UNCOVERING THE REALITIES OF SIMULATION

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Part I of this series
(May, pp. 42–52) raised the point
that even using the best hardware
and software does not necessarily
generate the proper results.
Here, the authors examine this
problem and provide guidelines
to overcome these problems.

At the end of Part I of this series, we presented basic thermodynamic relationships for enthalpy, entropy, and isobaric heat capacity. If we have an equation of state (EOS) and the ideal-gas heat capacities, we can calculate not only phase equilibria, but also all the needed thermodynamic properties for a comprehensive model of an entire flowsheet. However, we do not solve all problems using these equations. The reason is partly historical, and partly need. Look at the basics first. Cubic EOS based on the van der Waals EOS were initially too simple to provide results sufficiently accurate for engineering calculations. Van der Waals theory basically states that all fluids at the same reduced coordinates have the same physical properties. Usually, the reducing parameters for the van der Waals EOS are the critical temperature and pressure, and, therefore, the original van der Waals EOS is a two-parameter corresponding states model.

Redlich and Kwong *(1)* made some progress on the issue, with a carefully crafted cubic EOS to provide better physical properties than the original van der Waals formulation, still using two parameters, critical temperature and pressure. Still, it was not enough for engineering calculations, as shown in Figure 1.

[References for Part II are found at the authors' Web site: www.virtualmaterials.com/cep2001.html. — Ed.]

Later, Wilson *(2)* made a simple modification of the attractive term of the van der Waals EOS, using it to predict the physical properties of gases such as ammonia. Unfortunately, Wilson's approach did not give accurate vapor pressures around the normal boiling point and so was not popular. Nevertheless, Wilson's suggestion about using the acentric factor as a third parameter for an EOS did not go unnoticed.

In 1972, Soave *(3)* created a clever parameterization using the acentric factor as a third parameter for cubic EOS that was accurate enough for general natural pro-

cessing calculations. It was quickly extended to refinery applications, and soon a model, which was accurate enough for significant process modeling, appeared. Soave's model was also simple enough to be useful with very few physical properties as input (basically, the critical pressure, temperature, and vapor pressure at 0.7 reduced temperature or the acentric factor). Other EOS quickly followed, such as the Peng-Robinson. Some enhancements were tried via additional correlating parameters, like dipole moments and radius of gyration (thus, creating four-parameter EOS), but only offered minor enhancements when compared with simpler EOS, while requiring more data.

The relative paucity of required experimental information by cubic EOS, combined with the ease of solution and the ability of estimating enthalpies and entropies in the shape cast by Soave intersected in an interesting way with the birth of microcomputers and the desire to do process simulation calculations inexpensively. With the introduction of Russell's inside-out method for distillation calculations *(4),* microcomputers of the mid-1980s were powerful enough to calculate flowsheets for the oil refining industry, including crude towers. This resulted in a revolution in process calculation, as discussed by Svrcek *et al. (5).* Table 1 shows the lineage of commonly used cubic EOS.

Table 1 does not even begin to cover the variety one finds in the literature related to cubic EOS. Copious references abound elsewhere *(6, 7, 8).* At any rate, it seems as if we could have accomplished almost everything without going through the tortuous path of activity coefficients and standard states.

Unfortunately this is not quite the end. We changed the shape of the problem by using thermodynamic relationships, but the nature of the problem remains the same. If we recall Eq. 7, we notice that the main temperature dependen-

cy on the phase equilibrium problem is the vapor pressure. Somehow, it seems, that by using an EOS, we have avoided this issue all together. That is, of course, not the case.

Successful EOS such as Soave's can be thought of as generalized vapor-pressure equations, which are, in turn, functions of the pure-component critical pressure, temperature, and acentric factor. This is easily seen if you look at Eq. 1 applied to a pure component. For a given temperature, the equality of fugacities in vapor and liquid phases determines the system saturation pressure — *i.e.,* the vapor pressure.

But nature does not conform to a simple three-parameter corresponding states correlation. What happens when we try to calculate the boiling point of something more difficult, but rather fundamental, such as water? Using published critical constants for water, you will notice that a two-parameter cubic EOS predicts a normal boiling point of about 82°C, while a three-parameter cubic EOS predicts one of about 102°C. Since steam is a rather basic substance, this inaccuracy is unacceptable. A possible solution may be to find a more-sophisticated EOS. But a more-sophisticated EOS still does not usually give us better answers, unless it is much more-sophisticated such as the fundamental EOS for steam *(9)* and a few other pure substances' EOS *(10)* that also require much more data.

So what do we do? The short answer is we cheat. Instead of looking for a more fundamental theory, we nudge the equation to give the right results by calculating what the attractive term of the equation should be for each saturation temperature corresponding to a temperature and then we fit this using a convenient function of reduced temperature.

This is not necessarily elegant, but does the job. For example, Figure 2 shows the correlated water vapor pressure using a modified Peng-Robinson EOS *(11)* with an empirically fitted attractive term vs. experimental data *(12).* The modified PR does a good job at calculating the vapor pressure of water. The price we pay is three empirical constants for water *(13).*

If you use a simulator and get the correct boiling point of water via a simple cubic EOS, then something similar to the above is taking place. With some experimentation, you will find out that an interaction parameter equal to 0.5 *(14)* between water and hydrocarbon
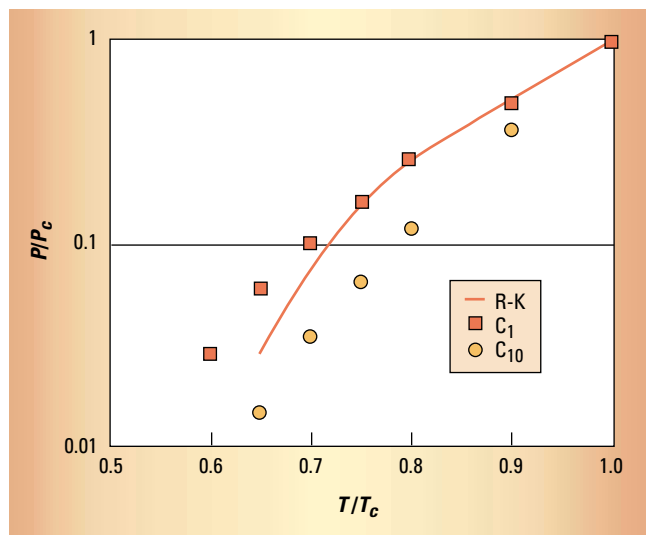

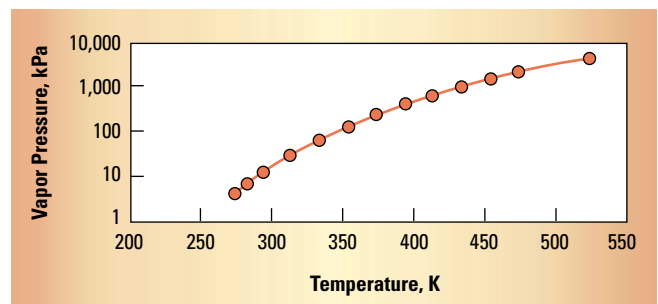■ Figure 1. Redlich-Kwong reduced vapor pressure vs. data for C_1 and C_{10}.

■ Figure 2. Water vapor pressure calculated via a modified Peng-Robinson EOS.

Table 1. Common cubic equations of state.				
Equation of State	**Repulsive part**	**Attractive Part**	**Engineering**	**Mixing Rules**
Van der Waals	$\dfrac{RT}{V-b}$	$-\dfrac{a}{V^2}$	A scientist's scientist EOS. Physics are simple, but we sick to the assumptions and consequences.	$b = \Sigma x_i b_i$
Redlich-Kwong	$\dfrac{RT}{V-b}$	$-\dfrac{a}{V(V+b)\sqrt{T}}$	Inspired but empirical modification. "a" term dependent on T.	$a = \Sigma\Sigma \sqrt{a_i a_j} x_i x_j$
Soave-Redlich-Kwong	$\dfrac{RT}{V-b}$	$-\dfrac{a(T)}{V(V+b)}$	Clever parameterization using $A = f(T, \omega)$; k_{ij} can be generalized HC*/HC pairs, water/HC, light gases and HC. Ch.e..at necessary for polar substances.	$b = \Sigma x_i b_i$ $a = \Sigma\Sigma \left(1-k_{ij}\right)\sqrt{a_i a_j} x_i x_j$
"Chemical" SRK	$\dfrac{RT}{V-b}$	$-\dfrac{a(T)}{V(V+b)}$	Sledgehammer parameterization using $a = f\left(T_r, \vec{c}\right)$ where the last term is a vector of parameters going (usually) from 1–5, unique for each substance. Flexible mixing rule based on activity coefficient models.	$b = \Sigma x_i b_i$ $a = b\left[\Sigma x_i \left(\dfrac{a_i}{b_i}\right) + \dfrac{G^E}{\sigma}\right]$

* HC = Hydrocarbon.

pairs will be adequate qualitatively. This value will force a phase split of the aqueous and hydrocarbon phases, and will, generally, estimate a reasonable amount of water dissolved in the hydrocarbon phase (the amount of hydrocarbon in the water phase is much less reasonable and caution should be used if you are using such model for an environmental study; refinements should be considered (15)).

Since the saturation pressure of nearly immiscible systems such as water/hydrocarbon is close to the sum of the water and hydrocarbon vapor pressures, simple cubics can be used for many natural gas and refinery problems (if you cheat and calculate good vapor pressures for water — a normal boiling point of ~102°C as predicted without a little nudge is of little practical interest).

Thus, if one can calculate the vapor pressure accurately for polar and nonpolar compounds, we can hope of calculating complex VLE if we have a sufficiently flexible mixing rule for the EOS. There are dozens of mixing rules (16); we are not going to discuss their merits here. Suffice to say that Gibbs-based mixing rules such as Huron-Vidal, used in Table 1 are successful at representing complex VLE, including for systems that one would not hesitate in using an activity coefficient model. So, finally, did we really get something significantly different by going towards the EOS route instead of the activity coefficient route?

What is really certain? EOS are compact models that can predict thermal properties without any supplementary data (except, of course, ideal heat capacities). They are consistent in that they provide a smooth transition between the liquid and vapor phases, allowing the modeling of processes near the critical point.

These are undeniable advantages. Nevertheless, some thought shows that the models are not that different when you look at phase equilibrium alone in terms of the necessary data for actual calculations.

Consider Table 2, and you will see that things are not that different. Note that we are assuming the pressure is sufficiently low to discard nonideality effects related to the gas-phase fugacity coefficient (if not, we would have to assume a model for the vapor phase).

The table is very general, and with exceptions it can always be found where these general observations will fail. Nevertheless, there is a trend. As the problems to solve become more involved, our models, either activity coefficient or EOS based, tend to be more complex, requiring more physical properties (either pure component or mixture) and are less predictive in nature.

This is the essence of where we are when using any of the common thermodynamic models in process simula-

tors. No matter how they are sold to you, in general, they are based on relatively simple theories that have to be tweaked to work under industrial situations. These tweaks are implementation-dependent and sometimes poorly documented. Predictions depend upon the model chosen, and their applicability is system-dependent. Generally, the more polar the system, the more experimental data will be needed for a reliable prediction, and these will be of less value.

A, perhaps, not immediately evident weakness of more-complex cubic EOS lies in their very strength. Because they are intrinsically consistent models, their predictions of varied sets of properties are intimately connected with the fundamental laws of thermodynamics. This is good in general, but it can hinder the model in such a way that it is not useful. For example, excess enthalpies will be automatically predicted when you use an EOS. These enthalpies will be found as a byproduct of the VLE modeling done to determine the parameters. In turn, these values may or may not be accurate. Traditional activity coefficient models (such as NRTL) have limitations on the magnitude of the excess enthalpies they can predict *(17)*. How these models behave inside cubic EOS for the calculation of derived properties is not well known, and is disappointing sometimes *(18, 19)*. So, if you are modeling a system with significant excess enthalpies using a Gibbs free-energy-based EOS and you have a good VLE fit, this does not automatically ensure you a good overall model (from an energy balance point of view).

Tips for simulations

Now we can suggest some pointers for real-life simulations. Before we proceed though, note that chemical engineering thermodynamics is a field under develop-

ment, and more sophisticated models other than the ones we mentioned are available. For example, significant advances in statistical mechanics-based EOS such as SAFT *(20, 21)* allow the creation of EOS with more physical flavor. Nevertheless, these more complex models are still not based (at least not entirely) on a fundamental physical theory, and some educated use of experimental information is needed. Thus, a healthy skepticism is useful when weighing the real and perceived value gained by using a more intricate model.

Likely, as more powerful computers are available on the desktop, "quantum process simulators" will be possible, in which calculations based on detailed quantum mechanical descriptions of molecules will be performed and physical properties will be calculated using this virtual laboratory. There is a good indication that this will be possible in the not-distant future *(22, 23),* and certainly some calculations, such as phase envelopes for some classes of mixtures and ideal gas properties, are already in the realm of feasibility.

Since we have to wait until the future catches up with our needs, what can we recommend? First of all, there is no panacea. Since the basic thermodynamics and basic thermodynamic models used by all simulators are well known, we can offer some guidance based on those. However, since we do not have a true fundamental theory guiding exactly how the models should be implemented, the results will depend on the brand of simulator you are using and its vintage.

Therefore, ensure that you read the section of your simulator's manual that describes the thermodynamic models used. Some simulation companies can provide you with validation material, which may help you to establish boundary conditions for the applicability of programmed models. This information is invaluable if you

Table 2. Equivalencies between simple EOS and activity-coefficient-based models.			
Problem Type	**EOS**	**Similar Activity Coefficient**	**Physical Properties**
Petroleum refinery	SRK, PR Special handling for water.	Generalized vapor pressure equation (*e.g.,* Lee-Kesler). Ideal solution or regular solution.	Critical pressure, critical temperature, and acentric factor. Special parameters for water (pure-component and mixture).
Petrochemicals	SRK, PR Special handling for water and other polar compounds.	Generalized vapor pressure (*e.g.,* Lee-Kesler) regular solution, one-parameter activity-coefficient models.	Critical pressure, critical temperature, acentric factor. Special parameters for water (pure-component and mixtures).
Chemicals	Modifications of SRK and PR as suggested by the "chemical"-SRK.	Antoine equations plus 2–3 parameter activity-coefficient models.	Empirical attractive-term equation plus 2–3 parameter Gibbs excess (activity-coefficient) model.

consider moving your simulated design from the state of fiction to fact. Assuming that you have read the manual and have a clear idea of the model and how it was implemented, we should go over some specifics.

1. Vapor pressure is king

Unless you are modeling a system you know is grossly superheated or subcooled, accurate vapor pressures are fundamental. Regardless of the sophistication of your thermodynamic model and the number of parameters in the mixing rule, you are in trouble if the vapor pressures are inaccurate. If you are not convinced, see Figure 3. No matter how many parameters your mixture model may have, the end points will always be calculated incorrectly.

2. Simple EOS do not use the Antoine equation

One of the most amusing tales (depending on the side you are on, of course) is how well the Antoine equation predicts the behavior of a given component, and how badly the prediction by the simulator compares when someone is using a simple EOS such as SRK or PR. These EOS predict the vapor pressure using critical temperatures and pressures, and acentric factors, and their predictions are independent of the equation used to fit the vapor pressure, such as the Antoine equation. This seems trivial, but we have seen this happen. Occasionally, one can adjust the acentric factor to create better vapor pressure predictions for the temperature range of interest.

This is risky. An EOS gives a compact way of calculating many properties. But, tinkering with the acentric factor to get better vapor pressures may create unreasonable densities, enthalpies, or heat capacities.

3. More complex EOS may or may not use empirical vapor pressure data

Remember our "sledgehammer" based EOS? It corresponds closely to having an empirical equation (such as the Antoine) for fitting vapor pressures using an EOS. Make sure you understand how your simulator calculates those constants. If they come from a database, they may not change if you determine better Antoine constants from more relevant vapor pressure data for your process conditions. Check the accuracy of the vapor pressure prediction to ensure the empirical parameters used by the EOS can reproduce vapor pressures with sufficient accuracy.

4. Do not get careless because the problem is simple

Almost ideal separations such as ethyl benzene/styrene separations and isomer separations are apparently simple systems to model. The activity coefficients are small and, many times, an ideal liquid solution will suffice. Pressures for separation are usually modest (for ethyl benzene/styrene, there is a relatively high vacuum) thus, gas-phase nonidealities play a minor role and can usually be neglected. Therefore, the key to the proper modeling of this kind of system is the accuracy of pure component vapor pressures as shown by Sadeq *et al. (24)*.

For example, small inaccuracies in vapor pressures for isomer separation may create problems ranging from gross
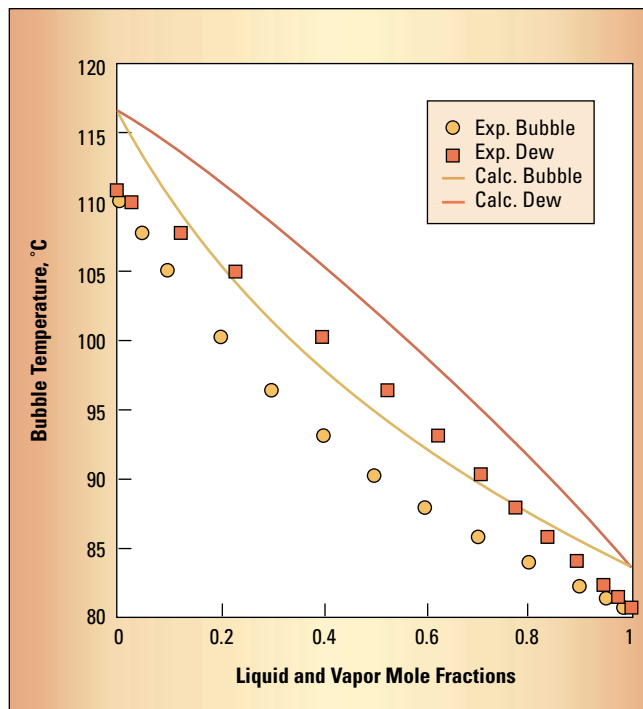

Figure 3. VLE with incorrect vapor pressures — bubble and dew point curves.

errors in the number of theoretical stages to the prediction of nonexisting azeotropes caused by crossing vapor pressure curves. Superfractionation operations are prone to this kind of error as shown by Haines *(25)*. To illustrate this, write Fenske's equation:

$$N_m = \frac{\log\left[\left(\dfrac{x_{LK,D}}{x_{LK,B}}\right)\left(\dfrac{x_{HK,B}}{x_{HK,D}}\right)\right]}{\log \alpha_{LK}} \tag{1}$$

Since in dealing with superfractionators, the relative volatilities are rather small, let us do a simple experiment. Imagine that the correct relative volatility is 1.1, and the model has a 10% error, thus predicting a relative volatility of 1.21. This means that, for a given set of bottoms and top heavy and light key specifications, our minimum number of trays will be incorrect by a factor of two!

You can think from a simulation point of view, in which the number of trays is fixed. In that case, your specifications will be tied by Eq. 2, rewritten in a slightly different form:

$$\left(\alpha_{LK}\right)^{Sm} = \left(\frac{x_{LK,D}}{x_{LK,B}}\right)\left(\frac{x_{HK,B}}{x_{HK,D}}\right) \tag{2}$$

Thus, the inaccuracy in the model is raised to the minimum number of trays. When looking at systems that may have well over 100 trays, there may be a very significant

error indeed.

5. Use simple models to your advantage

Depending upon your modeling challenge, you can take advantage of the simple models in simulators and play with them like clay. Say you need to model a triple-effect evaporator to concentrate caustic soda. One way to do this is by using an electrolyte model. A simpler way would be to make a component behave like caustic, at least within some concentration ranges. We want a component that has virtually no vapor pressure, but, at the same time, would participate in the VLE, thus changing the solution's boiling point. This is easy when using a simple activity coefficient model. Start by setting all of the Antoine constants equal to zero, except A, which we will make a negative value such as –20. This will give us a component with very small vapor pressure and will behave, for all practical purposes, as a solid. Then, we collect some boiling elevation data. Finally, we fit the interaction parameters for any activity coefficient model (models such as Margules, van Laar, and NRTL are simpler, because they do not need any pure-component molecular parameters such as molar volumes or van der Waals areas or volumes).

Provided that you keep your perspective (*e.g,* trying to calculate the boiling point of pure caustic using this approach will evidently not work), a simple model like this can give a reasonably good result quickly.

A related example: Assume you need to model the crystallization of an organic salt from an aqueous mixture. Start by characterizing the solid as above. Here, we want to model the formation of a solid phase and a saturated mother liquor. Assume that your simulator has a good, reliable three-phase flash. So, albeit physically incorrect, for mass and energy balance purposes, we can model the crystallizer as a flash vessel and a heat exchanger (the heat exchanger is needed to account for the heat effects related to crystal formation), where the crystal is modeled as a second, liquid phase.

All we need to do now is to determine the interaction parameters for an activity coefficient model that will predict two liquid phases, one with the proper concentration of salt in the mother liquor, the other with a small amount of liquid to model the solid phase. With a bit of finesse, even multicomponent crystallization can be modeled this way with only simple solubility curves easily found in the lab.

Finally, let us say you need to model a polymer/solvent mixture. This can be challenging to solve rigorously. But, if a preliminary mass balance is desired, we can quickly create a simple model that will provide a reasonable prediction for the effect of the polymer on the activity of solvent. Use an EOS such as the SRK. Start by estimating thecritical properties, which would be close to a polymer. In general, the critical properties of polyethylene as predicted by Tsonopolous (*AIChE J.,* **33**, 12, pp. 2080–2083, Dec. 1987) work quite well, and

can be used as a template for defining a "polymer" component. Afterwards, we get the vapor pressure of a mixture of solvent and polymer and determine the interaction parameter between them. Simple, but within limits, this can prove to be rather effective.

Extrapolation and documentation

The problem with these simple models is not so much the applicability to your current conditions, but, rather, how well they will extrapolate. That is where care and attention are needed. This brings us to the not so pleasant, but permanent, need to document the simulation work. Simulation models tend to live longer than their creators ever imagined, and information about assumptions, data used, and estimated limits of applicability will be invaluable for those coming after you.

We have identified vapor pressure as a fundamental property, to which we should give much attention before embarking into a simulation. In our previous discussion on EOS and activity coefficient models, we had two kinds of problems.

If we have a generalized EOS such as the Soave or Peng-Robinson, the quality of vapor pressure predictions will be a function of the quality of the critical temperature, pressure, and acentric factor. The quality will also depend upon whether the component in question conforms to a corresponding states theory based on three parameters (there is little you can do about this other than to "sledgehammer" the needed behavior into the theory by having empirical parameters such as the Mathias-Copeman constants).

If we have an activity coefficient-based model, we will need an empirical correlation for vapor pressures. This will usually be based on a data fit using an Antoine-type equation or on an estimate using a correlation, again based on a corresponding states theory, such as Lee and Kesler's equation — in which case, you have the same problem as when using a simple EOS for vapor pressure estimation.

Now, we appear to be considering rather simple properties. We should have determined them with a rather high degree of confidence. After all, critical properties have been known since Andrews' time *(c. 1869, 26, 27)* and, therefore, we should have them all. One of the best available pure-component databases off the shelf is that published by the AIChE's Design Institute for Physical Properties (DIPPR) *(28)*. This database has endured the test of time and usefulness, being continuously updated, revised, and expanded — and an industrial consortium actively supports it. Nevertheless, it contains many estimated properties for rather simple components. Actually, one of DIPPR's greatest contributions is the estimation and recommendation of physical properties based on open literature and specially created estimation methods.

How come we do not know everything? Some problems are technical. For example, heavy hydrocarbons thermally crack when we approach their critical points and, therefore, a direct measurement is difficult or sometimes impossible.

Some systems are dangerous to work with. But, it seems that the largest problem is focus. Well-conducted experiments are difficult and expensive. Unfortunately, we are seeing less work on experimental measurements of physical properties. It is our hope that this trend will stop, and vigorous research programs will be restarted in North America and elsewhere. It is easy to do theoretical work and check it against literature data, but it is also easy to start a cycle of inbreeding with this easier path, and the actual merit of what is published slowly (but certainly) decreases. New experimental results push theories and, in turn, allow us to craft better theories. Better theories lead to better plant designs.

Enough of philosophy. Our job is to get a robust model, and we were looking at vapor pressures. A problem that you should be aware of with many of the generalized vapor pressure equations is that they were developed using data from the normal boiling point up to the critical point. Therefore, they extrapolate poorly under vacuum and, if you are doing a vacuum separation design, the predicted relative volatilities may not be accurate. For some specific systems, such as the ones usually found in refining, special correlations for heavy hydrocarbon vapor pressures are available (29).

Also, you may be faced with modeling the separation of heavy organic compounds for which apparently no vapor pressure information exists. Since one of the thermodynamicist's jobs is to develop something from apparently nothing, one should consider a simple approach and verify what is already published. For many compounds, the "CRC Handbook" (30) tabulates the vapor pressure of an organic compound not at its boiling point, but at vacuum. Thus, how can we extend this information and get a vapor pressure equation that we can use? Pailhes (31) published a useful method based on group contributions, which can extend vapor pressure data from a single point to a complete, two-parameter Antoine equation. For heavy hydrocarbon processing, some recent work by Soave (32) is of interest, as well as an earlier paper by Twu et al. (33).

The less attractive area — densities, enthalpies, entropies, and others

Physical properties also may be fundamental for the success of your simulation. Some information on the performance of some commonly used EOS for the prediction of densities can be found in the works of de Hemptinne and Ungerer (34), Ungerer and Batut (35), Mathias et al. (36), Monnery et al. (37), and de Sant'Ana et al. (38). These should be consulted to develop a feeling for the accuracy of the models when predicting volumetric properties. For aqueous systems, significant volumetric changes may occur upon mixing, which are not well represented by standard EOS or corresponding states-based models.

Enthalpies are key for the construction of energy balances and, unfortunately, not much is available in the open literature on comprehensive evaluations on the perfor-

mance of EOS when estimating enthalpies, entropies, and heat capacities. Useful resources are the works by Starling et al. (39), Daubert (40, 41, 42), Trebble and Bishnoi (43, 44, 45), Satyro (46), and Barreau et al. (47).

You may need to calculate accurate excess enthalpies, which may call for an empirical expression for calculating liquid heat capacities, plus one for excess enthalpies and heat capacities. For example, depending on the concentration, the excess heat capacity for ethanol/water mixtures can be up to 10% of the value of the ideal mixing heat capacity (48). Ignoring this will render the enthalpy balance inherently inaccurate, even for simple liquid/liquid heat exchangers under modest temperatures and pressures.

Accuracy vs. precision

One of the most heartbreaking experiences for a thermodynamicist is to watch someone spending a large effort refining a model with far more precision than the basic data allows. Of more concern is that people feel obliged to do significant work on the results that use the thermodynamic model, such as optimizing a process based on heat exchangers' small-temperature approaches, when the enthalpy model is only good to within ±15%.

For some reason, error analysis seems to be a lost art, and novice users of process simulation tools seem to forget that, although their simulator may display temperatures to four decimal places, only rarely will more than one actually make any sense. For some whimsical reason, it seems that the computer replaces the lab such that it provides results with quasi-infinite accuracy.

It is beyond the objective of this article to talk about error analysis and error propagation extensively, since excellent references are available (49, 50, 51), but we will touch on at least two important definitions. We hope that this will make you a healthy skeptic when looking at simulation results, as well as fixing simulation parameters for case studies and optimization.

Let us do a simple thought experiment. Imagine that we have NASA working for us (it's a thought experiment, right?) and the agency produces ten blocks ranging from one to ten centimeters in height. The blocks have their heights measured with such precision and accuracy that, for all practical purposes, they are exact. Only I know this. I have also asked NASA to build a very accurate laser interferometer to measure heights with variable accuracy (*i.e.,* I can set the smallest scale to be millimeters, centimeters, etc.) and adjustable bias (*i.e.,* I can play a dirty trick without the user's knowing and make this measured value be larger by *x* units of measurement).

Give the blocks and the instrument to Person A with the instrument set to give smallest unit of measurement as 0.5 cm and no bias. Now, for Person B, set the smallest unit of measurement to 0.1 cm and a bias of 0.5 cm (assume that Persons A and B are unable to suspect significant measurement errors). If this seems too hypothetical, consider the

relationship between the density of MTBE and methanol at 25°C from the top of your head. Replace our NASA laser rulers by densitometers, and you will perceive that things are not so far fetched. Now look at the heights of the blocks measured by A and B, with the error bars.

A's results are not very precise (they are within 0.025 cm), but they are accurate in the sense that, outside the inaccuracy of our measuring device, there are no other errors. B's results are precise (they are within 0.005 cm), but they are inaccurate with a bias of 0.5 cm. B's scenario is exactly that of a user of a process simulator. Barring any programming errors, the results are precise, basically limited by the computer's numerical word length and tolerance in convergence methods, but are not necessarily accurate.

This is easy to understand, because we do not know how good the models and parameters are in the models extrapolated from the regions where they were found (they are based in semitheoretical models at best), we do not know how the models were implemented, we do not know the inaccuracies of the estimation methods used to fill in missing properties, and, finally, we do not know how the errors propagate from one part of the model to another.

Therefore, a fundamental skill one has to gain when using simulators is to gauge how accurate are the results being generated by the machine, and exercise a healthy skepticism that balances the claims of software accuracy against the reality of the basis of the models. How does one go about learning this skill? Again, there is no fast and hard answer, but it is a must to do spot checks on basic properties that may be important for the use of your model:

1. We repeat here — for most chemical process simulations, vapor pressure is king. Make sure it is as good as needed for the desired accuracy of your model and that you understand what has been estimated by the simulator and how.

2. Check your pure-component and mixture densities. Do you have aqueous mixtures? Excess volumes will be present. Are they important? It depends on what you are doing, as you will recall from the ethanol volume-fraction example.

3. Check your pure-component and mixture enthalpies and heat capacities if you are going to do any calculations related to energy balances. Thinking about having a pinch point approach of 0.3°C in your superduper optimized flowsheet? If you are using a generic EOS, your enthalpies are within 15%, so think about this before asking lots of bucks for your proposed modifications.

4. Are you going to design heat exchangers? It is a good idea to check your transport properties. There is much less work on those properties than on VLE, so make sure to cover your bases.

5. Are you designing trays? Pressure drop is important and surface tension plays a key role in pressure drop calculations. Surface tension is another property for which much less work is available than for VLE, so when designing a

vacuum system, be careful.

6. Do you have azeotropes? Do you suspect they may exist? Check them out before proposing a modification that will violate the second law of thermodynamics *(52, 53)*.

7. Trace components should not be brushed aside. Nonidealities are extreme at low concentrations, and components behave in apparently unexpected ways (methanol in depropanizers, water in demethanizers, as examples).

8. Talk to people. Modeling in general and thermodynamics in particular are intellectual exercises, which develop better if discussed. Likely, there are people in your company who can help you gather ideas that will help you to create a better model.

9. If you are going to design a new process, try to interact with chemists as much as possible. When chemists and chemical engineers work together in the early phases of project, a positive synergy may happen. An optimum amount of knowledge can be gathered in a short time, building on the strengths of both disciplines.

10. Talk to the process simulation vendor and inquire about available background information that may be useful for establishing reliability criteria for important parts of your process.

11. Beware of using estimated parameters and interaction parameters when screening process alternatives. You may spend considerable time refining a proposal that is thermodynamically infeasible, or screen out a solution that is valid. If a solution looks promising, but the supporting thermodynamic background is questionable, get some experimental data if the economic importance of the new or modified process warrants the interest.

12. Simulation is a means, not an end, no matter how much effort you put into the model. Once, after finishing a large simulation model with several hundreds of unit operations, one of us had to spend many hours fixing the model, because air leakage into the equipment was not taken into account (the process had many pieces of equipment under vacuum). The model was good from a thermodynamic point of view, but, without the leaks, it was not the process we were interested in.

13. Go see the plant, touch the hardware, get a feeling for what is hot, what is cold, etc. Plant personnel are usually helpful, and they know how things behave. Their insight and your knowledge of modeling can form a strong bond for problem solving.

A simple model well understood is more useful than a complex model poorly understood. It is that simple. No matter what the theoretical sophistication and marketing hype, if you do not understand the basics of your model, you are subject to belief, not science.

Useful references

Useful reviews on physical property needs for industrial applications can be found in Cox *(54)* and Liles *(55)*. Economic impact studies relating physical properties to plant

Simulating Reality

performance can be found in Elliot *et al. (56),* Zudkevich *(57),* and Murthy and Zudkevitch *(58).* One of the few studies that actually names process simulators and their relative performance for VLE calculations is by Benso and Bertucco *(59).* Dewan and Moore *(60)* present an exhaustive review of physical-property-data resources that can save you quite a bit of legwork. Mathias *et al. (61)* offer a comprehensive review of EOS calculations inside process simulators. Mathias and Klotz *(62)* give a good review of thermodynamic models and should be read in conjunction with this article. Useful pointers can be found in Carlson's paper *(63).*

Finally, we strongly recommend Soave's article *(64)* as an example of how to approach physical property modeling in general. His clear exposition on how one can transform a simple EOS by adding fixes here and there until an industrial grade EOS is produced is insightful and a pleasure to read.

The Feynman effect

So, we come to the end of this series. Perhaps, it is a bit disappointing that we did not write a completely exhaustive list of tests and check points, and reduced the subject to a recipe. In honesty, no matter how complete a list we would write, we can guarantee that we could break it.

Chemical engineering thermodynamics is not a set of simple rules and recipes, but rather, an intellectual framework for reasoning. No matter how well packaged and sold, the use of thermodynamics for making decisions about chemical processes is an intellectual exercise that carries all the thinking burdens and pleasures of a well-played chess game. The beauty of the usual models we have to play with when modeling processes is that they are simple enough for any determined chemical engineer to understand, they are semitheoretical to the point that they carry some physical flavor, and, by looking at their physical basis, they can be modified and extended to model more processes than their original creators dreamed about.

It may seem we are suggesting that process simulators are not reliable. Not at all — process simulation companies have transformed simulators from expert tools to desktop appliances used by virtually all chemical engineers. What we suggest is that the problems simulators address are too complex and interrelated to be thought of as completely solved and closed issues. Far from it, the problems are usually open, and there is always room for improving the results one would get from the original package, because you will know the problem at hand much better than the software developers, and you will be able to get better, more reliable results if you take the time to learn a bit of science and use it.

We leave you with a few words from physicist Richard Feynman *(65)* that describe his involvement in the investigation of the Challenger disaster. Feynman was a very dear figure to us who represented the best in honesty and integrity related to science. His down-to-earth way of looking at the world to solve complex problems and no-holds-barred attitude towards established "reality" is a continuous source of inspiration to us on how to solve real problems. If you replace some of the words below by "dew points" or "effluent composition" you will see how much power — and responsibility — are riding on your hands.

"There was no way, without full understanding, that one could have confidence that conditions the next time might not produce erosion three times more severe than the time before. Nevertheless, officials fooled themselves into thinking they had such understanding and confidence, in spite of the peculiar variations from case to case. A mathematical model was made to calculate erosion. This was a model based not on physical understanding but on empirical curve fitting. Specifically, it was supposed that a stream of hot gas impinged on the O-ring material, and the heat was determined at the point of stagnation (so far with reasonable physical, thermodynamic laws). But, to determine how much rubber eroded, it was assumed that the erosion varied as the 0.58 power of heat, with the 0.58 being determined by the nearest fit. At any rate, adjusting some other numbers, it was determined that the model agreed with the erosion (to a depth of one-third the radius of the ring). There is nothing so wrong with this analysis as believing the answer! Uncertainties appear everywhere in the model. How strong the gas stream might be was unpredictable; it depended on holes formed in the putty. Blowby showed that the ring might fail, even though it was only partially eroded. The empirical formula was known to be uncertain, for the curve did not go directly through the very data points by which it was determined. There was a cloud of points, some twice above, some twice below the fitted curve, so erosions twice those predicted were reasonable from that cause alone. Similar uncertainties surrounded the other constants in the formula, et cetera, et cetera. *When using a mathematical model careful attention must be given to the uncertainties in the model.*" [Italics added by the authors.]

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