt. % (salt-free) water (■), 80 wt. % water (△), 60 wt. % water (▲), 40 wt. % water (○), 20 wt. % water (●), 10 wt. % water (▽), 0 wt. % water (▼) (Papaiconomou et al., 2002).

and the second part is, essentially, an osmotic virial series in electrolyte concentration. Regrettably, this power series requires several system-specific coefficients that depend on temperature. However, because we have a large body of experimental results for aqueous salt solutions over a reasonable temperature range, we now have a fair inventory of Pitzer parameters. To extend Pitzer's model to multisalt solutions, it is necessary to make some simplifying assumptions or else to introduce one or more ternary parameters. Pitzer's model has been applied toward optimizing process design for salt recovery from Trona mines as discussed by Weare (Harvey et al., 1984), and for designing a recovery process for radioactive salts from aqueous solutions (Felmy and Weare, 1986).

To illustrate Pitzer's theory for an aqueous system containing two salts (potassium chloride and sodium chloride), Figure 22 shows experimental and calculated salt solubilities in the region 0 to 200 °C.

An alternate model for activity coefficients in aqueous electrolyte solutions was developed by Chen et al. (1982, 1986, 2001) who used the NRTL equation to account for ion–ion and ion–solvent interactions beyond those given by DH theory. An advantage of Chen's model is that, in at least some cases, it requires fewer binary parameters than Pitzer's model. Figure 23 shows an application of Chen's model to aqueous organic electrolytes. A similar theory, based on the UNIQUAC equation, was presented by Iliuta et al. (2002) who gave particular attention to solubilities of heavy-cation salts. Figure 24 shows calculated and observed solubilities of various hydrates of $Zn(NO_3)_2$.

When augmented by chemical equilibria, a much simplified version of Pitzer's model has been used by Edwards (Edwards et al., 1978) to correlate multicomponent vapor-liquid equilibria for aqueous solutions of volatile electrolytes (NH_3, H_2S, CO_2, SO_2) that are frequently encountered in chemical pro-
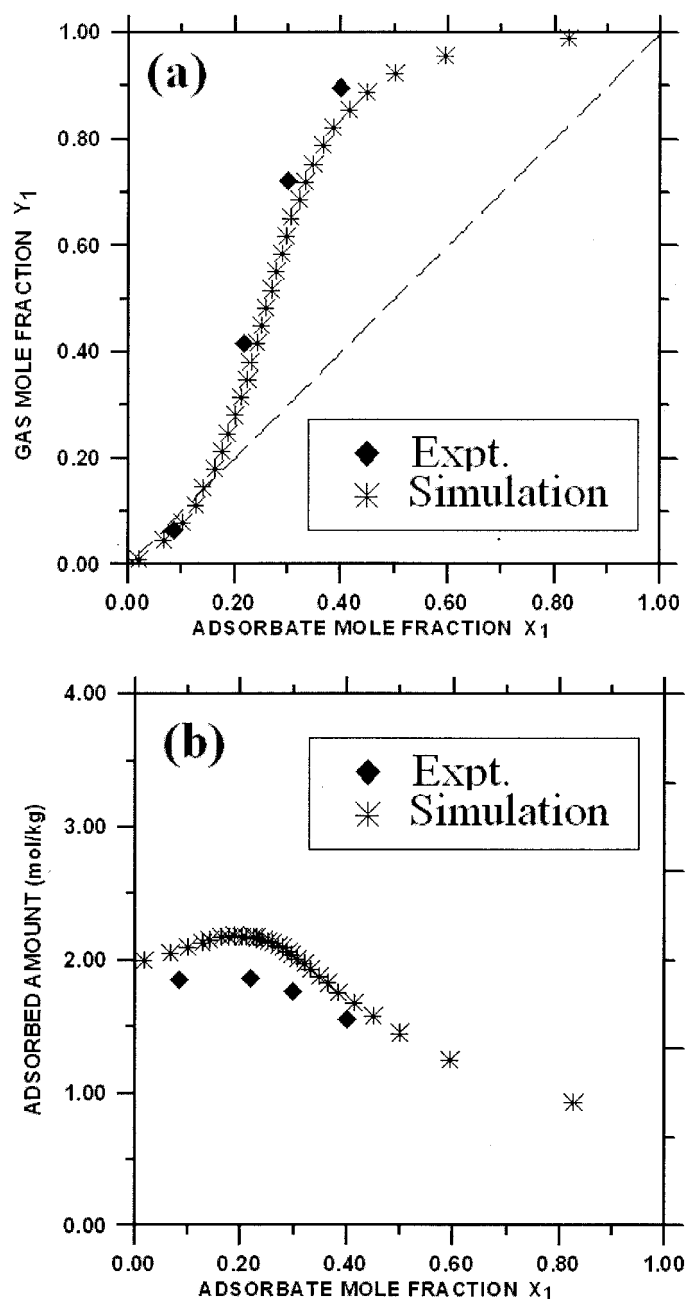
Figure 28. Comparison of Monte Carlo simulations with experimental data for adsorption of binary mixtures of propane (1)- H_2 S(2) on H-mordenite at 8.13 kPa and 30°C.

Parameters were obtained from each pure-component adsorption isotherm. (a) gives the phase diagram, and (b) gives the total amount of gas adsorbed (Cabral et al., 2003).

cesses. To illustrate, Figure 25 shows the total pressure as a function of SO_2 concentration for aqueous mixtures of SO_2 and NH_3 at 100°C.

The early theory by Edwards has been much improved by applying the full Pitzer theory. Maurer and coworkers have presented an extensive correlation of VLE for aqueous solutions of weak electrolyte gases with or without selected added salts (Rumpf et al., 1993; Bieling et al. 1995, Kamps et al., 2002, Kamps et al., 2003).

Integral-equation theory can be used to establish a theoreti-

cal basis for describing electrolyte solutions as discussed by Papaiconomou et al. (2002). To account for electrostatic and free-volume interactions of ions in solution, including the concentrated region, these authors used the integral theory of solution coupled with Blum's mean spherical approximation; the effects of van der Waals attractive forces are provided by an equation similar to NRTL. This theory is readily applicable to a salt in a solvent mixture; to illustrate, Figure 26 shows calculated and observed mean-ion activity coefficients for KCl in methanol–water mixtures at 25°C.
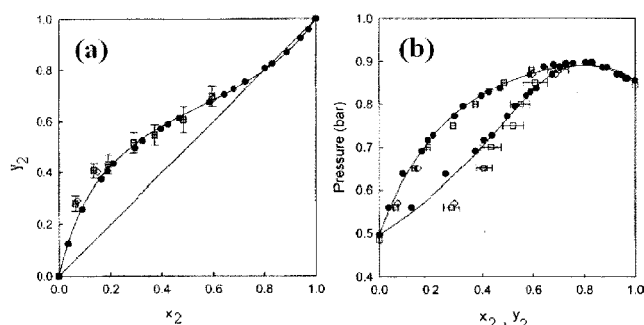
Figure 29. Calculated and experimental VLE phase diagrams for acetronitrile(1)-methanol(2) at 60.31 °C.

Phase diagrams show (a) vapor vs. liquid mole fraction and (b) pressure vs. vapor and liquid mole fraction. Filled circles are experimental data (DECHEMA), and open squares and diamonds are predictions from Gibbs-ensemble Monte Carlo NPT and NVT simulations, respectively; the solid line is the best fit of the experimental data (Sum et al., 2002).

Integral-equation theory can also be used to establish an EOS for describing electrolyte solutions as discussed by Jin and Donohue (1988, 1988), Wu and Prausnitz, (1998), and Myers et al. (2002).

Depending on pH, proteins carry an electric charge. Therefore, a description of the thermodynamic properties of protein solutions must include electrostatic effects in addition to van der Waals forces, as discussed, for example, in Albertsson's (1986) book on separation of protein mixtures by extraction in aqueous two-phase systems. Such systems are formed upon dissolving two water-soluble polymers, for example, dextran and poly(ethylene glycol) (PEG). A measure of how these two aqueous phases differ is provided by the length of a tie line on a plot where the percent PEG in one phase is plotted against the percent dextran in the other. Figure 27 shows calculated and observed distribution coefficients for three dilute proteins in a two-phase aqueous system as a function of the difference between the two phases (Haynes et al., 1991). Because this system also contains a small amount of KCl that partitions unequally between the two aqueous phases, and because the charges on the three proteins are not identical, the distribution coefficients differ widely, facilitating protein separation.

Molecular Simulations

An alternative to algebraic expressions for activity coefficients or equations of state is provided by molecular simulations as discussed in several textbooks, notably that by Sadus (1999) and that by Frenkel and Smit (2002).

Molecular simulations are attractive because they require as input only quantitative data for molecular structure, and for the potential of molecule–molecule interaction. The disadvantage of molecular simulations is that results are restricted to a particular case; these results are not easily generalized.

The last 15 years have produced a large number of articles showing how molecular simulation can be used to calculate phase equilibria for a large variety of systems based on the Gibbs–ensemble method of Panagiotopoulos (1987). Although

numerous authors have contributed to this important development, particularly noteworthy are the articles by Cummings and coworkers (for example, McCabe et al., 2001; Rivera et al., 2003) and those by de Pablo et al. (for example, Nath et al., 1998; Yan and de Pablo, 2001; de Pablo and Escobedo, 2002; Jendrejack et al., 2002). To illustrate applicability to process design, Monte Carlo simulations can be used to describe the adsorption of pure gases and their mixtures on solid surfaces as discussed, for example, by Smit and Krishna (2003), and by Steele (2002). To illustrate, Figure 28 shows calculated and experimental gas-solid adsorption equilibria for mixtures of propane (1)- H_2S (2) on H-mordenite (Cabral et al., 2003).

Because the results from molecular simulations are sensitive to the potential function that describes intermolecular forces, it is necessary to obtain that potential function from the reduction of some experimental data. For some cases, the extent of required experimental data can be reduced by quantum mechanics.

Application of Quantum Mechanics

One of the most promising recent developments in chemical engineering thermodynamics is provided by applying quantum mechanics for calculating thermodynamic properties, in particular, activity coefficients of components in liquid mixtures. Quoting from Sandler's review (Sandler, 2003):

"In the most direct and computational intensive form, computational quantum mechanicsis used to obtain information on the multidimensional potential energy surface between molecules, which is then used in computer simulation to predict thermodynamic properties and phase equilibria. At present, this method is limited to the study of small molecules because of the computational resources available. The second method is much less computationally intensive and provides a way to
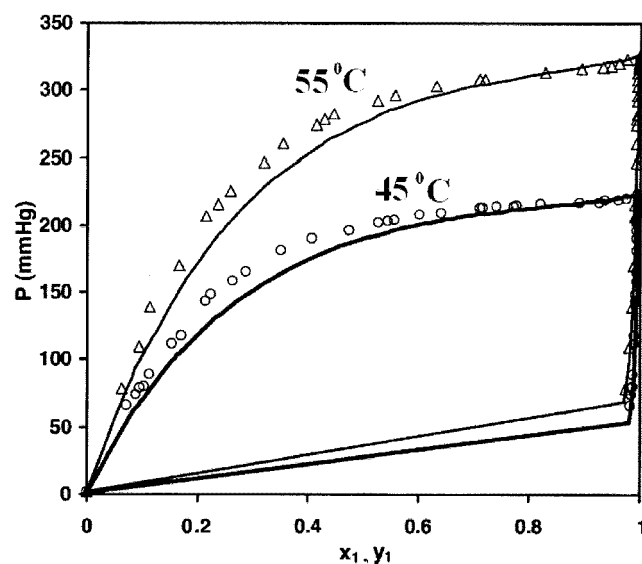
Figure 30. Calculated and experimental VLE for benzene(1)-N-methyl formamide(2) at 45 and 55 °C; calculation with the COSMO-SAC model (Lin and Sandler, 2002).

Circles and triangles are experimental.

improve group-contribution methods by introducing corrections based on the charge and dipole moment of each functional group that is unique to the molecule in which it appears. The third method is based on the polarizable continuum model, in which the free energy of transferring a molecule from an ideal gas to a liquid solution is computed, leading directly to values of activity coefficients and phase equilibrium calculations."

For typical polar molecules, such as acetonitrile or methyl fluoride, it is now possible to establish a reliable two-body potential that depends on all distances between the atoms of one molecule and those of the other. In some cases, the potential can be simplified by considering only the distance between the center of mass of one molecule and that of the other in addition to angles of orientation. For polar molecules having less than (about) 100 electrons, knowing the geometric and electronic structures of the molecules is sufficient to establish the two-body potential; for more difficult cases (for example, methanol), a well-measured thermodynamic property (typically the second virial coefficient) is used to augment results obtained from quantum mechanics.

For a binary mixture containing components 1 and 2, we need three two-body potentials: one each for 1–1, 2–2 and 1–2 interactions. Some, or perhaps all of these potentials may be obtained from quantum mechanics. These potentials are then used in a Monte Carlo-simulation program to generate vapor-liquid or other phase equilibria. Although this promising type of calculation is likely to see increasing popularity, at present, for industrial application, it suffers from two disadvantages: typical simulation calculations are limited by the additivity assumption (the total potential energy of a system is given by the sum of all two-body interactions), and by insufficiently powerful computers. Although corrections for nonadditivity are not simple, they are often significant, especially for hydrogen-bonding systems. A highly computer-intensive method for calculating multibody potentials is provided by Car and Parrinello (1985), but as yet this method is not sufficiently sensitive for application to mixtures of ordinary liquids (Trout, 2001).

Figure 29 shows a successful application of quantum mechanics-plus-Monte Carlo simulation for vapor-liquid equilibria for methanol-acetonitrile at 333.46 K (Sum et al., 2002). It is remarkable that, although no mixture data were used to generate Figure 29, the calculations give the correct pressure and composition of the azeotrope.

More than a century ago, Mossotti derived an equation for the change in energy experienced by a dipolar molecule when it is transferred from an ideal gas into a continuous liquid medium characterized by its dielectric constant (Israelachvili, 1992). Similarly, more than eighty years ago, Born indicated how the free energy of a charged molecule changes when it goes from one dielectric medium to another (Israelachvili, 1992). In the same spirit, but with more powerful physics, Klamt and coworkers (Klamt, 1995; Klamt and F. Eckert, 2000) have developed a method for calculating the activity coefficient of a solute dissolved in a continuous polarizable medium. This method does not use functional groups but uses surface charges for atoms that depend not only on the particular atom, but also on the identity of other atoms in the same molecule. Thus, Klamt's method, in effect, overcomes one of the serious limitations of UNIFAC. Klamt's method is attractive for engineering because computational requirements are
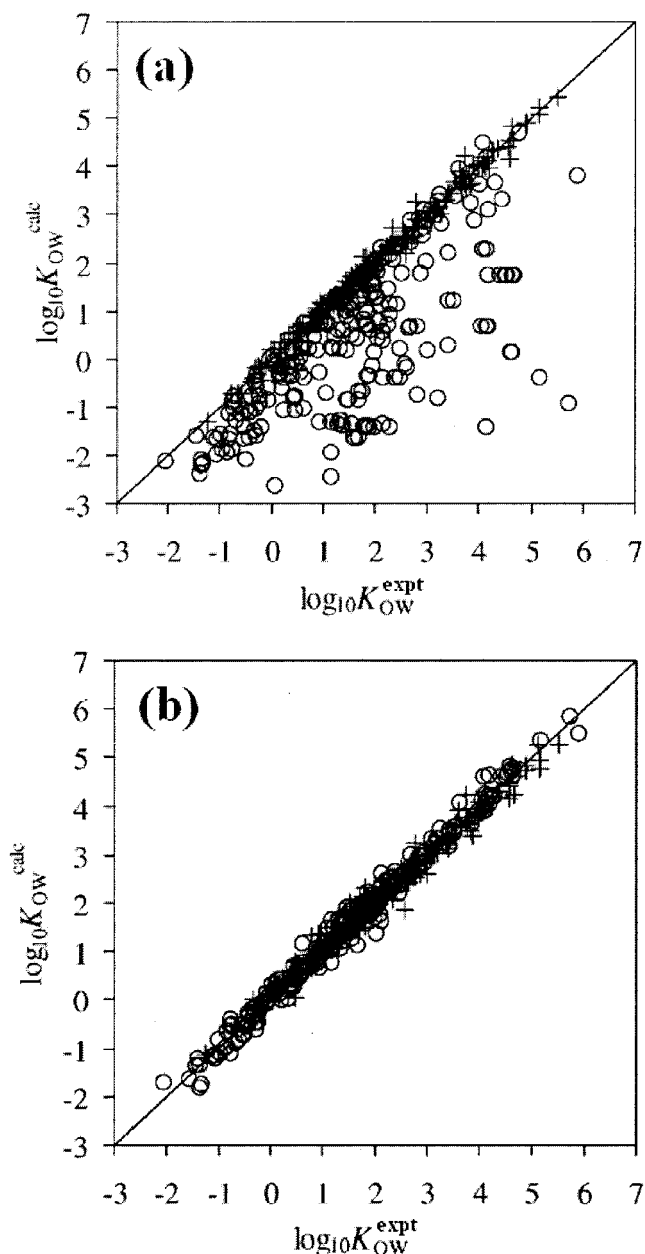
Figure 31. Comparison of calculated and experimental distribution coefficients for a large number of solutes distributed between water (W) and octanol (O) at high dilution, near room-temperature.

The partition coefficient is defined by the ratio of solute molar concentrations (mol/L). Crosses are for monofunctional molecules, and circles are for multifunctional molecules (Sandler, 2003).

relatively low. However, at present this method is limited to activity coefficients of solutes in dense liquids, that is, liquids well below their critical temperatures; it is not (yet) applicable to gaseous mixtures or to low-density liquid mixtures encountered in the vapor-liquid critical region. Figure 30 shows a successful example of Klamt's COSMOSAC model for vapor-liquid equilibria in the benzene–N–methyl formamide system (Lin and Sandler, 2002)

Quantum Mechanics for Group-Contribution Parameters

The popularity of UNIFAC (and other group-contribution methods) has encouraged numerous authors toward seeking improvements that overcome some of UNIFAC's well-known limitations. Perhaps the most important limitation of UNIFAC is its neglect of neighbor effects; in UNIFAC, the interaction between a functional group X and a functional group Y is assumed to be independent of the identities of whatever functional groups are bonded to X or Y. For example, in UNIFAC, a chloride group in say, $CH_3 - CH_2Cl - CH_3$, is equivalent to that in say, $CH_3 - CH_2Cl - CH_2OH$. With quantum mechanics, it is now possible to correct UNIFAC group–group interaction parameters for the proximity effect because of neighboring bonded groups. For molecules that contain only one polar functional group, proximity corrections are not large. However, for molecules that contain two or more polar functional groups, proximity corrections are often significant, especially if two polar functional groups are in close proximity as found, for example, in biomolecules and pharmaceuticals. To illustrate, Figure 31 presents calculated and experimental distribution coefficients for a large number of dilute solutes distributed between water (W) and octanol (O) near room-temperature (Lin and Sandler, 2000; Sandler, 2003). Part (a) of Figure 31 shows UNIFAC calculations without proximity corrections, whereas Part (b) shows calculations with quantum-mechanical proximity corrections. For monofunctional molecules there is little difference; however, for multifunctional molecules, proximity corrections produce a large improvement in agreement with experiment.

There is good reason to believe that, as computer speed rises, we will see increasing use of molecular simulations, and increasing use of quantum mechanics for the calculation of thermodynamic properties. It is likely that extensive use of rigorous *ab initio* calculations is still in the indefinite future. However, it is now clear that the time is ripe for with molecular simulations and quantum mechanics to extend and improve current methods for calculating phase equilibria.

Conclusion

This brief and unavoidably incomplete survey is limited to 50 years of progress in applications of thermodynamics for more-or-less classical operations in conventional chemical engineering. That progress follows primarily from two mutually-supporting fortunate developments since 1950: first, increasing availability of ever more powerful computers, and second, increasing willingness of chemical engineers to base correlations and design procedures on insight from physical chemistry, molecular physics and statistical mechanics. As chemical engineering expands into a variety of new (high-tech) areas, it is clear that these two developments will provide the essential background for future application of thermodynamics in chemical engineering science and practice.

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