ChE classroom

ERROR BARS IN PROCESS SIMULATION

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In the first place, all men agree with the familiar maxim, "If you don't have a thing, simulate it."

Desiderius Erasmus [1]

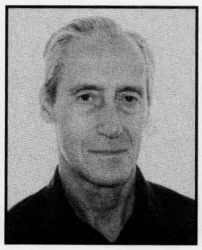
This early reference to simulation points up a certain ambiguity in our current use of the word. On one hand, a simulation (especially a computer simulation) tends to be regarded as a representation or prediction of the behavior of a real thing to a considerable degree of accuracy. On the other hand, the word can also mean *making a pretense of* —so a simulation could be a counterfeit or sham object. Error bars are usually lacking in the results of a simulation for process design, and this may fool us into believing that our simulation is of the first kind when it is actually of the second kind.

To illustrate this, consider a simple separation process based on an example in Douglas' *Conceptual Design of Chemical Processes.*[2] In this process, acetone is to be removed from an air stream (containing ~1.5 mol % acetone) by absorption at atmospheric pressure in water at 25°C. The aqueous solution is subsequently distilled to recover the acetone. Design specifications call for 99.5% of the incoming acetone to be removed in the absorber, and 99.5% of the acetone in the resulting feed to the distillation column to be recovered in the top product at a composition of 99% acetone. The entering air stream flows are 687 lb mol/hr air (G) and 10.3 mol/hr acetone.

A pencil-and-paper calculation, using the absorption factor (L/mG) as a parameter, shows that when

$$\frac{L}{mG} = 1.4$$

the required water flow (L) is 1943 lb mol/hr and, from the Kremser equation, 12.1 ideal stages are required in the absorber.[2] But a computer calculation by the Chemos modeling program (developed at the University of British Columbia) shows that the desired acetone removal cannot be obtained at the hand-calculation design point and that much higher water flows are needed. The difference is due to greatly differing values for the predicted equilibrium ratio, m, in the absorption factor, where



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$$m = \frac{y^*}{x} \approx \frac{\gamma_1 P_1^0}{P}$$

where

P	total pressure
P_1^0	vapor pressure of pure acetone at system temperature
γ_1	activity coefficient of acetone in solution

While P is specified and P_1^0 can be predicted to good accuracy, the value of γ_1 may be in some doubt.

The value used by Douglas ($\gamma_1 = 6.7$, giving $m = 2.02$) is referenced to page 14-15 of Perry's Handbook[3] where it occurs in a table used in an example calculation (Example 2), but no source is given for the table. The value used by the Chemos program came from a binary data bank containing parameters for the Wilson equation obtained from Hirata.[4] But the only entry then present in the Chemos data bank for the acetone-water system was set 504 from Hirata, which refers to equilibrium at 150°C. The default method used by the program for extrapolating to other temperatures assumes that the values of

$$(\lambda_{12} - \lambda_{11}) \quad \text{and} \quad (\lambda_{21} - \lambda_{22})$$

in Eqs. (9) and (10) are independent of temperature and gives a value for the activity coefficient of acetone at infinite dilution in water at 25°C to be

$$\gamma_1^{\infty} = 19.61$$

Alternatively, the "athermal model" could be chosen, which

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assumes that $\Delta G^E/RT$ is independent of T and gives (see Eq. 7)

$$\gamma_1^\infty(25°C) = \gamma_1^\infty(150°C) = 12.64$$

Obviously, either of these predicted values would require proportionately larger liquid flows to keep the absorption factor at a reasonable design value. Since all of this extra water has to be distilled, the size and energy requirements of the recovery column would also be greatly increased.

Extrapolation of activity coefficient values from one temperature to another always introduces extra uncertainty.[5;p.262] It can be avoided in this case since the Hirata data collection contains results at 25°C.[4: set 503] Using the values of the Wilson parameters calculated by Hirata for that data gives

$$\gamma_1^\infty = 4.69$$

which would reduce the water flow to 70% of the amount originally calculated. Gmehling's data collection[6] has this same data[7; 6, set 232] and one other at 25°C.[8; 6, set 245] Gmehling's fit of the Wilson equation to the Beare[7] data gives

$$\gamma_1^\infty = 7.00$$

and to the Taylor[8] data gives

$$\gamma_1^\infty = 6.44$$

Since data set 503 in Hirata is the same as data set 232 in Gmehling, the difference between the calculated γ_1^∞ values (4.69 versus 7.00) must either be due to different assumptions made in data reduction or be caused by different criteria for goodness of fit.

DATA REDUCTION

Each of the referenced authors assumes that all non-idealities may be described by the liquid-phase activity coefficient (γ_i) so that the phase equilibria may be represented by

$$y_i = \frac{x_i \gamma_i P_i^0}{P} \qquad (1)$$

where the mole fractions in the vapor and liquid phases (y_i and x_i) and the total pressure (P) are from the experimental data, and the pure component vapor pressure (P_1^0) is given by the Antoine equation

$$\log_{10}\left(P_i^0\right) = A - \frac{B}{(t+C)} \qquad (2)$$

The coefficients (A,B,C) used by the two authors differ slightly: Hirata, *et al.*, calculate the values of

$$P^0_{acetone} = 230.05\ \text{mm Hg} \quad \text{and} \quad P^0_{water} = 23.76\ \text{mm Hg}$$

while Gmehling, *et al.*, use

$$P^0_{acetone} = 230.91\ \text{mm Hg} \quad \text{and} \quad P^0_{water} = 23.69\ \text{mm Hg}$$

at 25°C. The effect of these differences is very slight, as can be seen in Table 1.

EXPERIMENTAL DATA FITTING

The Wilson equation for the activity coefficient of each component in a binary mixture can be written

$$\ell n\,\gamma_1 = -\ell n(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \qquad (3)$$

$$\ell n\,\gamma_2 = -\ell n(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \qquad (4)$$

A nonlinear regression method must be used to find the values of Wilson's parameters (Λ_{12},Λ_{21}) that best fit a set of experimental data. The choice of the measure of goodness of fit (objective function to be minimized) and of the regression method may affect the final values of the parameters.

Hirata, *et al.*, use a nonlinear least-squares method to minimize the function

$$F = \sum_{i=1}^{n}\left(Q_{exp} - Q_{calc}\right)^2 \qquad (5)$$

where n is the number of experimental points and

$$Q = x_1\ \ell n\,\gamma_1 + x_2\ \ell n\,\gamma_2 \qquad (6)$$

The independent variables are the values of L_{12} and L_{21}. Since the excess free energy of mixing is given by

TABLE 1
Experimental and Calculated Activity Coefficients for Acetone(1) in Acetone-Water system at 25°C

	Hirata, *et al.*		Gmehling, *et al.*	
x_1	$\gamma_{1\ exp}$	$\gamma_{1\ calc}$	$\gamma_{1\ exp}$	$\gamma_{1\ calc}$
(0)	(6.0)*	(4.686)	(6.0)*	(6.998)
0.0194	5.876	4.403	5.854	6.284
0.0287	5.774	4.274	5.753	5.978
0.0449	5.642	4.070	5.621	5.517
0.0556	5.454	3.942	5.434	5.241
0.0939	4.875	3.535	4.857	4.426
0.0951	4.870	3.523	4.852	4.404
0.1310	4.127	3.202	4.111	3.826
0.1470	3.905	3.075	3.890	3.610
0.1791	3.406	2.843	3.393	3.238
0.2654	2.554	2.348	2.545	2.518
0.3538	2.029	1.978	2.021	2.041
0.5808	1.365	1.394	1.360	1.381
0.7852	1.114	1.109	1.109	1.105

* Obtained by linear extrapolation for the first four data points.

$$\Delta G^E = RT(x_1 \ell n \gamma_1 + x_2 \ell n \gamma_2) \quad (7)$$

Hirata's solution best fits the excess free energy for an isothermal data set.

Gmehling, *et al.*, use the non-linear simplex method to minimize the function

$$F = \sum_{i=1}^{n}\left[\left(\frac{\gamma exp - \gamma calc}{\gamma exp}\right)_1^2 + \left(\frac{\gamma exp - \gamma calc}{\gamma exp}\right)_2^2\right] \quad (8)$$

and they relate the values of Λ_{12} and Λ_{21} to the interaction energy between components i and j (λ_{ij}) by the relations

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp\left[-\frac{\lambda_{12}-\lambda_{11}}{RT}\right] = \frac{V_2^L}{V_1^L}\exp\left[-\frac{A_{12}}{RT}\right] \quad (9)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L}\exp\left[-\frac{\lambda_{21}-\lambda_{22}}{RT}\right] = \frac{V_1^L}{V_2^L}\exp\left[-\frac{A_{21}}{RT}\right] \quad (10)$$

where A_{12} and A_{21} serve as the independent variables for minimization of F. The molar volume of pure liquid i is V_i^L. Gmehling, *et al.*, use the volume at 25°C for all data sets, and Chemos calculates the saturated liquid volume at system temperature and uses this to extrapolate to other temperatures, assuming that $\lambda_{ij} - \lambda_{ii}$ remains constant.

The minimization function used by Hirata, *et al.*, (Eq. 5) is recommended on thermodynamic grounds by Reid, *et al.*,[5;p.259] but it weights the error in the logarithm of the activity coefficient of a component by the mole fraction of that component. Consequently, the final values of the parameters that result from minimizing this function are less influenced by errors in the activity coefficients of components at high dilution than are the corresponding values for the minimization of the function used by Gmehling (Eq. 8). The predicted value of the activity coefficient of acetone is less than the value obtained from the Beare data set over almost all of the composition range when Hirata's values of Wilson's parameters are used (see Table 1), whereas Gmehling's values exceed the experimental ones at the lowest concentrations.

If Wilson's equation fit the data perfectly, then the two minimization functions would give the same value of γ_1^∞. The observed difference could be because the equation is inappropriate, or the data is erroneous, or both are wrong. Leaving aside the choice of equation for the moment, two tests on thermodynamic consistency of the data are reported in Gmehling. The "area" test[9] evaluates

$$\int_0^1 \ell n\left(\frac{\gamma_1}{\gamma_2}\right) dx_1$$

which should equal zero for isothermal data. The "point" test[10] calculates y_1 from experimental T, P, and x_1 for each point, and evaluates

$$\sum \frac{y_1(calc) - y_1(exp)}{n}$$

This test requires values of $\partial P / \partial x_1$ which are obtained by fitting a smooth spline curve to the P-x_1 data. The Beare data set meets the criteria set by Gmehling for the area test but fails the point test, while the Taylor data fails both tests. The experimental acetone activity coefficient has an s-shaped curve with mole fraction instead of increasing with increasing negative slope as $x_1 \to 0$, and the experimental water activity coefficient has a minimum of 0.916 at a mole fraction of acetone of 0.147 instead of increasing monotonically from 1.0 at $x_1 = 0$. These differences may be the result of systematic experimental errors. In any event, they make prediction of the activity coefficient very uncertain at low concentrations of acetone ($x_1 < 0.15$).

PREDICTED VALUES

Prediction methods based on ASOG or UNIFAC can be used for this system. The ASOG method described by Pierotti[11] is summarized in Table 8-17 of Reid, *et al.*,[4] and predicts $\gamma_1^\infty = 7.78$ at 25°C. While prediction methods cannot be better than the data they are based on, Pierotti had access to Shell Oil Company data book values that may not be generally available. Using UNIFAC by running Aspen Plus®[12] predicts values of the Wilson equation parameters that give $\gamma_1^\infty = 11.49$.

SIMULATION EXPERIMENTS

Table 2 lists values of γ_1^∞ from various sources. Any one of these values (except perhaps the two highest) might be chosen as a basis for design in the absence of other information, but the most likely values to be selected are either of the two values from data compilations 4.69[4] and 7.00[6], or the Aspen/Unifac value of 11.49.

TABLE 2
Value of γ_1^∞ for the Acetone (1)-Water System at 25°C (Various Sources)

γ_1^∞	Source
4.69	Hirata, *et al.*, 1975[4] (Beare data)
6.44	Gmehling, *et al.*, 1977[6] (Taylor data)
6.70	Perry, *et al.*, 1973[3] (Example 14-15)
6.93	Perry, *et al.*, (1984)[13] (Example 14-21)
7.00	Gmehling, *et al.*, 1977[6] (Beare data)
7.78	Reid, *et al.*, 1987[5] (Table 8-17)
8.96	Perry, *et al.*, 1963[14] (Examples 14-31,14-32)*
11.49	Aspen/Unifac, 1991
12.64	Chemos - athermal extrapolated from 150°C
19.61	Chemos - default extrapolated from 150°C

* γ-value back-calculated from value of m used in examples

Table 3 lists the results of some Aspen simulations taking the same feed-gas flows and product specifications as were used in the hand-calculation example.[2] The absorber was represented by the ABSBR block (the RADFRAC block gave almost identical results), the equation-of-state option set was SYSOP8A (Wilson/Redlich-Kwong/Henry's Law), and N_2 (used instead of air as the non-absorbed gas component) was declared an unsymmetrical (Henry's Law) component. A specification statement was used to adjust the liquid flow rate to satisfy the design requirement on the acetone leaving in the gas stream. Since the entering gas contained no water vapor, the simulation showed some evaporation of the water (~23 lb mol/hr). This evaporation required more heat than was provided by the absorption of acetone so that in all cases the water leaving the bottom of the tower was cooler than the entering liquid—by 13°F at the lowest flow rates and by 3°F at the highest.

It was not possible to obtain convergence of the simulation model at absorption factors as low as 1.4. We used all three data sources to model a six-stage absorber which gave a liquid rate ranging from 1460 lb mol/hr for the lowest activity coefficient (Beare/Hirata) to 5030 lb mol/hr for the highest (Unifac/Aspen) (see Table 3). In a second series of tests, we increased the number of stages to the maximum that could be solved (minimum liquid rate that would converge). The solutions varied from six stages at 1460 lb mol/hr liquid (Beare/Hirata data) to ten stages at 3538 lb mol/hr (Unifac/Aspen). Even this considerable range may underestimate the extent of our ignorance since other equations (Van Laar, Margules, NRTL, Uniquac) could have been fitted to the equilibrium data. Also, we made no attempt to convert ideal stages to real packing—this step is commonly regarded as being much less accurate than the prediction of equilibrium relationships.

IMPLICATIONS FOR DESIGN

The minimum solvent rate from the absorber is an important parameter for design since it sets a lower bound for the energy requirements if this stream is to be subsequently distilled. Depending on energy costs, this may enable a go/no-go decision to be made for this route early in the design process. (Douglas[2] considers a number of other process alternatives.) If the go/no-go decision turns out to be dependent on γ_1^∞, then clearly it becomes essential to get better data.

If the range of γ_1^∞ values all lead to feasible absorber-stripper designs, and the designs are optimized, there is still no escaping the necessity to circulate more water when higher values of γ_1^∞ are assumed. If the process were designed and constructed based on the Hirata databook value, and the real value turned out to be that predicted by Unifac, then the process would fail to meet the required air-pollution discharge standards. The chemical engineer who replaced the original designer might spend some time trying to improve the packing or tray efficiency, to no avail. If the apparently conservative Unifac value was used and the Hirata value was correct, the process would work—but it would be more costly than it should be. A contractor proposing this design might find his bid rejected as being non-competitive.

TABLE 3
Simulation of Absorber for Acetone Using Aspen®
• Inlet gas flow rate: N_2 = 687 lb mol/hr
• Acetone = 10.3 lb mol/hr
• Design specification: 99.5% of acetone to be absorbed
• Inlet temperature (both streams): 77°F

	Data Source	Stages	Water Flow lb mol/hr	A=L/KG (geometric mean)	K(acetone)
1.	Beare/Hirata	6	1460	2.16	1.041 - 0.782
2a.	Beare/Gmehling	6	1738	2.16	1.212 - 0.943
2b.	Beare/Gmehling	8	1360	1.72	1.208 - 0.875
3a.	Unifac/Aspen	6	5030	2.18	3.305 - 2.984
3b.	Unifac/Aspen	10	3538	1.524	3.305 - 2.858

VARIATIONS IN HISTORICAL VAPOR-LIQUID EQUILIBRIUM DATA AT 760 mmHg

If the absorbed acetone is to be recovered by distillation, equilibrium data at constant pressure (760 mmHg) are required; it is much easier to make equilibrium measurements under these conditions, and many more data sets are available. Whereas Gmehling, *et al.,* only list two data sets for acetone-water at 25°C, they report ten sets for the same system at atmospheric pressure. Table 4 lists the γ_1^∞ values (predicted from the Wilson equation parameters at 100°C) for these data sets, arranged by year of publication. For four of these sets, the γ_1^∞ values are also available from data compilations of Hirata, *et al.,*[4] and of Ohé,[15] who used the same measure of fit as Hirata. In some cases the different fitting methods have resulted in greatly different values of γ_1^∞ (34.83 compared to 11.81 for the 1952 data set, for example), even though that data satisfies both measures of thermodynamic consistency.

The more extensive data allow different activity coefficient equations to be compared. Hirata only fits the Wilson equation, but Gmehling fits each data set with five equations (Margules, Van Laar, Wilson, NRTL, and Uniquac) and compares their goodness of fit by evaluating

$$\Sigma \frac{|y_{1\,exp} - y_{1\,calc}|}{n}$$

Table 4 lists the equations that are reported to best fit the data and the corresponding γ_1^∞ predicted by that equation. No clear picture emerges, since NRTL is best for five sets,

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Margules for two, Wilson for two, and Uniquac for one. Restricting the comparison to the six sets of data that satisfy both of the thermodynamic consistency tests gives a score of three for NRTL, two for Wilson, and one for Unifac.

Based only on the "good" data, only on the Gmehling measure of fit, and only on the Wilson equation, this subset still yields values of γ_1^∞ ranging from 7.41 to 11.81. If the Hirata measure is also included, the range is from 7.41 to 34.83. For many distillation calculations the different data sets would yield similar results, but in this example, if the bottom product from the tower has to have a very low acetone concentration to meet discharge standards, or to be recycled to the absorber, then γ_1 approaches γ_1^∞ and the scatter is important.

At first sight it appears that the more recent sets of data show less variation, but note that three of these sets are smoothed data, at equal x increments. Some of these may have been obtained by interpolating smoothed bubble-point and dew-point curves, with no simultaneous measurements of x and y. Applying the point consistency test to these data may be tautologous.

TABLE 4

Value of γ_1^∞ for Acetone(1)-Water System at 760 mm Hg, 100°C from Experimental Data

Year Data Published	Wilson's Equation Fit by (Hirata, '75)/(Ohé, '89)		Wilson's Equation Fit by (Gmehling, '77)		Notes				
	Data Set	γ_1^∞	Data set	γ_1^∞	S[1]	A[2]	P[3]	E[4]	γ_1^∞ (Best)[5]
1942			251	5.546			√	N	5.39
1943			234	9.268		√	√	N	8.90
1945			241	9.273			√	M	8.64
1947	496(H)	20.100	244	6.731				N	6.56
1950			235	7.411		√	√	M	8.96
1952	497(H)	34.833	242	11.810		√	√	W	11.81
1953			249	6.820	√		√	U	7.56
1958			236	10.434	√	√	√	N	10.09
1968	495(H)	10.070	237	10.172	√	√	√	W	10.17
1973	510(O)	11.277	250	9.961		√	√	N	7.85

[1] Points in experimental data set were smoothed
[2] Data met "area" thermodynamic consistency test
[3] Data met "point" thermodynamic consistency test
[4] Equation that best fit the data, based on smallest $\sum |y_{exp} - y_{calc}|$ from Gmehling: N-NRTL; M-Margules; W-Wilson; U-Uniquac
[5] Value predicted by equation indicated in Column E, as fit by Gmehling

CONCLUSION

The error bars in chemical engineering design may be much wider than is commonly believed. This is especially true for non-ideal systems at limiting concentration—a region of operation approached by many absorbers designed to meet discharge specifications for air pollution abatement. There are warnings in the literature:

> *Finally, it must be emphasized that the biggest limitation to further developing the models is not theoretical insight or computational shortcoming, but the lack of good, relevant, experimental phase equilibrium data.*
>
> ***Fredenslund***[16]

Most chemical engineering textbooks, however, are silent on this and treat experimental data as given, with no error bars. To avoid being fooled, or fooling others, data sources must be properly referenced. This may require finding out where the numbers in a computer data bank came from. When possible, the range of uncertainty of the input data should be reported and the consequences of that range carried through to the final design. At that point it may be necessary to put the simulation aside and go back to the laboratory.

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