Stability Calculations for Nonequilibrium Separation Processes

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Two of the most significant contributions in the last two decades to separation process are the numerical implementation of the tangent-plane criterion to check the stability of any given mixture and the use of mass-transfer models to solve separation-process problems. This work combines the use of the tangent-plane analysis with mass-transfer models to solve problems with multiple liquid phases. As in equilibrium-stage problems, the tangent-plane analysis works effectively with nonequilibrium-stage separation-process problems. An example is presented where the nonequilibrium model, when used in conjunction with the tangent-plane criterion, predicts the correct number of phases, while the equilibrium model predicts the incorrect number of phases.

Introduction

The necessary and sufficient condition for the global material stability of any mixture at any given temperature and pressure is the Gibbs tangent-plane criterion. This criterion states that the necessary and sufficient condition for stability of a mixture at a given temperature and pressure and overall composition is that the Gibbs energy surface be at no point below the tangent plane drawn at that overall composition (see Figure 1 for an example of an unstable mixture). In addition to providing a way to numerically implement the tangent-plane criterion, Michelsen (1982) has demonstrated that the results of the stability analysis can be used effectively to solve the liquid–liquid phase-equilibrium problem. Wasylkiewicz et al. (1996) demonstrated that the tangent-plane analysis could be used to detect cases where three liquid phases could exist as well.

Krishnamurthy and Taylor (1985) used a rigorous mass-transfer approach to solve vapor–liquid separation problems. Here, they separate the bulk liquid and vapor phases, and assume equilibrium at the interface. They take into account the mass transferred from one phase to the other as a result of the difference between the bulk and interface compositions and are able to obtain a more rigorous solution to the separation-process problem.

Lao and Taylor (1994) and Lao (1989) have extended and modified this approach to solve problems involving heterogeneous mixtures. Lao and Taylor also consider three-phase problems, and use an approach similar to that of Krishnamurthy and Taylor (1985) to solve the three-phase separation-process problem. To date there has not been any attempt to combine the tangent-plane analysis with rate-based heterogeneous separation-process calculations. This work is an attempt to do so and demonstrate with an example that this combination can not only provide better values of mole fractions but also provide the correct number of phases as well.

This article is organized as follows. First, a section deals with the pertinent features regarding stability analysis. The next section deals with two- and three-liquid-phase equilibrium calculations. Then, a description of the set of equations for the nonequilibrium model is presented, followed by the method of solution. These equations include the bulk-phase

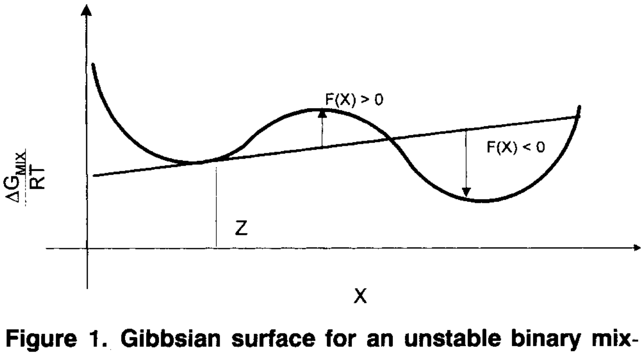

Figure 1. Gibbsian surface for an unstable binary mixture.

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material-balance equations, interface mass-balance equations, interface equilibrium equations, transfer-rate equations, and summation equations. A simple example is presented where the stability analysis is combined with the nonequilibrium model to produce a two-phase liquid–liquid solution. Finally, another example is presented where the equilibrium model incorrectly predicts three liquid phases, while the nonequilibrium model actually predicts the correct *stable* two-phase solution.

Stability Criterion

Gibbs (1873) proved that any given mixture at a given temperature pressure and overall composition would be globally stable if and only if the tangent to the Gibbs free-energy surface would never cut the surface. If z is the overall composition at a temperature T and a pressure P, and the chemical potential of the ith component, μ_i^0, then the molar Gibbs free energy of the mixture would be

$$g(z,T,P) = \sum_{i=1}^{c} z_i \mu_i^0 \tag{1}$$

and the equation to the tangent plane drawn at z, would be

$$L(x,T,P) = \sum_{i=1}^{c} x_i \mu_i^0. \tag{2}$$

The necessary and sufficient condition for stability is that the function $F(x)$ defined for all x within the composition domain as

$$F(x) = g(x) - L(x) = \sum_{i=1}^{c} x_i(\mu_i - \mu_i^0) \tag{3}$$

must be greater than or equal to 0. This was established analytically by Baker et al. (1981), Michelsen (1982), and Wasylkiewicz et al. (1996).

Michelsen (1982) showed that all the minima of $F(x)$ are located in the interior of the composition domain. This implies that if $F(x)$ is nonnegative at these minima, it must be nonnegative for the entire composition domain. Consequently, it is sufficient to check the value of $F(x)$ at the minima. In order to obtain these minima, one must differentiate the function $F(x)$. This would yield the stationary points where the sign of the function can be checked.

Differentiation of the function $F(x)$ with respect to the $c-1$ mole fractions along with the use of the Gibbs–Duhem equations yields the condition

$$\mu_i(\hat{x}) - \mu_i^0 = \mu_c(\hat{x}) - \mu_c^0 = \sigma \qquad (i = 1, \ldots, c), \tag{4}$$

where $\hat{x}$ is the mole fraction at the stationary point, and σ is a constant that depends on z and $\hat{x}$, but does not depend on the component index.

For liquid mixtures we can express the chemical potentials in terms of the activity coefficients, and the stability criterion can be written as

$$F(x)/RT = \sum_{i=1}^{c} x_i(\ln x_i + \ln \gamma_i(x) - h_i) \geq 0, \tag{5}$$

where $\gamma_i(x)$ is the activity coefficient evaluated at composition x, and

$$h_i = \ln \gamma_i(z) + \ln z_i, \tag{6}$$

which is constant for fixed feed conditions. Equation 4 can be written as

$$\ln \hat{x}_i + \ln \gamma_i(\hat{x}) - h_i = \beta, \tag{7}$$

where $\beta = \sigma/RT$ and γ_i represents the activity coefficient at the stationary point composition. Introducing new variables $Y_i = x_i \exp(-\beta)$, Eq. 5 can be rewritten as

$$\ln Y_i + \ln \gamma_i - h_i = 0. \tag{8}$$

Equation 8 can be solved using various techniques and admits multiple solutions.

If $\Sigma Y_i > 1$ for any of the solutions, then the mixture is unstable. For unstable mixtures we usually find two minima that provide excellent initial estimates for performing the phase-equilibrium calculations. The successive substitution method has been used for solving Eq. 8. A simple example would be the mixture ethanol, benzene, and water. Using the Uniquac model (Prausnitz et al., 1980), for a mixture at temperature 337.25 K and an overall composition (0.05, 0.67, 0.28), we find one of the solutions to be (1.87, 0.015, 0.003) and $\Sigma Y_i =$ 1.888, which is greater than 1, which means the mixture is unstable.

Equilibrium Calculations for Two and Three Liquid Phases

In this section, a very brief description of the use of the tangent-plane criterion to solve two- and three-liquid-phase equilibrium calculations is presented.

Two-phase calculations

For three-component systems that admit a stable two-phase solution, the stability analysis usually reveals two minima, which can be used to initialize the compositions by doing the two-liquid-phase calculations, as shown by Michelsen (1982) and Wasylkiewicz et al. (1996). The values of Y at these two minima are normalized and these values are used to do the two-liquid-phase calculations. We have used the Rachford–Rice strategy and also solved the material-balance and phase-equilibrium equations together using the Newton–Raphson technique. It is found that for both cases, as confirmed by Swank and Mullins (1985), the stability analysis reveals excellent initial estimates for the two-liquid-phase compositions.

As a simple example, consider the mixture water, acetic acid, and hexane at a temperature of 298.15 K, and overall composition [0.3062, 0.2252, 0.4686]. The NRTL model is used for calculating the activity coefficients and the binary interaction coefficients are taken from the DECHEMA chemistry data series (Sorensen and Arlt, 1980, p. 282). The values of Y_1 and Y_2 are [1.3488, 0.3489, 0.00167] and [0.0058, 0.0432, 1.3319]. The normalized values of Y_1 and Y_2 are [0.793, 0.206, 0.001] and [0.004, 0.0312, 0.964], while the compositions obtained as a result of the phase-split calculations are [0.003, 0.06303, 0.934] and [0.608, 0.386, 0.006].

It can be seen that the normalized values of Y are qualitatively similar to the actual values of the compositions, facilitating easy numerical computation.

Three-liquid-phase calculations

Wasylkiewicz et al. (1996) have developed a reliable strategy for identifying the existence of three liquid phases. First they solve the two-liquid-phase problem and then perform the stability analysis on the two-phase solution. If the two-phase solution is unstable, it would reveal three minima, which, *in the absence of a stable two-phase solution*, could be used to initialize a three-liquid-phase solution. After initialization, any numerical technique such as Rachford–Rice or a regular Newton method with finite difference derivatives, can be used to solve the material-balance and phase-equilibrium equations. As an example, consider the mixture toluene, *n*-propanol, and water at 5°C. When the NRTL model (Sorensen and Arlt, 1980, p. 580) was used to obtain the activity coefficients, both numerical techniques *independently* revealed the three-liquid-phase compositions that are in equilibrium with each other. Table 1 contains these compositions.

Other examples can be found in the article by Wasylkiewicz et al. (1996).

Rate-Based Model for Liquid–Liquid Phase Split Calculation

In the next few sections, a description of the equations for the rate-based liquid–liquid stage are presented. The set of equations is very similar to those presented by Krishnamurthy and Taylor (1985) and Lao (1989). The rate-based nonequilibrium stage is presented in Figure 2. In it F represents the feed, L represents the bulk liquid flow rate, while N is the flux of mass transfer. The equations for the rate-based liquid–liquid model include the mass-balance equations, transfer-rate equations, and interface-equilibrium equations. We differentiate between a bulk phase and an interface; equilibrium is assumed only at the interface. The mass balance takes into account the bulk-phase flow rates and compositions, along with the number of moles transferred from one phase to the other. These moles are the product of the fluxes and the interfacial area. The next few subsections deal with a detailed description of the equations that constitute the rate-based liquid-liquid model.

Mass-conservation equations

In a manner similar to that of Krishnamurthy and Taylor (1985) and Lao (1989), the two liquid phases are identified as L^1 and L^2, and unlike the equilibrium case, a separate material-balance equation is written for each liquid phase as

$$L^1 x_i^1 - F^1 z_i^1 + N_i^1 a = 0 \tag{9}$$

and

$$L^2 x_i^2 - F^2 z_i^2 + N_i^2 a = 0, \tag{10}$$

where i represents the component index; L^1 represents the first bulk-liquid phase, while L^2 represents the second liquid phase; a is the interfacial area; while N represents the interfacial flux of the mass transfer. The tangent-plane stability criterion can be used to provide excellent initial estimates for the bulk-phase compositions.

Table 1. Three-Liquid-Phase Equilibrium Solution

Component	Toluene	*n*-Propanol	Water
x_1	0.00155	0.0438	0.9546
x_2	0.6915	0.2434	0.0650
x_3	0.4055	0.3883	0.20606

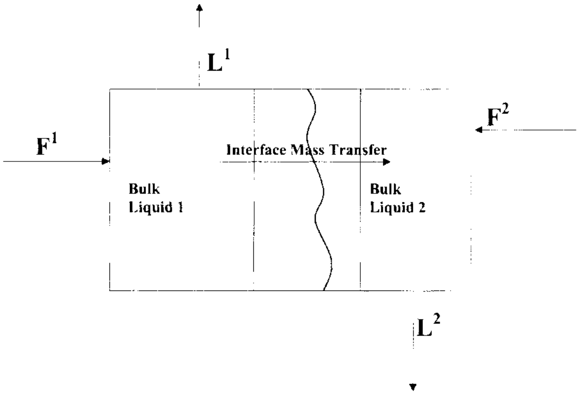

Figure 2. Rate-based liquid–liquid problem.

Transfer-rate equations

The molar fluxes will consist of a diffusive and a convective term as

$$N_i^1 = J_i^1 + N_t^1 x_i^1 \tag{11}$$

and

$$N_i^2 = J_i^2 + N_t^2 x_i^2. \tag{12}$$

The diffusive fluxes can be calculated from

$$J_i^1 = \sum_{k=1}^{c-1} k_{ik}^1 (x_k^1 + x_k^{1,\mathrm{I}}) \tag{13}$$

and

$$J_i^2 = \sum_{k=1}^{c-1} k_{ik}^2 (x_k^2 - x_k^{2,\mathrm{I}}), \tag{14}$$

where k_{ik} represents the interfacial mass-transfer coefficients and will usually be available in matrix form for the interaction of each component with the other. We represent this matrix as $[k]$. The method of Krishna (1977) is used to obtain this matrix. This is achieved through a solution of the generalized Maxwell–Stefan equations for a film model of mass transfer. For different types of interfaces, Krishna (1977) uses the continuity equation

$$\nabla \cdot N_i = 0 \qquad i = 1, \ldots, c, \tag{15}$$

and, assuming a molecular diffusion process to be restricted to a film, obtains a relation for $[k]$ as

$$[k] = [R]^{-1}[\Gamma][\Theta]. \tag{16}$$

This procedure is also described in Lao (1989). The matrix containing the coefficients k_{ij} is $[k]$. The matrix $[R]$ can be calculated from

$$R_{ii} = x_i/k_{ic} + \sum_{l=1, l \neq i}^{c} x_l/k_{il} \tag{17}$$

and

$$R_{ij} = -x_i\left(\frac{1}{k_{ij}} - \frac{1}{k_{ic}}\right), \tag{18}$$

where x is the mole fraction and k_{il} are the binary mass-transfer coefficients. Γ is the matrix of thermodynamic coefficients given by

$$\Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j}. \tag{19}$$

For ideal systems Γ reduces to the identity matrix δ_{ij}; Θ is a matrix of correction factors that accounts for the influence of mass-transfer rates on the mass-transfer coefficients and can be obtained by solving the equations

$$[\Theta'] = [\theta'][\exp[\theta'] - I]^{-1} \tag{20}$$

and

$$[\Theta''] = [\theta'']\exp[\theta''][\exp[\theta''] - I]^{-1}, \tag{21}$$

where $[\theta]$ is defined by

$$[\theta] = [\Gamma]^{-1}[\Phi]. \tag{22}$$

The matrix Φ is given by

$$\Phi_{ii} = \frac{N_i}{c_t k_{ic}} + \sum_{l=1, l \neq i}^{c} \frac{N_l}{k_{il}} \tag{23}$$

and

$$\Phi_{ij} = -\frac{N_i}{c_t}\left(\frac{1}{k_{ij}} - \frac{1}{k_{ic}}\right), \tag{24}$$

where c is the molar density.

The definitions of all these matrices can be found in Lao (1989). The routines for calculating all these matrices can be obtained from the internet site ftp.clarkson.edu. Then, as in Lao (1989), the rate equations can be written as

$$N_j^{\mathrm{I}} - N_{tj}^{\mathrm{I}}\left(x_j^{\mathrm{I}}\right) - c_{tj}\left[k_j^{\mathrm{I}}\left(x_j - x_j^{\mathrm{I,int}}\right)\right] = 0 \tag{25}$$

$$N_j^{\mathrm{II}} - N_{tj}^{\mathrm{II}}\left(x_j^{\mathrm{II}}\right) - c_{tj}\left[k_j^{\mathrm{II}}\left(x_j - x_j^{\mathrm{II,int}}\right)\right] = 0, \tag{26}$$

where int represents the interface, while c_t represents the molar density.

Interface equilibrium equations

Equilibrium is assumed at the interface, giving rise to the set of c equations

$$(\gamma_i x_i)^{\mathrm{I}} - (\gamma_i x_i)^{\mathrm{II}} = 0, \tag{27}$$

where γ is the activity coefficient at the given temperature and pressure and composition x.

Interface material-balance equations

The material-balance equations at the interface can be written as

$$N_i^{\mathrm{I}} + N_i^{\mathrm{II}} = 0 \qquad i = 1, \ldots, c. \tag{28}$$

This is equivalent to assuming equimolar counterdiffusion.

Summation equations

The summation equations for the interface compositions can be written as

$$\sum_{i=1}^{c} x_i^{\mathrm{I}} - 1 = 0 \tag{29}$$

$$\sum_{i=1}^{c} x_i^{\mathrm{II}} - 1 = 0. \tag{30}$$

Variables in the problem

The variables in the problem are

- Bulk-phase mole fractions for liquid 1; $c-1$ variables.
- Bulk-phase mole fractions for liquid 2; $c-1$ variables.
- Interface mole fractions for liquid 1; c variables.
- Interface mole fractions for liquid 2; c variables.
- Flux in phase 1; c variables.
- Flux in phase 2; c variables.
- The two-bulk liquid flow rates; 2 variables.

The total number of variables is $6c$.

Equations in the problem

The equations used are the material-balance equations for each of the bulk phases ($2c$ equations), the interface equilibrium equations (c equations), the transfer rates ($2c$ equations), and interface material balance (c equations). The total number of equations is $6c$.

Table 2. Nonequilibrium Two-Liquid-Phase Solution

Component	Water	Ethanol	Heptane
x-Bulk − 1	0.02565	0.1008	0.8740
x-Bulk − 2	0.5984	0.3544	0.04703
x-Interface 1	0.0153	0.0864	0.8983
x-Interface 2	0.6828	0.3096	0.0066
Flux 1	6.17×10^{-5}	2.691×10^{-5}	-9.29×10^{-5}
Flux 2	-6.17×10^{-5}	-2.691×10^{-5}	9.29×10^{-5}

Method of solution

The $6c$ equations are assembled in the form $F(X)=0$, where X denotes the $6c$ variables. The equations are then solved using the Newton–Raphson iteration method.

Example of two-liquid-phase rate-based solution

Consider the system water, ethanol, and heptane, at a temperature 298.15 K. Let the overall composition be 0.3062, 0.2252, and 0.4686. The NRTL model was used to model the activity coefficients and the data were taken from the DECHEMA series (Sorensen and Arlt, 1980, p. 376). The mixture is unstable, which is revealed by the Y-vectors [0.0261, 0.05735, 1.07798] and [1.3731, 0.1996, 0.00107]. The solution to this problem is presented in Table 2.

Example Where the Nonequilibrium Model Predicts the Right Number of Phases

In the problem involving toluene, n-propanol, and water, where the NRTL model predicted a stable three-liquid-phase solution, the nonequilibrium model actually demonstrated that a stable two-liquid-phase solution existed. In reality (Sorensen and Arlt, 1980), only two liquid phases existed, thereby demonstrating that the nonequilibrium model can actually predict the correct number of phases if used in conjunction with the tangent-plane criterion. Presented in Tables 3 and 4 are the unstable two-liquid-phase equilibrium solution and the stable two-liquid-phase nonequilibrium solution, respectively. The stable three-liquid-phase equilibrium solution is presented in Table 1.

Three-Liquid-Phase Nonequilibrium Example

For the mixture 1-hexanol, nitromethane, and water, when there exists three liquid phases in reality (see Wasylkiewicz et al., 1996; Sorensen and Arlt, 1980), the nonequilibrium model predicts three liquid phases. Details of the model description for the three-liquid-phase nonequilibrium problem are present in Torres (1998) and Sridhar and Torres (1998). The model is very similar to that of the vapor–liquid–liquid model of Lao and Taylor (1994), except that instead of each vapor–liquid interface we would have a liquid–liquid interface. In Table 5, we present the nonequilibrium three-liquid-phase solution for the mixture 1-hexanol, nitromethane, and water at 21°C, and a feed composition of 0.4, 0.3, and 0.3. The UNIQUAC model was used with the activity coefficient parameters from Sorensen and Arlt (1980).

Table 3. Unstable Two-Liquid-Phase Equilibrium Solution

Component	Toluene	n-Propanol	Water
x_1	1.5×10^{-3}	0.04363	0.9555
x_2	0.5086	0.3458	0.1456

Table 4. Stable Nonequilibrium Two-Liquid-Phase Solution

Component	Toluene	n-Propanol	Water
x-Bulk − 1	0.0063	0.093	0.8999
x-Bulk − 2	0.56011	0.3365	0.1032
x-Interface 1	0.00161	0.0537	0.9446
x-Interface 2	0.1423	0.42907	0.4286
Flux 1	6.6×10^{-5}	3.06×10^{-5}	-7.845×10^{-5}
Flux 2	-6.6×10^{-5}	-3.06×10^{-5}	7.845×10^{-5}

Table 5. Stable Nonequilibrium Three-Liquid-Phase Solution

Component	1-Hexanol	Nitromethane	Water
x-Bulk − 1	0.4582	0.2871	0.2547
x-Bulk − 2	0.0216	0.2533	0.7251
x-Bulk − 3	0.1900	0.4988	0.3112
x-Interface 1-2	0.4555	0.2789	0.2656
x-Interface 2-1	0.0012	0.0264	0.9723
x-Interface 1-3	0.4660	0.3039	0.2301
x-Interface 3-1	0.09978	0.8042	0.0959
x-Interface 2-3	1.242×10^{-3}	0.0270	0.9717
x-Interface 3-2	0.1936	0.6385	0.1678
Flux 1-2	-4.3646×10^{-5}	-2.905×10^{-5}	-2.983×10^{-5}
Flux 2-1	4.3646×10^{-5}	2.905×10^{-5}	2.983×10^{-5}
Flux 1-3	-1.216×10^{-5}	-6.362×10^{-5}	-4.496×10^{-5}
Flux 3-1	1.216×10^{-5}	6.362×10^{-5}	4.496×10^{-5}
Flux 2-3	4.308×10^{-5}	2.233×10^{-5}	-5.616×10^{-6}
Flux 3-2	-4.308×10^{-5}	-2.233×10^{-5}	5.616×10^{-6}

Conclusions

The tangent plane analysis, used so far to solve problems involving equilibrium problems, can be used to solve separation-process problems using mass-transfer models as well. The results indicate that the use of the mass-transfer models in combination with the tangent-plane analysis can predict the correct number of liquid phases, while the equilibrium model predicts the incorrect number of phases.

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Notation

L = total liquid flow
F = total feed flow
x = liquid mole fraction

Literature Cited

Baker, L. E., A. C. Pierce, and K. D. Luks, "Gibbs Energy Analysis of Phase Equilibria," Joint Symposium on Enhanced Oil Recovery, SPE/DOE, Tulsa, OK (1981).

Gibbs, J. W., "A Method of Geometrical Representation of the Thermodynamic Property of Substances by Means of Surfaces," *Trans. Connecticut Academy*, Hartford, p. 382 (1873).

Krishna, R., "A Generalized Film Model for Mass Transfer in Nonideal Fluid Mixtures," *Chem. Eng. Sci.*, **32**, 659 (1977).

Krishnamurthy, R., and R. Taylor, "A Nonequilibrium Stage Model of Multicomponent Separation Processes," *AIChE J.*, **31**(3) (1985).

Lao, M., "Nonequilibrium Models for Multiphase Separation Processes," PhD Thesis, Clarkson Univ., Potsdam, New York (1989).

Lao, M., and R. Taylor, "Modeling Mass Transfer in Three Phase Distillation," *Ind. Eng. Chem. Res.*, **33**, 2637 (1994).

Michelsen, M. L., "The Isothermal Flash Problem. Part 1, Stability," *Fluid Phase Equilib.*, **9**, 1 (1982).

Prausnitz, J. M., T. I. Andersen, E. A. Grens, C. A. Eckert, R. Hsieh, and J. P. O'Connell, *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1980).

Sorensen, J. M., and W. Arlt, *Liquid-Liquid Equilibrium Data Collection. Ternary Systems*, Vol. V, DECHEMA Chemistry Data Series, DECHEMA, Frankfurt (1980).

Sridhar, L. N., and M. Torres, "The Three Phase Nonequilibrium Problem," *Chem. Eng. Commun.* (1998).

Swank, D., and J. W. Mullins, "Evaluation of Methods for Calculating Liquid-Liquid Phase Splitting," *Fluid Phase Equilib.*, **30**, 101 (1985).

Taylor, R., and R. Krishna, *Multicomponent Mass Transfer*, Wiley, New York.

Torres, M., "Rate Based Heterogeneous Separation Processes," MS Thesis, Univ. of Puerto Rico, Mayaguez (1998).

Wasylkiewicz, S. K., L. N. Sridhar, M. F. Doherty, and M. F. Malone, "Global Stability Analysis and Calculation of Liquid-Liquid Equilibrium in Multicomponent Mixtures," *Ind. Eng. Chem. Res.*, **35**(4), 1395 (1996).

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