

Selecting Thermodynamic Models for Process Simulation of Organic VLE and LLE Systems

By Galen J. Suppes
Department of Chemical Engineering
The University of Missouri-Columbia

Introduction

Students and young chemical engineers often find themselves relying on powerful process simulation programs for coursework or job performance without having the proper background in applied phase equilibrium thermodynamics. This lack of experience becomes obvious when either a poor choice is made in selecting a physical property package or the actual selection process is completely overlooked. The heuristics presented in this text are designed to assist in selecting thermodynamic packages for process simulation without embarking upon the hours of effort that can be involved in getting similar information from other resources.

Background

Proper selection of thermodynamic models during process simulation is absolutely necessary as a starting point for accurate process simulation. A process that is otherwise fully optimized in terms of equipment selection, configuration, and operation can be rendered essentially worthless if the process simulation is based on inaccurate thermodynamic models. Because of this, good heuristics and appropriate priority should be placed on both selecting thermodynamic models and reporting the selections in process reports.

Simulation generally differs from hand calculations in two ways: (1) the simulator allows use of more sophisticated models without significantly expending more of the engineer's time and (2) simulations in chemical engineering typically involve VLE (vapor-liquid equilibrium) where the ideal gas EOS (equation of state) is inaccurate. Productivity is rarely diminished by selecting rigorous thermodynamic models as compared to models that make for easy calculations, and so, criteria for selecting thermodynamic models during simulation are based primarily on accuracy and not the optimal combination of accuracy and effort. However, acquiring accurate binary interaction coefficients or data still fall within the realm of increasing accuracy at the expense of increased effort.

During process simulation, thermodynamic model selection should be performed in at least two steps. Firstly, as with initial process configurations, the thermodynamic model should be chosen based on heuristics (heuristics) that provide for a good base case but may or may not provide the desired level of accuracy. Secondly, based on the results of the base case simulation (complete with cost estimate), improving the accuracy of the thermodynamic models should be prioritized relative to optimizing other design parameters such as the configuration of unit operations, optimization of specific unit operations, heat integration, and other degrees of freedom used to optimize processes. Optimization includes both economic and simulation accuracy aspects. Thermodynamic model definition should be revisited as often as necessary during process optimization.

This text summarizes heuristics for selecting thermodynamic models for base case simulation. Guidelines are also provided to help identify the priority that should be placed on efforts to improve thermodynamic models after completing the base case. The approaches described herein are largely a simplified version of those described by Stanley M. Walas in his text entitled Phase Equilibrium in Chemical Engineering. The format of this text provides a transitory approach for those engineers who have not studied applied phase equilibrium modeling beyond undergraduate material. This introduction should be sufficient to perform process simulation with confidence while not being overwhelmed with the detail provided by Walas. Walas provides a good source of explanation, theory, and examples beyond those detailed here.

Modeling Phase Equilibrium

Thermodynamic property package selection is, appropriately, one of the first necessary steps in process simulation. These packages typically include EOSs, activity (solution) models and other more specialized models for the purpose of taking account non-idealities in vapor and liquid mixtures. Table 1 summarizes the parameters that are calculated in these approaches. Vapor pressure models (e.g. Extended Antoine equation) are generally accurate provided the parameters are not specific to a range outside that of interest. Corresponding states methods for pure component fugacity coefficients (e.g. Chao Seader Model) are typically only called upon for pure component calculations when

alternatives are not available. Selection of either vapor pressure models, pure component fugacity models, or other methods such as interpolation of available data are typically performed automatically by simulation packages only as necessary and without operator interaction.

The present discussion is limited to the selection of EOS and solution models since these are used to solve the vast majority of organic chemical processes.

Table 1. Commonly used approaches to VLE by simulation packages.

Approach	Equation	Interpretation
	$\hat{f}_{iV} = \hat{f}_{iL}$	Condition of Equilibrium Between a Vapor and Liquid
EOS	$\hat{\phi}_{iV} y_i P = \hat{\phi}_{iL} x_i P$	$\hat{\phi}_{iV}$ and $\hat{\phi}_{iL}$ are calculated using the EOS to solve for y_i and/or x_i when solving for the equilibrium condition.
Solution Model	$\hat{\phi}_{iV} y_i P = \hat{\gamma}_i x_i \hat{\phi}_i P^{s_i} (PF)_i$	$\hat{\gamma}_i$ are calculated using the solution model. An EOS is still needed to calculate $\hat{\phi}_{iV}$ and $\hat{\phi}_i$. Pure component vapor pressures (P^{s_i}) calculations are performed with a vapor pressure model, and the Poynting factor corrections (PF) are optionally calculated with liquid density data.
	$y_i P = \hat{\gamma}_i x_i P^{s_i}$	Modified Raoult's law form of solution model.
Henry's Constant	$\hat{\phi}_{iV} y_i P = H_i x_i$	Henry's constant form of equilibrium equation for use with gases having low solubility in the liquid phase. H_i is specific to the gas-liquid combination.

VLE Model Selection

As summarized by the EOS and solution model equations of Table 1, both an EOS and solution models can be used for VLE calculations. Due to the complexity of the EOS calculations, this approach to the solution of mixture VLE problems is typically not covered in undergraduate curriculum. Walas provides good examples and algorithms for these calculations.

The following heuristics provide a good approach to base case calculations:

1. When the highest reduced temperature for VLE processes as calculated by Kay's rule is greater than 0.75 and immiscible liquid phases are not anticipated, use an EOS for VLE calculations. For Kay's rule, $T_r = T / \sum y_i T_{ci}$. The EOS selection will typically be limited to cubic equations capable of VLE modeling such as the Peng Robinson (PR) or Soave Redlich Kwong (SRK) EOSs.
2. When selecting an EOS, EOSs that have binary interaction coefficients obtained from experimental data should be selected over EOSs in which these are not available. Check the simulator's listing of these binary interaction coefficients through options that are typically provided by the simulator after an EOS is selected.
3. When the reduced temperature as calculated by Kay's rule is less than 0.75, use a solution model for the liquid phase and an EOS for the vapor phase.
4. The better-known solution models include equations Margules, van Laar, Wilson, NRTL, and UNIQUAC models. Of these, based on frequencies of best fits, the following choices are best when only one liquid is anticipated:
 - for aqueous organics, NRTL
 - for alcohols, Wilson
 - for alcohols and phenols, Wilson
 - for alcohols, ketones, and ethers Wilson or Margules (Wilson is preferred due to its improved ability to correct for changes in temperature)
 - for C₄-C₁₈ hydrocarbons, Wilson
 - for aromatics Wilson or Margules (Wilson is preferred due to its improved ability to correct for changes in temperature)

When in doubt for VLE calculations, use the Wilson equation. Apply this rule under the assumption that binary interaction coefficients are available or can be estimated.

5. When performing simulation that involves LLE, do not use the Wilson equation since the Wilson equation is not capable of performing LLE calculations. Alternative to the Wilson equation use the TK Wilson equation or the NRTL equation. Apply this rule under the assumption that binary interaction coefficients are available or can be estimated.
6. If your simulation package does not provide the ability to estimate binary interaction coefficients with the Wilson, NRTL, or TK Wilson equations and does offer this ability with the UNIQUAC equation, then use the UNIQUAC solution model with UNIFAC estimation of binary interaction parameters.
7. If the critical properties of a component are not available, the use of a cubic equation may not be an option. If within this same simulation, some process conditions have a reduced temperature at VLE conditions greater than 0.75, several approaches are available. a) the use of solution models may be extended with increasing inaccuracy to reduced temperatures of about 0.9, b) the process may be separated into different sub-processes that can be modeled using different thermodynamic packages, c) the process may be modified for simulation purposes only to allow it to be divided into sub-processes that can be modeled using different thermodynamic packages, and d) the critical properties may be estimated for those components for which critical properties are not available. If critical properties are not available for certain components and it is anticipated that processes will have VLE processes near the component critical point, this should indicate a potential problem to the engineer. For example, in the case of ethylene oxide, critical properties are not available because it explodes prior to experiencing its critical point. In the case of oleic acid, the acid simply degrades prior to reaching its critical point. In both of these cases, it would be impractical to design a process to operate with these components at VLE near their critical points.

The use of reduced temperature for selecting EOS models over solution models is based on two premises. Since solution models are specifically designed for liquid phases and are fitted to data in the conventional liquid phase as compared to near-critical fluids, solution models will tend to be more accurate than EOSs for liquids. With increasing temperatures and at a reduced temperature of about 0.75, the liquid phase begins to expand rapidly to the point where polar and hydrogen bonding forces that dominate liquid phase properties become less dominating. Since these polar and hydrogen bonding forces largely determine the binary interaction coefficients, the binary interaction coefficients become increasingly invalid and the model becomes increasingly inaccurate. EOSs are specifically designed to be useful in these near-critical regions, and so, they are preferred. The best reduced temperature to use as a point of transition is dependent upon the engineer, but the use of values from 0.7 to 0.8 can be readily justified by studying compressibility charts.

The choice of which EOS is substantially personal preference provided the EOS is capable of performing the desired tasks—this typically translates to limiting the selection to cubic equations if an EOS is used to model both liquid and gas phases. When teaching design for the first time at The University of Kansas, I asked Professor Walas which equation of state was generally the best, he responded that whenever somebody develops and reports a new EOS, they claim it to be better than the previous EOS options. The SRK EOS appears to be the most favorite with the PR EOS a close second. Walas reports binary coefficients for several systems and most simulation packages have these or other binary interaction coefficients built into their databases.

Table 2 summarizes a comparison of solution models presented by Walas. These data were used to derive heuristic 4. Heuristic 4 is also based on the ability of the model to go beyond fitting data, and specifically, to the ability of the solution model to accurately account for the impact of temperature. Based on the ability to accurately account for changes in temperature, the Wilson equation was selected over the Margules equation even though the Margules equation may provide a slightly better fit to the data.

The heuristics described above are designed to provide a starting point for selection of thermodynamic packages to use for base case process simulation. Depending upon process and availability of data, the best choices of thermodynamic packages will vary.

It is interesting to note that even though the development of the UNIQUAC solution model in combination with the UNIFAC group contribution was groundbreaking work, the UNIQUAC model does not consistently fit experimental data well. When using UNIFAC or other group contribution methods, different binary coefficients will be estimated based on LLE versus VLE options. The applicable options or options should be chosen during process simulation.

Table 2. Frequency with which each equation provided the best fit in DECHEMA Vapor-Liquid Equilibrium Data Collection. Summary if is from Walas.

Mixture Classification	Wilson	NRTL	UNIQUAC	Best Fit
Aqueous organics	0.240	0.403	0.143	NRTL
Alcohols	0.395	0.223	0.131	Wilson
Alcohols and phenols	0.342	0.225	0.102	Wilson
Alcohols, ketones, ethers	0.243	0.155	0.155	Wilson
C4-C6 hydrocarbons	0.365	0.232	0.099	Wilson
C7-C18 hydrocarbons	0.260	0.209	0.136	Wilson
Aromatics	0.225	0.160	0.172	Wilson

Selection of Model for Gas Solubility in Liquids

The equilibrium of a gas with a liquid can and should be separated into two separate types of separation problems a) the separation of a volatile organic from a gas like nitrogen and b) the separation of the gas from a liquid.

The separation of volatile organic compounds from purge gases is commonly encountered in industry. For this system, the gas is typically sparingly soluble in the liquid, and because of this, solution models such as the Wilson equation accurately estimate the vapor pressure of the volatile organics.

In contrast, accurate modeling of a sparingly soluble gas in a liquid is typically only achieved if experimental values are available to specify binary interaction coefficients at the low concentrations of the gas. As seen by Table 3 (Walas), the solubility of a gas can vary considerably depending upon the liquid. Furthermore, when comparing estimates of the SRK EOS to the Wilson equation, the estimated solubility can easily vary by greater than an order of magnitude. This second type of gas-liquid solubility problem requires further discussion to develop successful strategies.

Table 3. Examples of the solubility of gases in liquids. Values are in mole percent. Data is summarized from work of Walas.

Liquid	Nitrogen Solubility
Water	0.001%
n-Hexane	0.140%
n-Octane	0.130%
Isooctane	0.154%
Cyclohexane	0.076%
Benzene	0.045%
Toluene	0.057%
n-Perfluoroheptane	0.388%
Hexafluorobenzene	0.180%
Carbon tetrachloride	0.065%
Chlorobenzene	0.044%
Methanol	0.027%
Ethanol	0.036%
Acetone	0.054%
Dimethyl sulfoxide	0.008%

By far, the best resolution of uncertainty issues related to the solubility of gases in liquids is to do a sensitivity study. This could be a formal simulation sensitivity study or a thought process. In many instances, equipment sizes and configurations as well as bottom-line economics are substantially not impacted even if gas solubility in a liquid is varied by two orders of magnitude. In such instances, even if the thermodynamic model is off by a factor of 10, the soundness of the

design is not impacted. When the gas solubility does impact equipment design or economics data should be pursued. Walas does provide a listing of many gas solubilities that can be converted to Henry constants or solubility parameters for extrapolation to a range of conditions. In the rare instance involving a gas not covered by Walas or other publications, it may be warranted a) to purchase experimental time to acquire data or b) to design for an estimate of the worst case.

Prioritizing The Need to Improve Thermodynamic Model Accuracy

After a base case simulation is complete, the subject of thermodynamic model selection should be revisited in addition to a host of other process specifications designed to optimize the overall process. Changes in thermodynamic model selection will generally have a greater impact on simulation accuracy than they will on process economics.

The following additional heuristics will provide guidance as to the priority that should be placed on improving the thermodynamic model accuracy:

8. Use the activity coefficient as a guide to determine the impact of the thermodynamic model on simulation accuracy. If the infinite dilution activity coefficients are all less than 1.3 and no azeotropes are encountered, it is likely that any of a number of thermodynamic models will model the system with reasonable accuracy. Use a composition of 0.1% to determine infinite dilution activity coefficients if values are not available as extrapolated to zero composition. If an EOS is used to model liquid phases, convert the partial molar fugacity coefficients to activity coefficients to apply this approach.
9. If the infinite dilution activity coefficients are greater than 1.3, literature research or experimental investigation may be necessary to get improved data. The following should be considered: a) if the simulation package has binary interaction coefficients in its database these interaction coefficients may be suitable (check out any references for the binary interaction coefficients that may be available with the simulator to see if the conditions used to estimate the coefficients are similar to the conditions in the simulation) and b) conduct a sensitivity analysis using the simulator to determine how sensitive the actual design and economics are to the binary interaction coefficients and respective activity coefficients. Options a and b can be used to present a case for not expending time performing a literature search or money obtaining experimental data.

Heuristic 8 is based on the fact that solution models are more accurately described not as models for estimating activity coefficients, but rather, as models for estimating how activity coefficients deviate from the ideal case of the activity coefficient being equal to 1.0. And so, if a solution model estimates an activity coefficient of 1.1 it is more accurately described as estimating an activity coefficient variation of +0.1 from the ideal case of 1.0.

Consider the case of 0.1 mole fraction of water in two unspecified organics at a temperature of 100 C ($P_{sat} = 1$ bar). In one case, the activity coefficient is 1.1 while in the other case the activity coefficient is 2.0. If in each case, the correction estimated by the activity coefficient has an error of 50%. This translates to the actual partial pressures potentially ranging from 0.105 to 0.115 bar for the first case and 0.15 to 0.25 bar for the second case. The implications of a 0.01 bar uncertainty in the partial pressure are far less than the uncertainty of 0.1 bar in partial pressure. Hence, the simple but effective heuristic 8 provides a useful guide as to the need to expend additional time in defining thermodynamic models. The value of 1.3 as a decision point is justified; however, the range of values from about 1.2 to 2.0 could be considered a transitory range where values less than 1.2 would have very little error while values greater than 2.0 could easily have considerable error.

When a system exhibits LLE, infinite dilution activity coefficients are typically >7.0 . In such instances even small errors in the activity coefficients may lead to inaccurate prediction of the existence of LLE or the compositions of the LLE. For these applications, a sensitivity analysis can provide insight into how a typical solution model inaccuracy would impact process designs.

Conclusions

Thermodynamic modeling including the selection of the best models for use with process simulation is a recognized topic in chemical engineering that is held in the same regard as process simulation. However, richness and complexity of the phase equilibrium topic should not prevent engineers from using heuristics as a starting point for tapping into the ability of powerful simulation packages.