

# Don't Gamble With Physical Properties For Simulations

*Finding good values for inadequate or missing physical property parameters is the key to a successful simulation. And this depends upon choosing the right estimation methods.*

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Chemical engineers use process simulation to perform a variety of important work. This work ranges from calculations of mass- and energy balances of large flowsheets to prediction of the performance of process alternatives that can save millions of dollars. An engineer very quickly can define a complex flowsheet and all the process conditions. Desktop computers now allow rating, sizing, optimization, and dynamic calculations that previously required large mainframe computers. In the past, these simulations were often built by a group of experts, including a physical property expert. Now, simulators such as ASPEN PLUS, ChemCAD III, HYSIM, PRO II, and SPEEDUP are easier to use and more powerful than the standalone programs of the past. Today, a single engineer can set up the basic simulation specifications, including the physical properties, in very little time.

Missing or inadequate physical properties, however, can undermine the accuracy of a model or even prevent you from performing the simulation. That some required information is missing is not an oversight in the simulator. After all, for most compounds, physical property parameters are not known for every thermodynamic model or for all temperature or pressure ranges. Models have built-in assumptions and practical limits that should apply.

In this article, we will provide practical tips and techniques to help you accurately describe the physical properties needed in a simulation. As an engineer,

you always will have to make assumptions in terms of physical properties, however. The goal of this article is to outline the appropriate assumptions and to provide techniques when properties are missing.

## The five important tasks

Successfully describing the physical properties to be used in a simulation involves five tasks:

1. selecting the appropriate physical property methods;
2. validating the physical properties;
3. describing nondatabank components (chemical species or compound) and missing parameters;
4. obtaining and using physical property data; and
5. estimating any missing property parameters.

It can be argued that these tasks are not sequential and, to some degree, they are concurrent. During simulation development, however, you will need to visit each area to be confident that your simulation is as accurate as possible — so that important decisions can be made based on the results of your simulations.

## Selecting the appropriate physical property methods

This essential first step will affect all subsequent tasks in developing accurate physical properties in your simulation. Indeed, the choice of the physical property models for a simulation can be one of the most important decisions for an engineer. Several factors need to be consid-

ered, and no single method can handle all systems. Table 1 lists some thermodynamic models available in simulators.

The four factors that you should consider when choosing property methods are:

- the nature of the properties of interest;
- the composition of the mixture;
- the pressure and temperature range; and
- the availability of parameters.

To ease the selection of the right physical property methods, we suggest using the decision trees shown in Figures 1–3. These trees are based on the four factors for selecting property methods, and can be used when the chemical components and approximate temperature and pressure ranges are known. While these diagrams are simplifications, they do show the basic steps of the decision-making process, while the notes in the sidebar amplify some of the key points.

*The nature of the properties of interest.* A question that you may ask yourself when starting a simulation is “Does the choice of physical property methods matter?” The answer is an emphatic YES. The choice can strongly affect the prediction of the simulation. You should be selecting a collection of methods that will best predict the properties or results of interest to you.

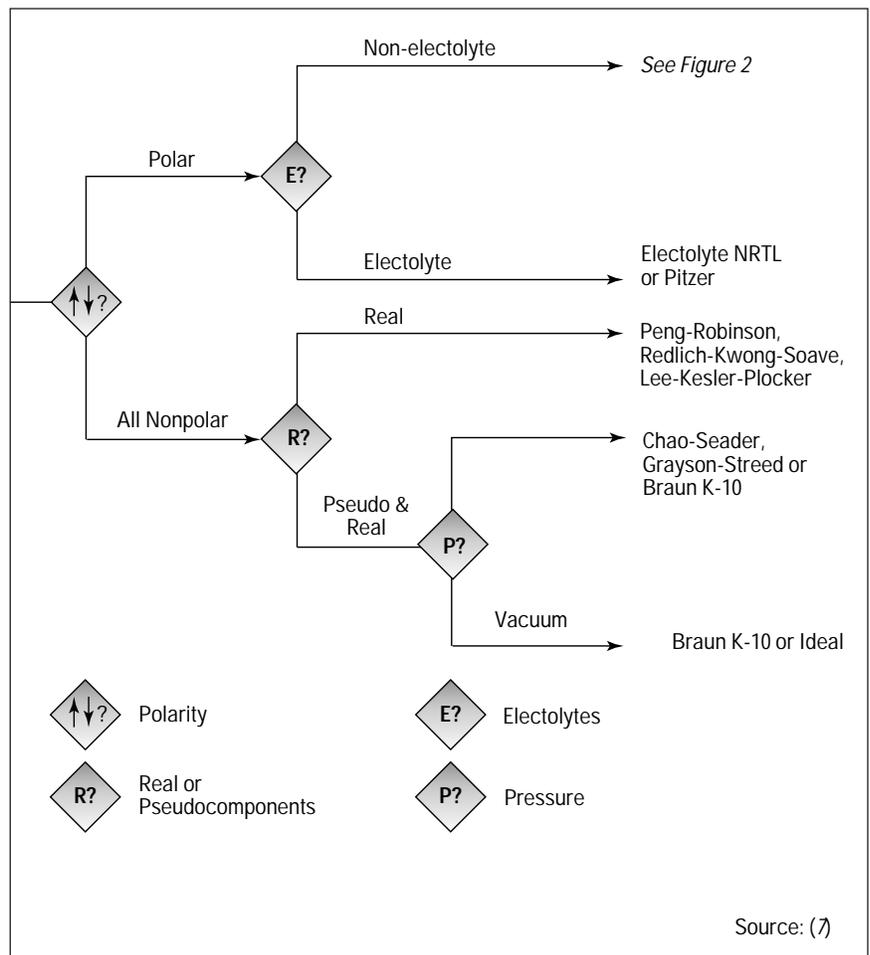
Because many chemical process simulations include distillation, stripping, or evaporation, one important potential consideration for the choice of physical property models is vapor/liquid equilibrium (VLE). This is the area in which the most physical property work is focused in chemical engineering. Liquid/liquid equilibrium (LLE) also becomes important in processes such as solvent extraction and extractive distillation.

Another critical consideration is pure-component and mixture enthalpy. Enthalpies and heat capacities are important for unit operations such as heat exchangers, condensers, distillation columns, and reactors.

**Table 1. Thermodynamic property models available in a simulator.**

| Equation-of-State Models                                | Activity Coefficient Models |
|---|-----------------------------|
| Benedict-Webb-Rubin(BWR)-Lee-Starling                   | Electrolyte NRTL            |
| Hayden-O’Connell*                                       | Flory-Huggins               |
| Hydrogen-fluoride equation of state for hexamerization* | NRTL                        |
| Ideal gas law*  | Scatchard-Hildebrand        |
| Lee-Kesler (LK)   | UNIQUAC                     |
| Lee-Kesler-Plocker                                      | UNIFAC                      |
| Peng-Robinson (PR)                                      | Van Laar                    |
| Perturbed-Hard-Chain                                    | Wilson                      |
| Predictive SRK  |                             |
| Redlich-Kwong (RK)                                      |                             |
| Redlich-Kwong-Soave (RKS)                               |                             |
| RKS or PR with Wong-Sandler mixing rule                 |                             |
| RKS or PR with modified-Huron-Vidal-2 mixing rule       |                             |
| Sanchez-Lacombe for polymers                            |                             |
|   | Special Models              |
|   | API sour-water method       |
|   | Braun K-10                  |
|   | Chao-Seader                 |
|   | Grayson-Streed              |
|   | Kent-Eisenberg              |
|   | Steam Tables                |

\* Not used for the liquid phase



Source: (7)

**Figure 1. The first steps for selecting physical property methods.**

## Navigating the decision trees

Here are some pointers to help you navigate the decision trees that appear as Figures 1–3.

*What are pseudocomponents?* In many applications where only non-polar molecules are present (such as in hydrocarbon processing and refining), the mixture is so complex that instead of representing it by all the known constituents, it is easier to group the constituents by some useful property such as boiling point. In this way, a mixture of hundreds of constituents can be reduced to 30 or fewer. The properties of these grouped constituents, called pseudocomponents, are represented by an average boiling point, specific gravity, and molecular weight. If you do not use pseudocomponents, the constituents should be described by a molecular formula and are referred to as real components.

*Why are electrolyte mixtures different?* Electrolyte mixtures include components that are charged molecules (ions) or that form salts. Some simulators allow calculation of electrolyte reaction equilibrium with phase equilibrium. This is a very powerful method and its usage covers many applications such as caustic scrubbing, neutralization, acid production, and salt precipitation. The nonideality of electrolyte solutions, usually containing water, can be observed in boiling point elevation, salting out of gases (that is, adding salts to the solution to change the solubility of gases), and salt precipitation. The most common electrolyte methods are the Pitzer model, and the modified-NRTL activity coefficient model of Chen and coworkers. Some electrolytes, like formic acid and acetic acid, are very weak and an electrolyte method is not required.

*Which type of method should be chosen for mixtures containing polar components but no electrolytes?* There are two groups of methods — based on activity coefficients or equations of state. Use activity-coefficient-based methods when pressures are low to medium (typically less than 10 bar or 150 psia) and if no components are near critical point. Activity coefficient models also often are used to accurately predict non-ideal liquid behavior such as for VLE and for LLE. In contrast, equation-of-state methods excel in their ability to represent data and extrapolate with temperature and pressure up to and above the mixture critical point. Now, however, methods relying on cubic equations of state with predictive mixing rules effectively combine the strengths of the two methods. (See Table 2.) For higher pressures (and temperatures), these special equations of state are better as they were developed to apply to a wider range of temperatures. These methods incorporate activity coefficients in the calculation of component interactions represented by excess Gibbs free energy. Most of the latter use a UNIFAC-based activity coefficient model as the default, but you can use any activity coefficient.

At simulation pressures less than 10 atm and where there are no near critical components, for the best results use the Wilson, NRTL, or UNIQUAC binary parameters that may be available in built-in databanks, or fit binary parameters to experimental data (if available) using activity coefficient models. These parameters may have been determined at different temperatures, pressures, and compositions than you are simulating, though, so you may not obtain the best possible accuracy. If interaction parameters are not available, however, you can use the UNIFAC method.

*When should UNIFAC be used?* UNIFAC and other UNIFAC-based activity coefficient models are predictive approaches that use structural groups to estimate component interactions. From structural information about organic components usually available in the built-in databank, UNIFAC is able to predict the activity coefficients as a function of composition and temperature. You can make use of UNIFAC when you do not have experimental data or binary parameters or when an approximate value is acceptable (for instance, for a component with low priority). In

recent years, there have been improvements to UNIFAC (see Table 3) that can better predict VLE, heat of mixing, and LLE over a wider temperature range. Recent extensions to UNIFAC proposed for molecules such as refrigerants and sugars may be useful, and you can add the groups and parameters to your simulation. Simulators may have the ability to generate binary interaction parameters for Wilson, UNIQUAC, or NRTL from UNIFAC.

Not all components can be described using UNIFAC, however, and not all group interactions are available. Examples of components that do not have UNIFAC groups include metals, organometals, and phosphates. So, we highly recommend always doing a search for available data on binary or ternary systems of interest.

*How should the vapor phase be treated?* The choice of the VLE method using an activity coefficient model also requires a choice of model for the vapor phase properties. If vapor phase association is observed (as in the case of acetic acid), then the vapor phase model should be Hayden-O'Connell or Nothnagel. A system containing hydrogen fluoride may require a special model to represent the high degree of association due to hydrogen bonding. Association in the vapor phase can have a strong effect on phase equilibria and enthalpy.

*When should defaults be overridden for other physical property methods?* Prediction of density, enthalpy, and viscosity also are important in simulators, and you shouldn't automatically accept the default methods. Check the simulator documentation for the default method and mixing rules.

Vapor density is calculated by an equation of state or the ideal gas law. Mixture liquid densities can be calculated by an equation of state, a temperature-dependent model such as that of Rackett, or by a temperature- and pressure-dependent model such as the COSTALD. For pseudocomponents, an American Petroleum Institute (API) method typically is employed. The Rackett model is recommended for general use.

Vapor enthalpy usually is calculated via an ideal gas assumption or an equation of state. The equation-of-state methods calculate a departure from ideality called the vapor enthalpy departure. For components such as acetic acid, the Hayden-O'Connell model is best, and will calculate a larger-than-normal vapor enthalpy departure.

Liquid enthalpies are calculated by a variety of methods. If the simulator uses the ideal gas as the reference state, then the pure-component liquid enthalpy is calculated from the ideal gas enthalpy and a liquid enthalpy departure. This can be written as

$$H^{*l} = H^{*lg} + (H^{*l} - H^{*lg}) \quad (1)$$

where  $H^{*l}$  is the pure-component liquid enthalpy,  $H^{*lg}$  is the ideal gas enthalpy, and  $(H^{*l} - H^{*lg})$  is the liquid enthalpy departure. This departure includes the heat of vaporization, the vapor enthalpy departure from the ideal pressure to the saturation pressure, and the liquid pressure correction from the saturation pressure to the real pressure. Simulators also allow separate calculations for a liquid enthalpy directly from the liquid-heat-capacity polynomial. For some components, the method in Eq. 1 will not be accurate enough for liquid-heat-capacity predictions. This can be very important if you are exporting your property information to another program such as one for rigorous heat-exchanger design. You can use the latter liquid-heat-capacity (CpL) method to improve the accuracy of liquid heat capacities.

Viscosity is another important property for sizing of piping, pumps, heat exchangers, and distillation columns. There are various vapor and liquid methods for calculating viscosity and, generally, the parameter requirements for these methods are substantial.

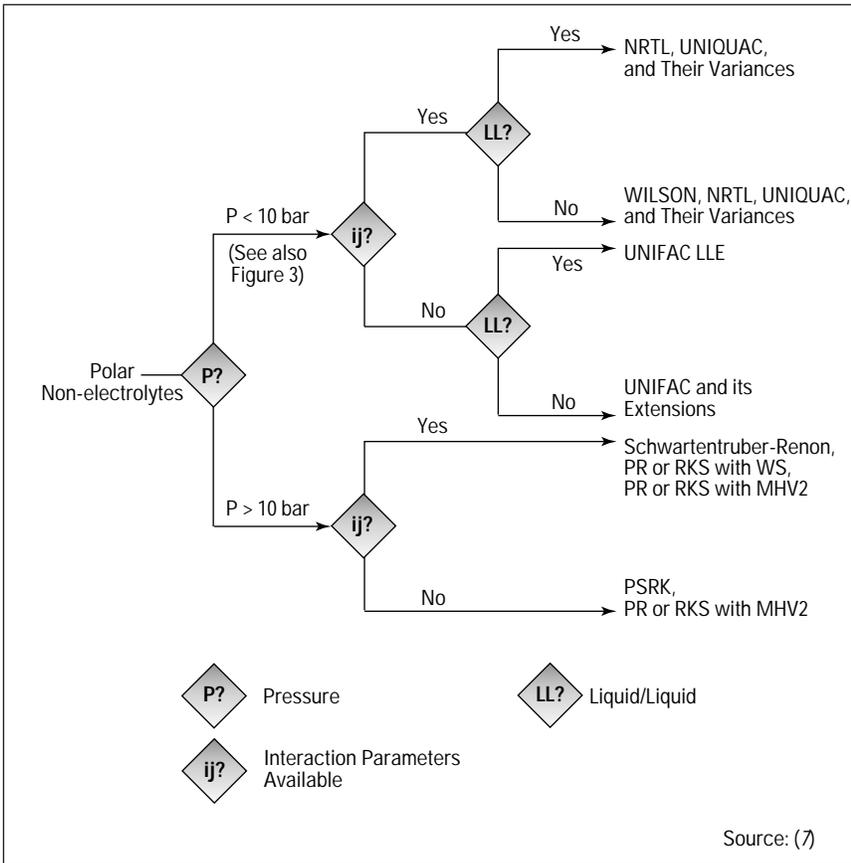


Figure 2. Proceeding for polar and nonelectrolyte components.

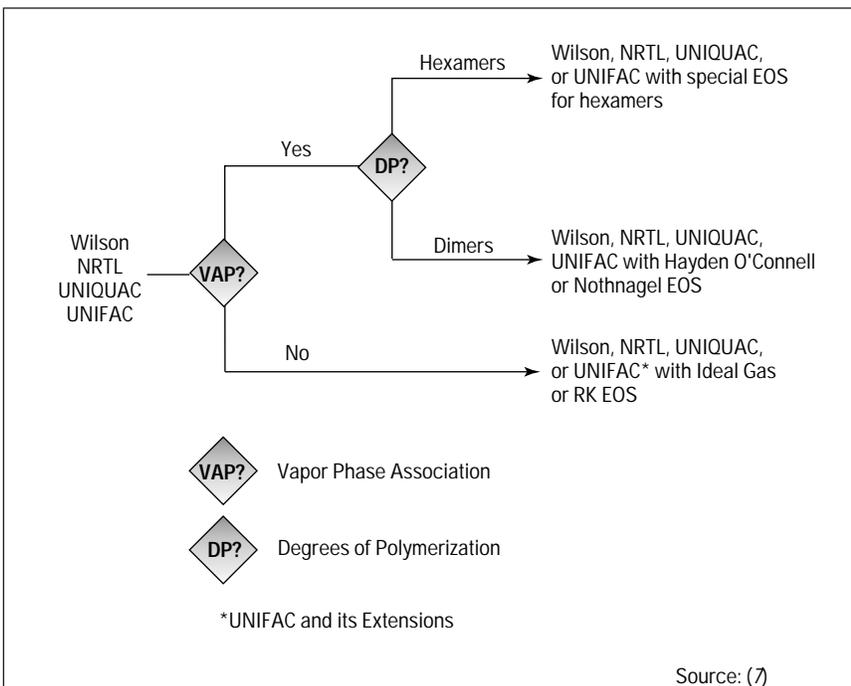


Figure 3. Options for vapor-phase calculations with activity-coefficient models.

Table 2. Examples of special equations of state.

|   |
|---|
| Predictive SRK (PSRK)                       |
| PR with modified Huron-Vidal-2 mixing rule  |
| PR with Panagiotopolous mixing rule         |
| PR with Wong-Sandler mixing rule            |
| RKS with modified Huron-Vidal-2 mixing rule |
| RKS with Panagiotopolous mixing rule        |
| RKS with Wong-Sandler mixing rule           |

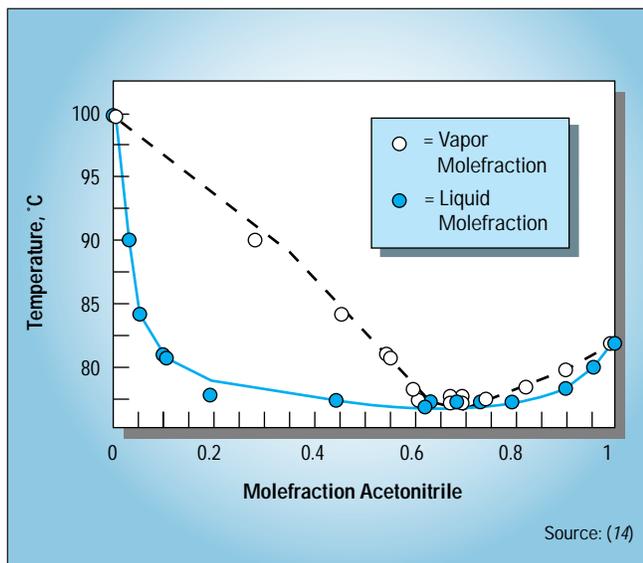
Table 3. UNIFAC revisions and extensions.

| Model                               | Predicts                                       |
|-------------------------------------|--|
| Dortmund-modified UNIFAC (1993) (8) | VLE, LLE, H <sup>F</sup> , $\gamma^{\infty}$ * |
| Kleiber extension (1994) (11)       | VLE of fluorinated hydrocarbons                |
| Lyngby-modified UNIFAC (1986) (13)  | VLE, H <sub>E</sub> (Excess Enthalpy)          |
| UNIFAC, LLE (1980) (12)             | LLE  |
| UNIFAC, revision 5 (1991) (9)       | VLE  |

\*Infinite-dilution activity coefficient

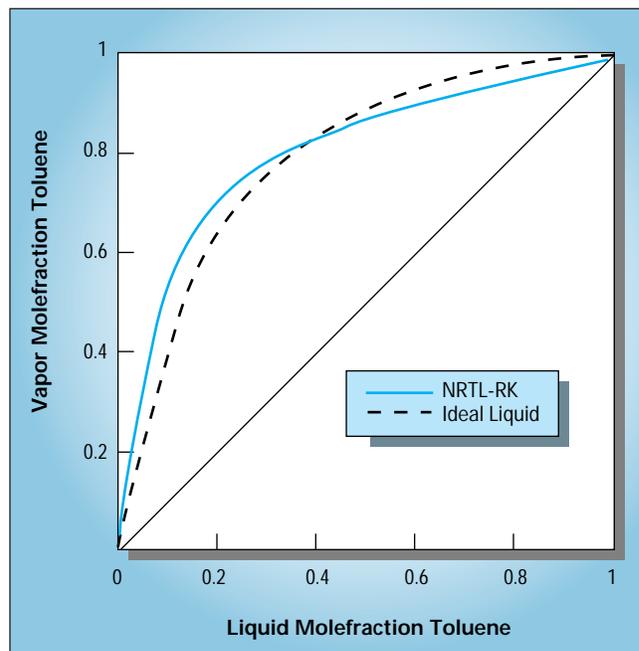
In addition, density, viscosity, pH, and thermal conductivity may be essential for other process calculations. Transport properties are important when doing equipment sizing calculations. Also, processes such as metallurgy and mining will require calculations for phase equilibria including solids.

*The composition of the mixture.* Composition will influence all properties, due to the way mixture properties are calculated. It will affect phase equilibria greatly because of the interaction of the components in the mixture. Usually, the interaction in the liquid phase is the more important because of the close proximity of the molecules in that phase. The nature of the vapor phase also can be significant if the components form complexes. The important intermolecular forces are electrostatic, induction, attraction, and repulsion between nonpolar components, and chemical forces such as hydrogen bonding. A good overview of these forces is given in Ref. 1.



■ Figure 4 (above). VLE of acetonitrile/water system at 1 atm.

■ Figure 5 (right). VLE of toluene/phenol system at 1 atm.

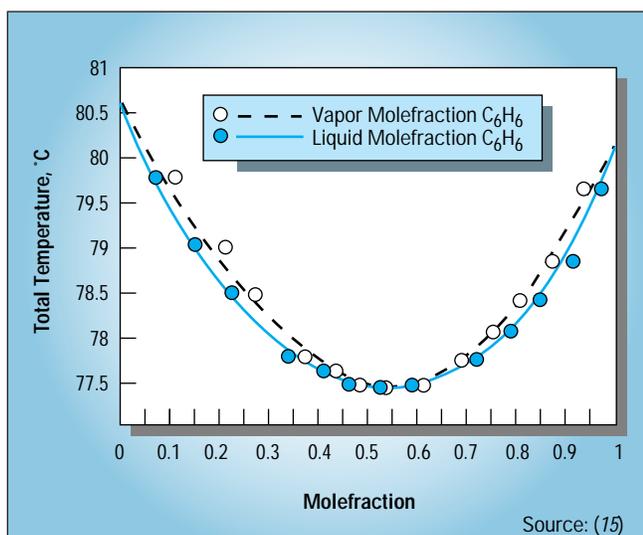


The magnitude of the electrostatic and induction forces is related to the polarity of the components. Components such as water, acetone, formaldehyde, and methyl chloride are strong dipoles. Many polar compounds are associative, and form complexes or dissociate into ions. Components like ethane and *n*-heptane are nonpolar. You can use your

simulator to report the dipole moments of databank components as one measurement of polarity. In general, mixtures of nonpolar components will exhibit less nonideal behavior.

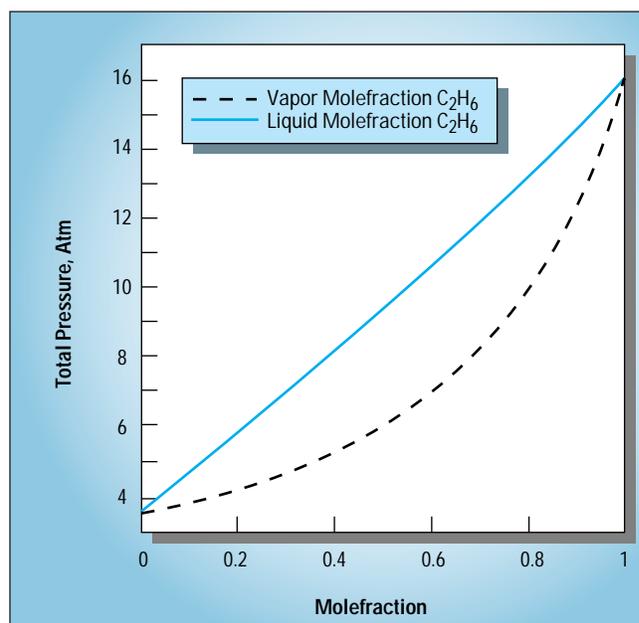
Figures 4–7 illustrate the effect of polarity on binary vapor/liquid equilibria. Figure 4 shows the predicted and experimental VLE of two highly polar components, acetonitrile and

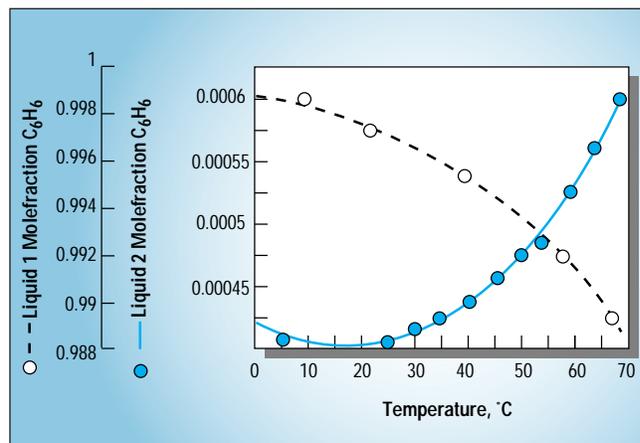
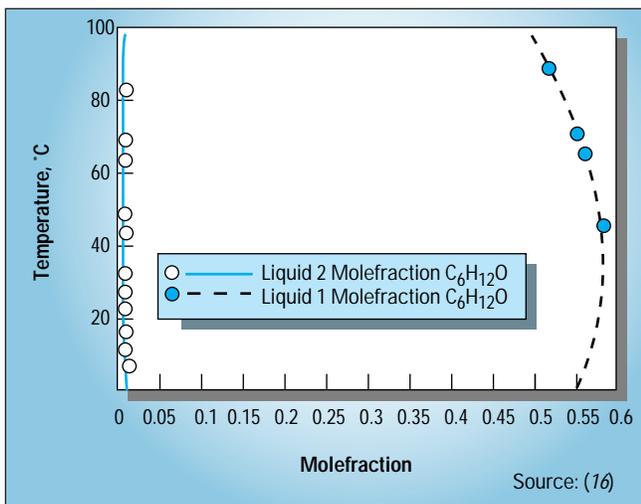
water, at 1 atm. The azeotrope is accurately predicted at approximately 0.7 mole fraction of acetonitrile. Figure 5 presents VLE for a mixture of two slightly polar compounds, toluene and phenol, at 1 atm. The deviation from ideality is shown by comparing the predicted curve from an ideal liquid assumption to that from a method predicting nonideality



■ Figure 6 (above). VLE of cyclohexane/benzene system at 1 atm.

■ Figure 7 (right). VLE of ethane/propylene system at 40°F.





■ Figure 8 (left). LLE of cyclohexanol/water system at 1 atm.  
 ■ Figure 9. (above). LLE of benzene/water system at 1 atm.

(the nonrandom two-liquid activity coefficient model (NRTL) and Redlich-Kwong equation of state for the vapor phase). Figure 6 depicts the VLE of a mixture of cyclohexane and benzene at 1 atm. Here, the interaction of seemingly similar molecules with a difference in boiling point of less than 1°C causes an azeotrope at a composition of about 0.54 mole fraction of benzene. A mixture such as ethane and propylene (Figure 7) is an almost ideal one, and does not deviate much from Raoult's law.

Mixtures of nonpolar and polar compounds, such as water and hydrocarbons, often will form two liquid phases that are very immiscible. Figures 8 and 9 show examples of miscible and immiscible systems of liquid/liquid equilibria, respectively, at 1 atm. In Figure 8, cyclohexanol is immiscible in the water phase but the organic phase contains up to 0.50 mole fraction water (0.10 mass fraction water). Figure 9 shows the high degree of immiscibility in both the organic and water phases for a mixture of benzene and water where there is less than 0.06% by mole benzene (0.3% by mass). Because of this behavior, some simulators have a special property method to treat the water phase as organic-free (also called Free-Water).

Most simulators offer collections of property methods in predefined

sets based upon methods that frequently are used for certain types of mixtures. Usually the sets are identified by the method used for phase equilibria. When these sets use an equation-of-state model, the same model is used for many properties, including those for phase equilibria.

*The pressure and temperature range.* This is especially important in choosing the method to perform phase equilibria calculations. Methods that are based on Raoult's law or that use activity coefficients are not accurate at high pressure or when the temperature is above the critical temperature of a component. You can use Henry's law when you have light gases in subcritical solvents, but it generally is not recommended for concentrations of solute greater than 5%. In general, equations of state are better suited to predict VLE over a wide temperature or pressure range, especially at high temperature and pressure.

*The availability of parameters.* Without sufficient pure-component and binary parameters, you will be unable to calculate pure-component or mixture properties. You must choose among obtaining and using experimental or literature data, estimating parameters, or choosing a less rigorous method. This should be investigated for all physical property methods including those shown in Figures 1–3.

### Validating the physical properties

A necessary step in any simulation project is validation of the physical properties. This involves reporting, tabulating, or plotting pure-component and mixture properties and comparing the results to known data or expected behavior. This is an important step in any simulation and should be performed for databank as well as nondatabank components. Simulators can provide these calculated properties in tabular and plot format. This is a useful tool for understanding how pure-component and mixture properties, such as density, heat capacity, and excess properties, vary with temperature, pressure, and composition, and how they behave when extrapolated. Similarly, such results can be used to generate plots of VLE and LLE to compare to diagrams in the literature and actual field data. Some simulators have the capability to generate residue curves for distillation of ternary mixtures. The residue plot capability also is a powerful tool for distillation analysis.

Use the tabulation and plotting tools to determine the cause of discrepancies in properties. If a mixture property is incorrect, investigate if a single component is the cause by reporting pure-component properties. Another useful technique is to compare the same flowsheet or property-table results while using different physical property methods.

By default, most phase equilibria calculations are performed assuming vapor and liquid phases. If your process involves two liquid phases (VLLE), be sure to specify three-phase calculations. If not, you will get incorrect results. As a part of the validation, you also should check that your property methods do not falsely predict two liquid phases.

Simulators let you specify that only one phase is present in a stream or a unit operation. If vapor and liquid phases are possible, however, you should use the two-phase specification.

### Nondatabank components and missing parameters

When you want to simulate nondatabank components or have components for which parameters are missing, ask yourself the following:

- Is this a major component in the mixture? If it is minor, can I take it out of the simulation?
- Does the component take part in VLE?
- Is the component non-volatile?
- Is it polar or nonpolar?
- Will reaction (including decomposition) cause this component to be depleted?
- What properties need to be accurate for the chosen property methods?

These questions will help you to identify the parameters that are needed based on your choice of physical property methods. If these parameters are not available or cannot be determined through literature search, regression, or estimation, then you will have to reevaluate your choice of physical property methods or obtain data by measurement.

You should determine what the parameters will default to if the simulator does not find any available. It is dangerous to assume that the physical property parameters were available just because the simulator did not give you an error message. Use the simulator manuals and on-line help to

create a list of parameters that are missing. You should detail this information when communicating the assumptions of the simulation to other users or your management.

Certain property parameters always are required for a simulation. These can include molecular weight, vapor pressure, and ideal-gas heat capacity constants. The need for other parameters depends upon your choice of physical property methods. The simulator manuals should include the information about the parameter requirements (7). There also are parameters that will be required for calculating the heat of reactions or the reaction equilibrium constants. This includes the heat of formation and the Gibbs free energy of formation of all components that participate in the reactions.

### *Techniques to remove or minimize the impact of specific parameters should be used with caution.*

You can use your judgment about the importance of a parameter to set nominal values for unimportant properties. For example, if you know that a component is very nonvolatile and are using Antoine's equation for vapor pressure ( $\ln P = A + B/(T+C)$ ), you can set the value of parameters  $A$ ,  $B$  and  $C$  to -100, 0, and 0, respectively. ( $T$  is temperature.) This will assign the vapor pressure used in Raoult's Law a very small value, almost zero ( $3.7 \times 10^{-44}$ !). This and similar techniques to remove or minimize the impact of specific parameters should be used with caution, however.

If you can't find a component in the simulator's databanks, make sure you check for synonyms. For example, methoxybenzene may be listed as methyl phenyl ether or anisole. A good approach is to search for the component using its formula. When selecting the component by formula,

check for different ordering of atoms. For instance, ammonia can be described as  $H_3N$  instead of  $NH_3$ . Ref. 2 contains a formula index of organic compounds and is a good resource for alternative names.

Once you have determined the parameter requirements that are not satisfied, the next stage should be obtaining and using physical property data.

### Obtaining and using physical property data

*Sources of data.* To provide parameters for nondatabank components or to do regression for pure-component and binary parameters, you will need to search for available data. Such data may be found in a variety of sources, including data-compilation references, handbooks, journals, and internal data collections.

While most streams in simulations contain mixtures, accurate property calculations are not possible without accurate pure-component properties. The importance of pure component data should not be underestimated as they are the basis for both pure-component and mixture properties. For instance, pure component properties such as vapor pressure will be used in phase equilibria calculations. Table 4 contains common sources for pure component properties, while Table 5 lists common sources for mixture properties.

The recommended order of data search is:

1. critically evaluated data sources;
2. nonevaluated sources;
3. experimental measurements; and
4. estimation techniques.

*Binary parameters for phase equilibria.* Because of the large number of binary pairs in even a simulation of only ten components, we recommend ranking the components so as to prioritize the pairs and focus the literature search and measurement efforts on the most important param-

**Table 4. Examples and reliability of sources of pure component data.**

| Source   | Evaluated     | Generally Reliable? |
|--|---------------|---------------------|
| Critical Data of Pure Substances, DECHEMA*                 | Critically    | Yes                 |
| CRC Handbook of Chemistry and Physics (Beilstein)*         | Noncritically | Yes                 |
| DIPPR Data Compilation*                                    | Critically    | Yes                 |
| Encyclopedia of Chemicals, Drugs, and Biologicals          | Noncritically | Yes                 |
| Encyclopedia of Polymer Science and Engineering            | Noncritically | Yes                 |
| ESDU Validated Engineering Data Index                      | Noncritically | Yes                 |
| Handbook of Thermophysical Properties of Gases and Liquids | Noncritically | Yes                 |
| JANAF Thermochemical Tables                                | Critically    | Yes                 |
| Lange's Handbook of Chemistry                              | Noncritically | Yes                 |
| Perry's Chemical Engineer's Handbook                       | Noncritically | Yes                 |
| Properties of Gases and Liquids                            | Noncritically | Yes                 |
| Selected Values of Properties of Chemical Compounds (TRC)* | Critically    | Yes                 |
| Vapor Pressure of Pure Substances                          | Noncritically | Yes                 |

\* Parts of these sources are available on-line from DIALOG Information Services, STN International, or Technical Databases Services, Inc. (TDS)

ters. First, divide the components into three groups: high, medium, and low priority. Base the priority on criteria such as composition, and the purity specifications of the process — if a component purity is specified, that component is important even if it appears only in low concentrations. Second, pair the components into high/high, high/medium, high/low, medium/medium, medium/low, and low/low groups. Search the available sources, including in-house ones, for any data for all groups. If certain component pairs are known to behave ideally, they can be excluded from the search. Next, use the UNIFAC method for the missing pairs in the medium/medium, medium/low, and low/low categories. UNIFAC is not recommended, however, for any pairs that include the components of high priority. A secondary literature search can be used to find binary data for similar compounds and those parameters then substituted. Propose experimental work if any binary parameter data are still missing or if data regression exposes data as inadequate (3).

### Regressing data

Data regression is a powerful tool for engineers not just to make the best of available data, but also to analyze the goodness of fit of a physical property model to the data. Most simulators include a data regression feature. Examples of commonly regressed data include binary VLE and LLE, vapor pressure, heat of vaporization, density, and heat capacity.

Data regression finds the best fit of parameter estimates to the experimental data. The best fit is represented by finding the lowest value of an objective function while matching the phase equilibrium or other constraints. One common regression technique is called Maximum Likelihood Estimation. The objective function for this method is:

$$\sum_j w_j (\sum_i ((C_i^m - C_i^e)/\sigma_i)^2) \quad (2)$$

where  $j$  is a data group,  $C_i^m$  and  $C_i^e$  are measured and estimated variables, respectively, such as temperature, pressure, composition, or heat capacity,  $\sigma_i$  is the standard deviation or the error in the measurement of the variable, and  $w_j$  is the weighting of the data group.

When fitting phase equilibria data, the regression algorithm attempts to reduce the objective function while the physical property method is being used to check that the components meet the constraints of phase equilibria.

The work of a successful regression involves selecting the right physical property model and parameters, representing the data properly, choosing appropriate standard deviations of the data, and starting with suitable initial estimates of the parameters. The following are general guidelines for data regression.

- *Make sure that you are regressing the right parameters.* Use the same physical property method and built-in databank that you will be using in the simulation. Choose parameters that have impact on the data being used. For example, when using an equation-of-state method such as Peng-Robinson or Redlich-Kwong-Soave, you should determine the acentric factor,  $\omega$ . But, if you are using an activity coefficient method, you should determine two or more constants for the Antoine model.

- *Estimate as few parameters as possible.* There is a tendency to use a large number of parameters when fitting a model to data such as temperature-dependent properties or binary phase equilibria. Try to regress the data with as few parameters as possible. If the regression results report that the standard deviation of the estimated parameters is of the same order of magnitude as the values of the parameters, you may be estimating too many parameters for your given data. The larger the temperature range of your data, the more parameters that you can estimate.

- *Watch out for incomplete data.* A regression may yield poor results if there are missing data points, particularly composition data. For example, some authors do not report all compositions in VLLE or immiscible LLE. You may need to estimate the missing compositions so that phase equilibrium can be calculated for all components. Find out how your sim-

ulator handles missing data to best deal with incomplete data.

- *Specify the right number of phases.* A regression will yield incorrect results if the number of phases is not specified correctly. This is a common problem in VLLE systems. For some literature data, the number of phases is hard to interpret because of the presentation of the data or lack of description. Often in VLLE data, only a total liquid composition is reported even though two liquid phases were present. The author may be reporting a heterogeneous azeotrope — an azeotrope where the vapor composition equals the total liquid composition but two liquid phases are present. When doing the regression of a heterogeneous azeotrope, divide the data into two groups, the VLE data and the VLLE data. This will ensure that the correct phase equilibria is considered. In regressions such as this, it is important to use the property tabulation and plotting features of the simulator to check that the parameter estimates correctly reproduce the original data.

- *Use a model's full functionality.* A physical property model may be used to calculate several properties. For example, you can use binary excess-enthalpy ( $H_E$ ) data and binary VLE or LLE data to determine binary parameters for activity coefficient models. For equation-of-state models, you simultaneously can use liquid- and vapor heat capacity, vapor pressure, and heat of vaporization data. If data are available for these properties, use these data together to estimate the parameters. Data groups of different types can be used together in the same regression.

- *If necessary, regress parameters even if values are available in the databank.* The physical property parameters found in the built-in pure-component and binary databanks generally are very reliable. You may find, however, that you need to determine new parameters to replace the databank values for your application. Check the built-in parameters to ensure that the recommended temperature, pressure, and composition range

Table 5. Examples of sources of mixture data.

#### Sources

Activity Coefficients at Infinite Dilution, DECHEMA Chemistry Series  
Binary VLE Data file\*, DIPPR  
Dortmund Databank (superset of DECHEMA data collection)\*  
Heats of Mixing Data Collection, DECHEMA Chemistry Series  
Liquid-Liquid Equilibrium Data Collection, DECHEMA Chemistry Series  
Phase Equilibria and Enthalpies of Electrolyte Solutions, DECHEMA Chemistry Series  
Vapor-Liquid Equilibrium Data Collection, DECHEMA Chemistry Series  
Vapor-Liquid Equilibrium Data for Electrolyte Solutions, DECHEMA Chemistry Series  
Vapor-Liquid Equilibrium for Mixtures of Low Boiling Substances, DECHEMA Chemistry Series  
Selected Values of Chemical Compounds, Texas A&M University  
Solid-Liquid Equilibrium Data Collection, DECHEMA Chemistry Series

\* On-line databanks

is not outside the range of your simulation. For example, vapor pressure parameters may not have been determined at temperatures below the normal boiling point. Most physical property models extrapolate outside the temperature bounds reasonably well — but at some compromise in accuracy. The parameter values also may apply to a very wide range of temperature and thus not provide as good a fit if you only need a narrow range in the simulation. For phase equilibria calculations, to improve the accuracy of VLE or LLE predictions, you may want to use ternary or quaternary data to fine-tune binary parameters that may be available in the simulator.

- *Check that the parameters reproduce the data.* The simulator will report qualitative results of the regression, including the residuals (experimental minus estimated variables). Use the property tabulation or plotting features to reproduce the data at the specified conditions. This can be performed in the same regression run. Check that the correct number of phases is predicted by allowing two-liquid-phase calculations for the property table or plot. In addition, your simulator may have an option where you can evaluate the fit using the existing parameters and model with experimental data without doing a regression.

- *Remove components not in phase equilibria.* If components that are solids or ions do not appear in a

phase, you can remove them from the phase equilibria constraints. This is useful in VLE.

- *Generate equilibrium data.* If you have binary parameters for an activity coefficient or equation-of-state model, your simulator may be able to generate VLE or LLE data for regression using these parameters. You can regress these “data” with another physical property model. This allows consolidation of known parameters into a single property method.

- *Fit other data.* Your simulator may have a data fitting feature that can be used for plant data. This method may not be as useful for predictive simulation, though, if the data are not from a wide variety of conditions.

#### Estimating missing property parameters

Property estimation usually is done after a data search is performed, to supply missing property parameters. You can use built-in estimation methods to fill in some gaps in your physical-property-parameter requirements. Simulators include one or more estimation methods for each of the most common parameters. There are two types of estimation methods for pure component parameters: structural group, and corresponding states.

Structural group methods are based on the idea that contributions of the parts or structural groups of the component are additive for properties such as

Table 6. Comparison of estimated and experimental parameters for phenetol (C<sub>8</sub>H<sub>10</sub>O).

| Property Name               | Units                 | Data         | Estimated Value | % Error | Estimation Method |
|-----------------------------|-----------------------|--------------|-----------------|---------|-------------------|
| Critical temperature        | K                     | 647.15       | 657.1265        | 1.54    | Joback            |
| Critical temperature        | K                     | 647.15       | 653.738         | 1.02    | Lydersen          |
| Critical temperature        | K                     | 647.15       | 652.7763        | 0.87    | Ambrose           |
| Critical pressure           | N/m <sup>2</sup>      | 3,420,000    | 3,577,070       | 4.59    | Joback            |
| Critical pressure           | N/m <sup>2</sup>      | 3,420,000    | 3,509,780       | 2.63    | Lydersen          |
| Critical pressure           | N/m <sup>2</sup>      | 3,420,000    | 3,474,970       | 1.61    | Ambrose           |
| Critical volume             | m <sup>3</sup> /kmole | 0.39         | 0.3935          | 0.90    | Joback            |
| Critical volume             | m <sup>3</sup> /kmole | 0.39         | 0.391           | 0.26    | Lydersen          |
| Critical volume             | m <sup>3</sup> /kmole | 0.39         | 0.389603        | -0.10   | Fedors            |
| Standard heat of formation* | J/kmole               | -101,600,000 | -105,400,000    | 3.74    | Benson            |
| Standard heat of formation* | J/kmole               | -101,600,000 | -104,140,000    | 2.50    | Joback            |

\* at 1 atm, 25°C for ideal gas.

Table 7. Estimated properties for propyl phenyl ether (C<sub>9</sub>H<sub>12</sub>O).

| Property Name               | Units                 | Estimated Value | Estimation Method |
|-----------------------------|-----------------------|-----------------|-------------------|
| Molecular weight            |                       | 136.1937        | Formula           |
| Critical temperature        | K                     | 668.6672        | Ambrose           |
| Critical pressure           | N/m <sup>2</sup>      | 3,085,350       | Ambrose           |
| Critical volume             | m <sup>3</sup> /Kmole | 0.442373        | Fedors            |
| Standard heat of formation* | J/Kmole               | -125,330,000    | Benson            |

\* at 1 atm, 25°C for ideal gas.

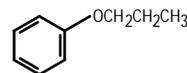
normal boiling point, critical temperature, critical pressure, ideal-gas heat capacity, and standard heat of formation. Some methods, such as that of Benson, contain additional corrections for next-nearest-neighbor atoms or for rings. Structural group contributions are determined by taking an average contribution based on known physical constants of many organic compounds. Because the Benson, Joback (10), and other structural-group methods are based mainly on data for organic compounds, they cannot be used for inorganics, including metals, or ions. In addition, structural group methods do not accurately represent very large organic molecules (that is, ones with a molecular weight > 200) such as proteins. New group-contribution methods like that of Constantinou and Gani (4) potentially may provide better estimations for organics. Other possibly useful methods are proposed in the literature but may apply to only certain families of components.

Corresponding states methods are based on empirical mathematical relationships among properties. For example, the Letsou-Stiel method relates liquid viscosity to critical temperature, critical pressure, and acentric factor. These methods most likely will be inaccurate when used for compounds unlike those upon which the correlation was based.

A good approach for both group contribution and corresponding states methods is to check the accuracy of as many methods as possible for compounds for which properties are known and which are structurally similar to the compound you are estimating. The following example shows the use of this concept.

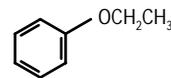
*Estimating the properties of propyl phenyl ether.* Let's say that you are modeling a process containing propyl phenyl ether (PPE), also called propyloxy benzene. The only data you have are its boiling point

(189.9°C), density at 25°C (0.9474 g/cm<sup>3</sup>), and molecular structure:



You want to estimate the properties of PPE using the most appropriate methods.

**Step 1.** Determine the best estimation methods for a similar phenyl ether. Select other compound(s) chemically similar to PPE for which you have experimental property data. (Of course, the more similar compounds you can use, the greater your confidence that you are selecting the most appropriate methods.) In this case, for simplicity, let's choose only phenetol:



Data for phenetol is available from the DIPPR data collection (5).

Use the simulator's built-in methods to estimate properties for phenetol. Then, compare the results of the various methods with the experimentally determined values to identify which methods give the best estimates for this class of compounds. Table 6 lists the results for the different methods for phenetol.

You can see that the Ambrose method gives the best overall predictions for critical temperature and pressure, the Fedors method for critical volume, and the Joback method for standard heat of formation for phenetol. So,

we will use these methods to predict the corresponding properties for PPE.

**Step 2.** Enter the available data and structure for PPE. Enter normal boiling point and molecular structure of PPE, and specify the methods that gave the best predictions for phenetol.

**Step 3.** Examine the estimation results for PPE. These appear in Table 7.

One area of property estimation that is more difficult is differentiating the properties of stereo isomers. Some group-contribution methods have corrections for *ortho*, *meta*, and *para* configurations, but few have built-in corrections for optical isomers. The separation of these isomers in a chemical process is based on their slightly different properties — relative volatility in distillation is one example.

### Employing simpler methods

In addition to structural group and corresponding states methods, another useful estimation approach is provided by series and family plots. Series plots look at the values of a property such as normal boiling point with increasing molecular weight or carbon number for compounds in a series that differ by one substituent group, such as the  $\text{CH}_2$ -unit in *n*-alkanes. Figure 10 is a series plot for the normal boiling point of *n*-alkylbenzenes. Family plots are similar, but the number of groups is larger. For example, Figure 11 shows a family plot of the critical pressure of methyl(hydrogen)chlorosilanes. You can use these plots to predict properties by extending the curve or to check your data for errors (6). To create a useful series or family plot, however, you must be careful about the components included.

When accuracy is not critical, consider the simple but powerful technique of component substitution. In this, you use the properties of another, similar component for all properties of the component of interest that you do not know. A similar component is one that has a comparable volatility (vapor pressure), density, and heat capacity. This is useful if the component is nonvolatile or is not involved in phase equilibria. For example,

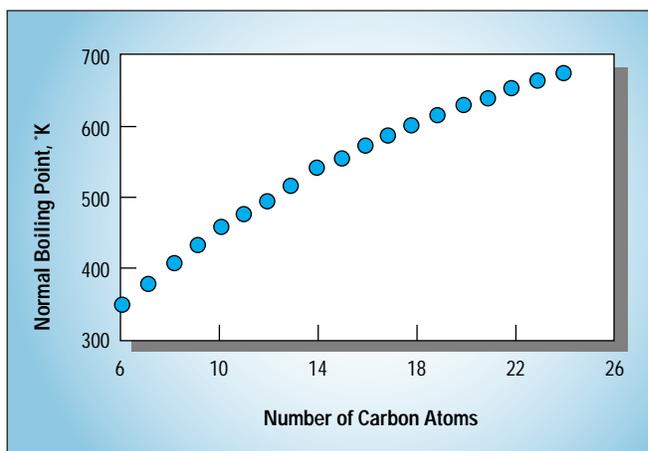
you have a small amount of a nonvolatile component in a stream that is at  $100^\circ\text{C}$  and 1 atm. You can access the properties of a nonvolatile component, say  $\text{C}_{20}\text{H}_{42}$  (molecular weight = 282.55, and boiling point =  $343.78^\circ\text{C}$ ), instead of estimating properties. This method is very efficient if you do not need accurate properties of the component. Take care, though, if you use this approach and one of the UNIFAC activity-coefficient methods, as you may change the assumptions made about the liquid phase.

Another technique to simplify a mixture of similar components is to represent them with a single component. This is a useful technique when components are not known exactly. For instance, Component  $\text{C}_{5+}$  could represent hydrocarbons of 5 carbon atoms and greater.

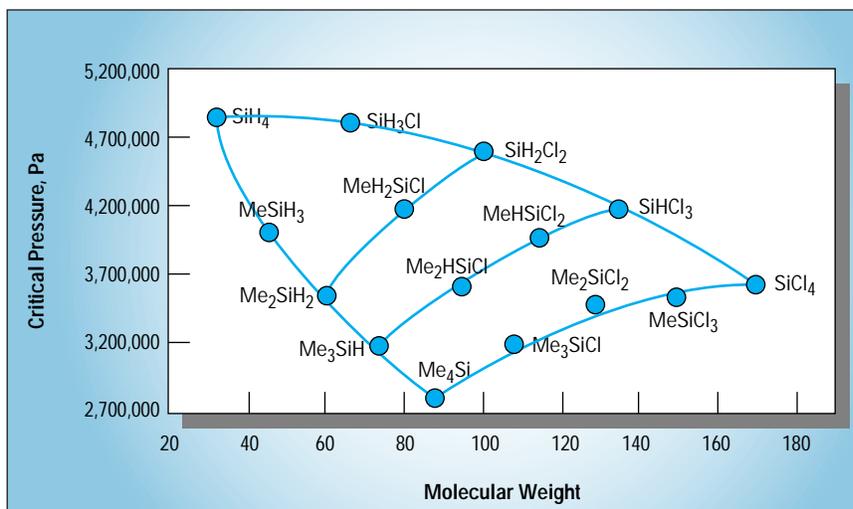
### Estimating binary parameters

You can estimate binary parameters for Wilson, NRTL, and UNIQUAC activity-coefficient models using two approaches: UNIFAC and infinite-dilution activity coefficients. UNIFAC-estimated binary parameters usually do not provide enough accuracy and, so, only are recommended for early stages of physical property data investigation and to “fill in the blanks” for components with medium or low priorities.

Better binary parameters can be estimated using infinite-dilution activity coefficient data. (Some simulators may include this feature under their regression tools.) This method is better because it is based on the components of interest, unlike the group contribution method, which averages



■ **Figure 10** (left). Series plot of normal boiling point for *n*-alkylbenzenes.



■ **Figure 11** (below). Family plot of critical pressure of methyl(hydrogen)chlorosilanes.

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the effect of group interactions from different components.

Estimation of physical properties can get you started in a simulation problem — but you should do an exhaustive literature search to find missing pure-component and binary parameters.

It is important to enter any known parameters before doing property estimation. First, experimental data generally are more accurate than estimated values. Second, corresponding-states estimation methods require other physical constants as input. Using an experimental value will improve the prediction of these property parameters. Otherwise, the error in estimating parameters such as normal boiling point, critical temperature,

and critical pressure propagates to other property parameters.

### Documenting what you've done

Simulation projects often have a long life at a company. New users may come along and be unfamiliar with the assumptions and recommended use of the simulation. You may find that you need to revisit a simulation a year or more later. Documenting the data sources, the range of applicability, and physical property assumptions is extremely important. This can be incorporated using the comment or descriptions fields in the simulator. Include a statement about any properties that were not well defined or components that should not

## Acknowledgment

The techniques and guidelines presented in this article are the results of experience helping simulation users solve engineering problems. I would like to thank the following colleagues at Aspen Technology for advice and information: Valentijn DeLeeuw, Marcelo Marchetti, Bill Mock, Andrea Takvorian, and Suphat Watanasiri.

be added given the physical property method employed — for instance, electrolytes when an equation-of-state method is being used. Keep track of the references for data and list them in the simulation, if possible. Include comments about properties, such as densities or heats of mixing, that were not of interest or not validated in the simulation. Keep the estimation, regression, and simulation files together. If possible, create a file containing all pure-component and binary parameters including those accessed in the built-in databanks. This way you will be able to reproduce your results in the future with upcoming simulation-software releases.

### Keeping the right perspective

The physical property system of the simulator is not a black box, but a well developed set of rules and relationships that can execute very complex calculations very quickly. It does not replace that most useful of all tools of a chemical engineer — common sense. Always use your judgment to evaluate simulation errors or suspicious results to find their source. That way, you'll make the best use of your simulator, and avoid unnecessary mistakes. CEP

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