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Simple Models for Nonideal Vapor-Liquid Equilibrium Calculations

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In process simulation and design the rigorous thermodynamic functions which model vapor-liquid equilibria (VLE) are evaluated many times and can account for up to 80% of the total computation costs (Westerberg et al., 1979). This computational effort can be substantially reduced by using simplified local models to represent the rigorous thermodynamic properties. Models of this type have been presented by Leesley and Heyen (1977), Boston and Britt (1978), and Barret and Walsh (1979). A new approach for process design calculations involving the use of local models was detailed by Chimowitz et al. (1982 a,b). Here, our purpose is to present some new insights into the properties of the local models and propose areas of process design which stand to gain from the use of the local model concept.

SIMPLIFIED VLE MODELS

Vapor-liquid equilibrium in a mixture of n components if often defined in terms of the equilibrium ratio, K, defined by:

$$K_i = y_i/x_i = (\gamma_i f_i^o)/(\phi_i P) \qquad (i = 1 \ldots n) \qquad (1)$$

where γ_i is the activity coefficient, f_i^o is the standard-state liquid fugacity, ϕ_i is the vapor fugacity coefficient, and P is the system pressure. In general, activity and fugacity coefficients are nonlinear functions of temperature, pressure and composition, and Eq. 1 cannot be solved explicitly for any of these variables.

TABLE 1. REPRESENTATIVE LOCAL K-VALUE MODELS

Model	Defining Equations	Model Type	Min. # of Data
1	$ln\,(K_i) = a_i + b_i\,ln\,f_r^o - ln\,P$	Temperature only. Same as Leesley and Heyen's (1977) at low pressure	2
2	$ln\,(K_i) = a_i + b_i x_i + ln\,f_i^o - ln\,P$	All composition dependencies lumped into one term (Chimowitz et al., 1982a)	2
3	$ln\,(K_r) = a_r\,ln\,f_r^o + b_r(1 - x_r)^2 + c_r - ln\,P$ $ln\,(K_i/K_r) = a_i/T + b_i(1 - x_r)^2 + c_i(1 - x_i)^2 + d_i$	Relative volatility model respect to reference component (Chimowitz et al., 1982a)	4

A number of simpler expressions may be derived from Eq. 1 by making various assumptions regarding the nonideality of the solution. For example, we may assume that the relative volatility α_i is constant (α_i is defined as K_i/K_r, with r indicating a reference component), or that K_i is a function of temperature only. We may also take into account the major composition effects, but with only a very approximate functional dependence.

Representative models based on these considerations are shown in Table 1 (Chimowitz, 1982). The presence of adjustable parameters in the model equations makes it possible to fit rigorous VLE data about a particular point or region of interest in the two-phase envelope. Thus, it is quite possible for a simple model to represent the rigorous thermodynamic K_i well, at least locally, even if some of the assumptions used to derive it may be considered very drastic.

PERFORMANCE OF LOCAL MODELS

The capabilities of the local models shown in Table 1 are most conveniently assessed by using them in bubble-point calculations. Resulting temperatures and compositions are compared to those obtained using rigorous thermodynamic subroutines (Prausnitz et al., 1980). The corresponding errors provide a measure of the performance of the models.

In making these comparisons, we distinguish between the ability of the models (a) to interpolate accurately in the range where the model was fit and (b) to be extrapolated outside this range. Both capabilities are important in process design and simulation calculations.

To illustrate, we first consider the binary mixtures shown in Table 2. For each mixture at an arbitrary composition of 50 mol %, rigorous equilibrium ratios were generated at the bubble point and dew point. The local models were fit to these rigorous data. Model 3 required two additional rigorous data points (calculated at intermediate conditions) to obtain its parameters. The models and their associated parameters were then used to compute the equilibrium curve throughout the entire composition range.

Table 2 compares temperature and vapor compositions predicted by the local models with the corresponding rigorous values. In general, greater accuracy is achieved as a more complex model is used. However, errors are usually within 1% for all models when limited to the region in which they were fit. Mixture A represents an exception. This binary has a wide composition range from the

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TABLE 2. TEST MIXTURES AND ERRORS IN BUBBLE POINT TEMPERATURE AND VAPOR COMPOSITIONS RESULTING FROM THE USE OF LOCAL *K* MODELS*

Mixture	Components		Test Region	Average % Error on T			Average % Error on y		
				Model 1	Model 2	Model 3	Model 1	Model 2	Model 3
A	Acetone	(1)	Range of data (a)	0.3	2.6	0.2	21.9	14.6	0.8
	Water	(2)	Two-phase region	3.4	2.4	0.2	17.8	12.6	0.9
B	Methanol	(1)	Range of data (a)	1.5E-2	3.1E-2	2.1E-4	1.3	4.9E-2	6.5E-3
	Acetone	(2)	Two-phase region	0.6	0.5	0.6E-1	16.3	1.2	0.3
C	Acetone	(1)	Range of data (a)	1.3E-2	0.8E-2	4.5E-4	0.6	0.5E-1	0.2E-2
	Chloroform	(2)	Two-phase region	1.2	0.5	0.6E-1	33.3	2.6	2.8
D	2-Butanone	(1)	Along AB (b)	0.1	0.2	6.8E-3	3.7	0.3	1.0E-2
	n-Heptane	(2)	Region 1 (c)	1.3	0.4	0.3	11.4	1.8	4.5
	Toluene	(3)	Region 2 (d)	0.5	0.8	0.8	13.7	6.4	15.0
			Along CD (b)	4.8E-3	7.9E-3	2.8E-4	1.6E-1	1.2E-2	1.5E-3
			Region 1 (c)	1.4E-2	2.2E-2	1.4E-2	0.7	2.4	1.1
			Region 2 (d)	2.2E-2	9.7E-2	3.1E-2	1.3	5.3	2.7

* % error = |local model value-rigorous value| 100/rigorous value.
(a) Parameters for local models evaluated using rigorous data in the range: $x_1 = 0.032 - 0.83$ (*mixture A*); $x_1 = 0.42 - 0.61$ (*mixture B*); $x_1 = 0.46 - 0.56$ (*mixture C*).
(b) Liquid composition at point A: x = (0.7, 0.2, 0.1); at point B: x = (0.1, 0.5, 0.4); at point C: x = (0.007, 0.003, 0.990); at point D: x = (0.183, 0.016, 0.801).
(c) Shaded area in Figure 4.
(d) Region between dashed lines in Figure 4.

bubble point to the dew point, and can only be adequately represented by the more complex model 3.

While all of the models are comparable when used for interpolation, they vary considerably in their ability to be extrapolated. The azeotropic mixture of methanol and acetone illustrates this point. The *K*-values for this mixture (at constant pressure) are shown in Figure 1. Because of the nonidealities of the liquid phase the *K*-values exhibit minima, while an ideal solution would have *K*-values which are monotonic.

Model 1 is a linear function of a fugacity expression (monotonic w.r.t. T), and therfore will yield *K*-values which either increase or decrease monotonically. If this model is used to fit a system where the monotonicity of the *K*-values is destroyed by the composition effects, we can expect very serious errors upon extrapolation. In fact, this model not only fails to reproduce the azeotrope, but it also predicts that methanol boils at lower temperature than acetone. The result is that there are two temperatures for which the bubble point condition, $\Sigma_i K_i x_i = 1$, is satisfied, Figure 2. The presence of this multiplicity is obviously quite undesirable.

We have found that all local models with a temperature dependence given by an Antoine-type expression will exhibit similar behavior when used for highly nonideal liquid systems. The other models used here, having both a temperature and composition contribution, reproduce the minima and provide better extrapolation throughout the complete composition region.

With the simpler models, accurate quantitative results should not be expected when the range fit is too wide. For example, Figure 3 shows the $x - y$ diagram for the acetone-water system and the calculated equilibrium obtained using model 2. Although this local model agrees qualitatively with the rigorous data, it could not be used quantitatively. For a more accurate representation the model parameters should either be fit to a more limited region, or more than two rigorous data points should be used, or we should switch to a more accurate model. For this mixture, model 3 with parameters fit using five rigorous points predicts an equilibrium curve essentially coincident with the rigorous one.

The performance of the models with multicomponent systems is illustrated using the nonideal ternary mixture: 2-butanone(1), n-heptane(2), and toluene(3). Two liquid compositions were established, corresponding to an estimate of the liquid composition on two trays in a distillation column section (points A and B).

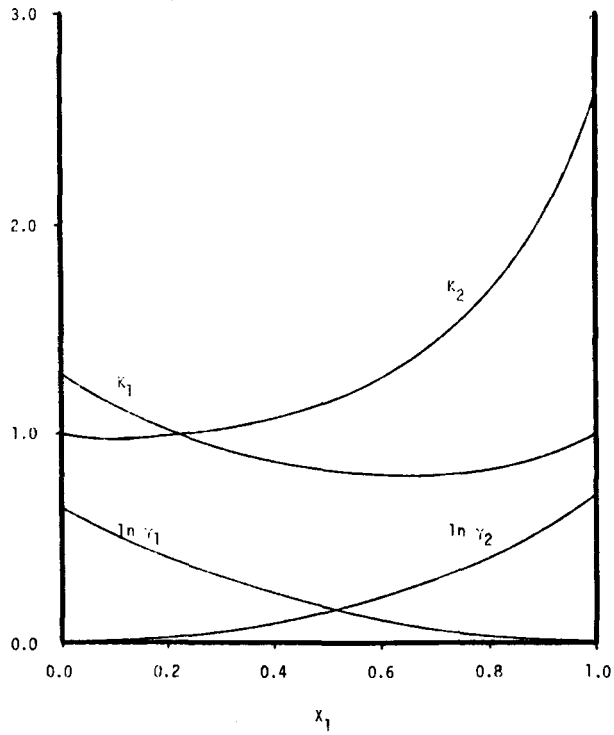

Figure 1. Rigorous equilibrium *K*-values and activity coefficients for the methanol(1)-acetone(2) mixture at atmospheric pressure.

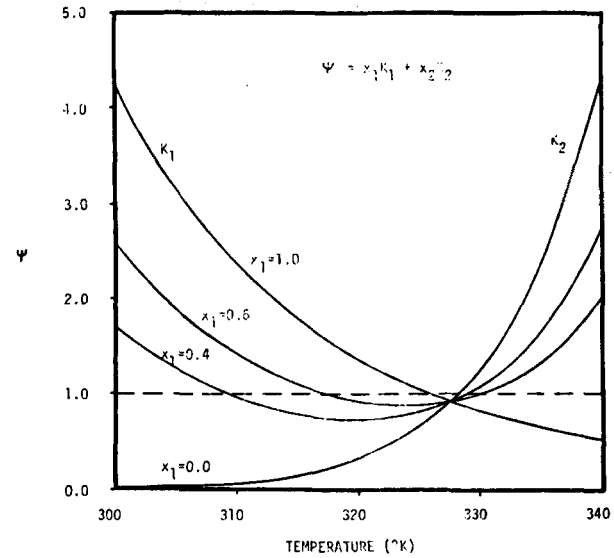

Figure 2. Sum of vapor mole fractions function for the methanol(1)-acetone(2) system. *K*-values computed using local model 1 at atmospheric pressure.

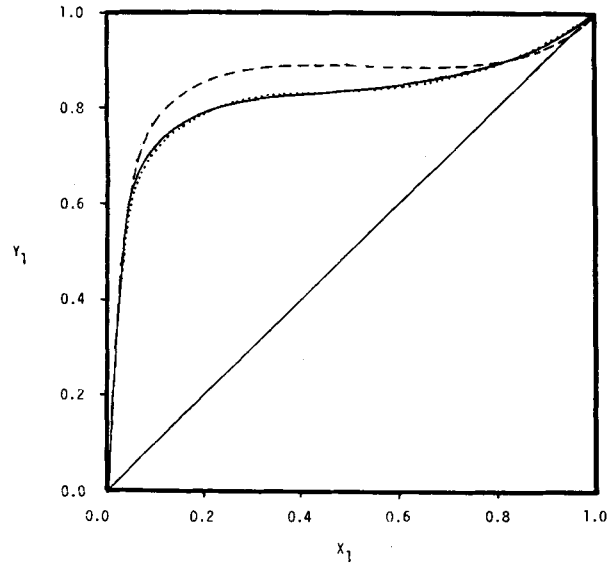

Figure 3. Equilibrium curve predicted for the acetone(1)-water(2) system at atmospheric pressure by a rigorous model (continuous line), local model 2 (dashed line) and local model 3 (dotted line).

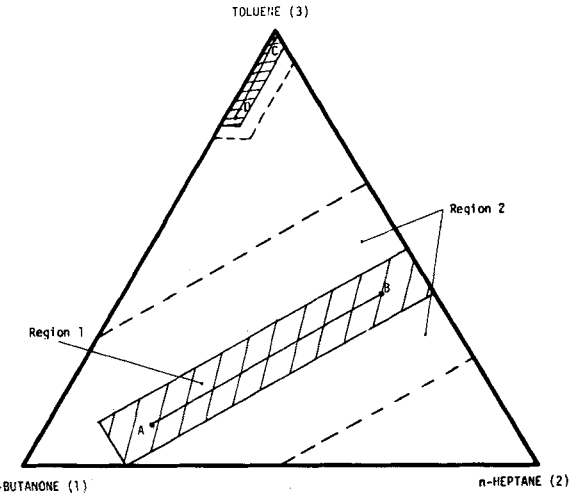

Figure 4. Ternary diagram for mixture D. Points A and B indicate the assumed end compositions in a distillation tower section. Points C and D represent end compositions in the near pure toluene region. Shaded area covers test Region 1 and test Region 2 is between dashed lines.

Rigorous equilibrium K-values were calculated at these points and at two linearly interpolated compositions between them, and the model parameters were estimated via standard least squares. The accuracy of each model was checked by recalculating the equilibrium conditions along line AB, in a narrow band around AB (Region 1), and in a wider composition range (Region 2), Figure 4. Results are shown in Table 2.

Again interpolation in the region where the models are fit yields an excellent representation of the VLE data, especially with models 2 and 3. Extrapolation to surrounding regions is increasingly less accurate as we move away from line AB. The temperature only model 1 predicts vapor compositions with large errors even for small extrapolations (Region 1), while the other models do better. Eventually all models become less accurate (Region 2). The same testing procedure yields similar results (last entry in Table 2) when repeated in the near pure toluene region, where the composition effects of diluted components are strongest (around points C and D in Figure 4).

APPLICATION TO PROCESS DESIGN

Even the simplest model can fit any VLE surface if any region, provided the region is small enough and care is taken not to extrapolate well beyond it. When extrapolating outside of this region, the model dependent on temperature only is not very reliable. Introduction of composition dependence, even in the simple form of model 2, gives the functional ability to reproduce fairly complex mixture behavior such as an azeotrope.

All models can be used with some confidence in a region outside of the original rigorous data, however large extrapolation should be considered with caution. It will be necessary to update the model parameters to better fit the new region. We have found that local models with composition dependence are more accurate, hold over wider regions, and thus require fewer parameter updates.

The convenience of using simple K models may be appreciated if we consider the solution of a set of equations which include equilibrium relations, via a Newton-Raphson type method. Let:

$$g_i = y_i - K_i(x,y,T,P)x_i = 0 \qquad (i = 1, \ldots, n) \qquad (2)$$

be a subset of the overall set and let J be the Jacobian matrix of partial derivatives pertaining to this subset. In the general case this matrix is full, since for an n component mixture, there are $2(n^2 + 1)$ partial derivatives to be computed, analytically or by perturbation. The assumption that K is independent of y, which is reasonable in most cases, reduces the number to $n(n + 2)$, which is still proportional to n^2. The adoption of a simple model leads to a Jacobian matrix with $4n$ partial derivatives only, with values obtained analytically by extremely simple expressions. In the case of multistaged equilibrium problems the difference in both storage and computational load can be very significant (1–2 orders of magnitude). In fact, this difference may determine the viability of using a Newton-Raphson method at all.

The strong computational attractiveness of the local models and their ability to give a good local representation of VLE surfaces suggest their use with two types of multistage separation problems: (1) steady-state solution with continuation-type methods (Wacker et al., 1978); and (2) dynamic simulation.

Both algorithms have very good stability characteristics. This is because of the ability to control the length of each continuation or integration step so that every new solution is close to a previous one. The main drawback in both instances is represented by the large cost normally associated with providing the necessary thermodynamic properties at every iteration.

Our experience with local models indicates that this cost can be reduced by several orders of magnitude. The model parameters must be occasionally updated using rigorous thermodynamic data as the solution moves from one temperature-composition region into an adjacent one. Preliminary results indicate that such a recursive procedure allows the algorithms to follow VLE surfaces with good accuracy, while mantaining the computational advantages of the simple models (Macchietto, 1982). Research in this area is under way and will be reported in the future.

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NOTATION

a,b,c,d	= local model parameters
f^0	= standard state liquid fugacity
g	= equilibrium equation
J	= Jacobian matrix
K	= equilibrium ratio
n	= number of components
P	= pressure
T	= temperature
x,y	= liquid, vapor mole fraction

Greek Letters

α = relative volatility
γ = activity coefficient
ϕ = vapor fugacity coefficient
ψ = sum of vapor mole fractions

Subscripts

i = ith component in a mixture
r = reference component

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Simulation of Test Conditions for Typical Pulverized Coal Combustors

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INTRODUCTION

The mixing of heterogeneous phases of gas and particles has varied applications. Processes commonly encountered are the MHD power generation system, air breathing missiles, and catalytic reactors. Of interest to us, however, is the pulverized coal combustor where an air jet issues along with particles. This dust makes significant contribution to the mass and momentum transfer of the mixture and its study is of considerable value in estimating the extent to which the mixing is affected. Control of a pulverized fuel combustor is dependent on the effect of the particles on the eddies that generate the turbulence and influence the entrainment. A study of particle effects should include velocity and concentration profile measurements and a look at the distortion in the jet development due to the presence of particles.

Figure 1 shows a schematic diagram of a round air jet. The round jet is seen to be made up of a central potential core of constant velocity and this is surrounded by an annular region where the velocity profile decays to a value equal to zero at the jet edge. The velocity and concentration profiles are believed to be similiar in the annular shear layer and our aim is to check this similarity.

In recent years considerable study has been directed to the near field of a round jet. This surge in interest is due to a desire to comprehend and alleviate the jet noise problem and also due to a growing recognition of the fact that the large-scale structure in a turbulent jet is intimately related to the developmental stages of flow in the mixing layer. Browand and Laufer (1975) and Yule (1978) have shown that the emerging physical picture is interesting. The shear layer leaving the nozzle whether laminar or turbulent becomes unstable to form a train of vortex rings which become unstable to azimuthal disturbances and ultimately disintegrate into a large number of vortical fragments distributed across the jet.

The purpose of this research, however, is to study the turbulent shear layer with particles present under conditions that would simulate industrial pulverized coal furnaces and entrained gasifiers.

PREVIOUS WORK

Laats and Frishman's (1970) work is the only detailed study available on the development of a solid/air jet. They determined the mean velocity distribution for different particle sizes and concentrations, mainly in the fully developed region. The radius of the two-phase jet was found to be less than that of the single-phase jet. An increase in the axial concentration of solids close to the nozzle was observed for some case and a rapid decrease was observed in other experiments. The data reported, therefore, seem to be confusing.

Brush (1962) studied the diffusion of glass beads in a submerged

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