

SATURATION POINT CALCULATIONS

MICHAEL L. MICHELSEN

Instituttet for Kemiteknik, Bygning 229, DK-2800 Lyngby (Denmark)

(Received September 18, 1984; accepted in final form April 16, 1985)

ABSTRACT

Michelsen, M.L., 1985. Saturation point calculations. *Fluid Phase Equilibria*, 23: 181–192.

A method for the calculation of approximate saturation temperatures or pressures for multicomponent mixtures with iteration in only a single variable is described. The basis for the method is that errors with magnitude of order ϵ in the assumed composition of the incipient phase result in an error of order ϵ^2 only in the corresponding saturation temperature or pressure.

Simple relations that must hold at the cricondenterm and the cricondenbar are given. These relations can be used for direct determination of temperature or pressure maxima along the phase boundary, and two procedures based, respectively, on direct substitution and Newton–Raphson iteration are described.

INTRODUCTION

The determination of saturation points, i.e., bubble- or dewpoint temperatures at specified pressure or pressures at specified temperature, is one of the basic phase equilibrium calculation problems. When separate models are used for the fluid phases saturation point calculations are deceptively simple and essentially reduce to the determination of the root for a single monotonic function. The saturation point calculation is actually sufficiently simple to warrant its use as an initial stage in e.g., adiabatic flash calculations (Prausnitz et al., 1980). This picture changes completely when the same model is used for both fluid phases. Firstly, a unique solution is no longer ensured. As an example, consider the dewpoint calculation at specified pressure, where the number of solutions depends on the specified pressure as follows: one solution for $P_{\text{spec}} < P_{\text{crit}}$, two solutions for $P_{\text{crit}} < P_{\text{spec}} < P_{\text{max}}$ and no solutions for $P_{\text{spec}} > P_{\text{max}}$, where P_{max} is the largest pressure at which two equilibrium phases are found. Secondly, inaccurate initial estimates will often lead to the so called “trivial” solution with equilibrium phases of

identical composition. The present paper is concerned with methods for alleviating problems associated with high pressure saturation point calculations using an equation of state, but in no way pretends to provide a solution for all such problems.

BASIC RELATIONS

For a mixture of given composition \mathbf{z} determination of the saturation point at a specified pressure (temperature) requires calculation of the temperature (pressure) and the composition of the incipient phase. For convenience we shall assume in the following, unless otherwise stated, that pressure is specified and temperature is unknown, and the mole fraction vector for the incipient phase is denoted \mathbf{y} , regardless of whether this phase is a liquid or a vapour.

For an N -component mixture there are N unknown, i.e., the $N - 1$ independent mole fractions and the temperature. These can be determined from the condition of equal fugacity in both phases for all components

$$f_i = \ln y_i + \ln \phi_i(\mathbf{y}) - \ln z_i - \ln \phi_i(\mathbf{z}) = 0, \quad i = 1, 2, \dots, N \quad (1)$$

It is, however, convenient to treat the mole fractions y_i as independent. This requires the additional condition

$$f_{N+1} = 1 - \sum_i y_i = 0 \quad (2)$$

and in the evaluation of fugacity coefficients for the incipient phase the y_i are formally treated as mole numbers.

An equivalent set of equations is obtained by replacing eqn. (2) by a linear combination of the above set of equations, namely $Q_1 = f_{N+1} - \sum_i y_i f_i$, or

$$Q_1 = 1 - \sum_i y_i + \sum_i y_i \{ \ln y_i + \ln \phi_i(\mathbf{y}) - \ln z_i - \ln \phi_i(\mathbf{z}) \} = 0 \quad (3)$$

and in this form Q_1 equals the modified tangent plane distance used by Michelsen (1982) for stability analysis.

Stability at (T, P) of the mixture with composition \mathbf{z} requires that the modified tangent plane distance, eqn. (3), is nonnegative for all \mathbf{y} . Selecting \mathbf{y} such that the set of eqns. (1) is satisfied implies that \mathbf{y} is a stationary point for the tangent plane distance. At a saturation point, the stationary value equals zero.

Let the solution to the set of eqns. (1, 3) at $P = P_{\text{spec}}$ be $\mathbf{y} = \mathbf{y}^*$, $T = T^*$. Of course, if \mathbf{y}^* was known in advance it would be possible to determine T^* from eqn. (3) alone. More important, however, is that if an approximation to \mathbf{y}^* , $\mathbf{y} = \hat{\mathbf{y}}$, is available, substituting this approximation in eqn. (3) and solving for the corresponding temperature T yields an approximate saturation

temperature which is “more accurate” than the approximation \hat{y} . Quantitatively, if the error of the approximate y -vector is of order ϵ , the error $\hat{T} - T^*$ will be of order ϵ^2 . The reason to the reduced error in \hat{T} is that to the first approximation Q_1 is insensitive to y when y is close to the stationary point.

This result is obtained by means of a Taylor series expansion of Q_1 around (y^*, T^*) , i.e.

$$Q_1(y, T) = Q_1(y^*, T^*) + \sum_j \left(\frac{\partial Q_1}{\partial y_j} \right)_{y^*, T^*} (y_j - y_j^*) + \left(\frac{\partial Q_1}{\partial T} \right)_{y^*, T^*} (T - T^*) \\ + \text{higher order terms.} \quad (4)$$

Now, $Q_1(y^*, T^*) = 0$, and from Michelsen (1982),

$$\left(\frac{\partial Q_1}{\partial y_j} \right)_{y^*, T^*} = (\ln y_j + \ln \phi_j(y) - \ln z_j - \ln \phi_j(z))_{y^*, T^*} = 0 \quad (5)$$

Hence, to a first approximation, $Q_1(y, T) = 0$ requires that $T - T^*$ equals zero. Including second order terms and taking $y = \hat{y} = y^* + \epsilon_v$, where ϵ is small, results in

$$T = \hat{T} = T^* - \frac{1}{2} \epsilon^2 \left\{ \sum_i \sum_j v_i v_j \left(\frac{1}{y_i^*} \delta_{ij} + \frac{\partial \ln \phi_i(y)}{\partial y_j} \right) \right\} / \left(\frac{\partial Q_1}{\partial T} \right)_{y^*, T^*} \quad (6)$$

$$\text{with } \left(\frac{\partial Q_1}{\partial T} \right)_{y^*, T^*} = \sum_i y_i \left\{ \frac{\partial \ln \phi_i(y^*)}{\partial T} - \frac{\partial \ln \phi_i(z)}{\partial T} \right\}$$

The point (T, P_{spec}) satisfying $Q_1(T, P_{\text{spec}}, y) = 0$ cannot be located in the one-phase region for the mixture of composition z unless $y = y^*$ (or $y = z$), since the modified tangent plane distance equals zero at $y = y^*$, while its gradient is nonzero. This implies that negative values of the tangent plane distance are obtainable and hence that the mixture is unstable.

An alternative form is obtained isolating y_i from eqn. (1) and substituting into eqn. (3), i.e.

$$Q_2(y, T) = 1 - \sum_i z_i \phi_i(z) / \phi_i(y) \quad (7)$$

The equilibrium phase composition $y = y^*$ still represents a stationary point of Q_2 since

$$\frac{\partial Q_2}{\partial y_j} = \sum_i z_i \phi_i(z) / \phi_i(y) \frac{\partial \ln \phi_i(y)}{\partial y_j} \quad (8)$$

At the equilibrium point, eqn. (1) is satisfied, i.e.

$$z_i \phi_i(z) / \phi_i(y^*) = y_i^* \quad (9)$$

and, from the Gibbs–Duhem equation

$$\left(\frac{\partial Q_2}{\partial y_j} \right)_{y^*, T^*} = \sum_i y_i^* \left(\frac{\partial \ln \phi_i}{\partial y_j} \right)_{y^*, T^*} = 0 \quad (10)$$

Hence, if eqn. (7) is used to determine the saturation temperature, an error of order ϵ in \hat{y} again yields an error in temperature of order ϵ^2 .

In practice it turns out that the error in temperature based on Q_2 is smaller than that based on Q_1 provided the same approximate composition \hat{y} is used. We may note, for example, that for an ideal incipient phase Q_2 is unaffected by the choice of \hat{y} (leading to an error free determination of the temperature), while this is not the case with Q_1 . A slight price is paid for the improved accuracy of Q_2 : satisfaction of $Q_2(T, P, \hat{y}) = 0$ strongly indicates but does not guarantee that (T, P) is located inside or on the phase boundary. In practice, however, solving $Q_2 = 0$ for T will, for any reasonable choice of \hat{y} , lead to a point (T, P) in the two-phase region.

The conventional method for saturation point calculations (Prausnitz et al., 1980) uses Newton–Raphson iteration to correct T using eqn. (7), combined with direct substitution for revising y , i.e.

$$Y_i = z_i \phi_i(\mathbf{z}) / \phi_i(\mathbf{y}^{(k)}) \quad (11)$$

$$Q_2^{(k)} = 1 - \sum_i Y_i \quad (12)$$

$$T^{(k+1)} = T^{(k)} - Q_2^{(k)} / \frac{\partial}{\partial T} (Q_2^{(k)}) \quad (13)$$

and finally

$$y_i^{(k+1)} = Y_i / \sum_j Y_j \quad (14)$$

It is instructive to observe an example of the error history for the iteration based on eqns. (11–14). Figure 1 shows $\mathbf{e}_y^{(k)} \triangleq \|\mathbf{y}^{(k)} - \mathbf{y}^{(\infty)}\|$ and $\mathbf{e}_T^{(k)} = |T^{(k)} - T^{(\infty)}|$ as a function of k for a bubble point calculation. The mixture investigated contains 70% CH_4 , 15% CO_2 and 15% H_2S , and the phase diagram for this mixture, based on the SRK-equation, is shown in Fig. 2. The calculation for which the error history is given in Fig. 1 is a bubble point determination at $P = 50$ atm.

The iterative process is linearly convergent, but we notice that the slope of the \mathbf{e}_T -line is twice that of the \mathbf{e}_y -line. The error in temperature rapidly adjusts to the current error in composition according to $\mathbf{e}_T \sim \mathbf{e}_y^2$. It is easily shown that the slope of the \mathbf{e}_y -line ($\ln \mathbf{e}_y$ versus k) equals $\ln |\lambda_1|$, where

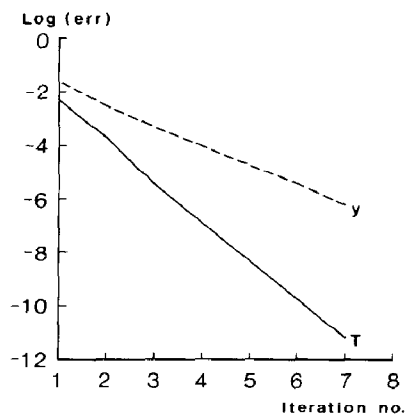


Fig. 1. Error in temperature (T) and composition (y) versus iteration no. for bubble point calculation at $P = 50$ atm for the mixture of Fig. 2.

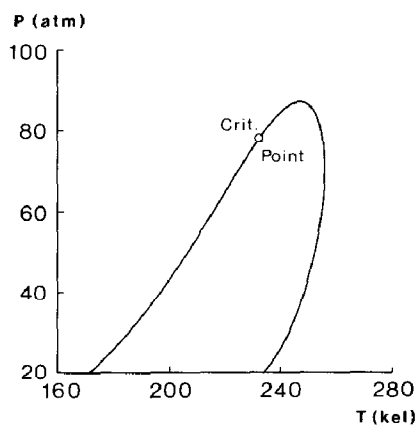


Fig. 2. Phase boundary for a mixture containing methane, carbon dioxide and hydrogen sulfide using the SRK equation of state.

$|\lambda_1|$ is the magnitude of the eigenvalue of largest modulus of the matrix given by

$$S_{ij} = - \left(y_j \frac{\partial \ln \phi_i}{\partial y_j} \right) \mathbf{y}_{(\infty)} \quad (15)$$

For the present example, $\lambda_1 = 0.2$.

APPLICATIONS

The use of Q_1 or Q_2 only for approximate saturation point calculations reduces these to one-dimensional problems which are easily solved. The

TABLE 1

Approximate phase boundary calculation using equilibrium composition at $P = 50$ atm

Pressure (atm)	Saturation temperature (K)		
	True	From eqn. (3)	From eqn. (7)
50	206.29		
52	208.16	208.20	208.17
54	210.01	210.20	210.06
56	211.85	212.3156	211.96
58	213.65	214.63	213.91
60	215.48	217.33	215.92

accuracy of the resulting approximations evidently depend on the quality of the estimate \hat{y} of the equilibrium phase composition.

Assume that the solution (y^*, T^*) to eqns. (1 and 2) is known at $P = P_{\text{spec}}$. At pressures close to P_{spec} , $P = P_{\text{spec}} + \Delta P$ with ΔP small, y^* represents a first order approximation to the equilibrium phase composition, with an error proportional to ΔP . Hence if the saturation temperature is calculated from $Q(T, P, y^*) = 0$, (with $Q = Q_1$ or Q_2) the error in T will be proportional to ΔP^2 . Furthermore the ratio $\Delta T/\Delta P = (T - T^*)/\Delta P$ is determined with an error proportional to ΔP , and therefore the derivative of the phase boundary, $(dT/dP)_{P_{\text{spec}}}$, ($\Delta P \rightarrow 0$) is exactly equal to the derivative found from $Q(T, P, y^*) = 0$, that is

$$\left(\frac{dT}{dP}\right)_{P_{\text{spec}}} = -\left(\frac{\partial Q}{\partial P}\right) / \left(\frac{\partial Q}{\partial T}\right) \quad (16)$$

The slope of the phase boundary can thus be calculated exactly, using only pressure and temperature derivatives of the fugacity coefficients. No composition derivatives are required, and contrary to general calculations of sensitivities (see, e.g., eqn. 27) solution of a set of linear equations is not required.

Table 1 gives, for the mixture of Fig. 2, approximate values of the bubble point temperature in the pressure range $50 \leq P \leq 60$ atm using, respectively, $Q_1(T, P, \hat{y}) = 0$ and $Q_2(T, P, \hat{y}) = 0$, where \hat{y} is the equilibrium phase composition at $P = 50$ atm.

If instead, temperature is taken as the independent variable, we find

$$\frac{dP}{dT} = -\left(\frac{\partial Q}{\partial T}\right) / \left(\frac{\partial Q}{\partial P}\right) \quad (17)$$

Similarly, one obtains

$$\frac{\partial P}{\partial \alpha} = -\left(\frac{\partial Q}{\partial \alpha}\right) / \left(\frac{\partial Q}{\partial P}\right) \quad (18)$$

where α represents any model parameter in the thermodynamic model used for evaluation of fugacity coefficients. This relation is of importance when the estimation of parameters in thermodynamic models is based on fitting calculated equilibrium pressures to measured equilibrium pressures. Each trial vector of model parameters requires saturation point calculations (at given temperature) for every set of experimental data. Once these are completed (and P and the equilibrium phase composition are available) the sensitivities of the calculated pressures to changes in the model parameters can be calculated at little extra cost using eqn. (18). The determination of such sensitivities is an integral part of all efficient parameter estimation procedures (see, e.g., Fletcher, 1980) and hence efficient evaluation is of importance.

The relation, eqn. (17), for the mixture vapour pressure has found surprisingly little use in phase equilibrium calculations, considering that it is well known. A similar relation for a binary mixture is, e.g., presented by Modell and Reid (1974, Ch. 9). One possible explanation for this is that the use of a single equation of state for calculating the properties of both fluid phases has only found widespread application during the last decade. When different models are used for the fluid phases, convergence problems in bubble- and dew point calculations are largely absent, and hence there has been little incentive to improve the traditional algorithms. As discussed in the introduction, when a single model is used for both fluid phases, good initial estimates are a vital necessity in saturation point calculations. It will subsequently be shown how the relations developed here can be used for providing such estimates.

TEMPERATURE AND PRESSURE MAXIMA

As can be seen from Fig. 2, the use of a single equation of state leads to a phase boundary with a pressure maximum as well as a temperature maximum. The determination of these maxima is of considerable interest and construction of the entire phase boundary (Michelsen, 1980) has been suggested as an indirect method of evaluation. Equations (16) and (17), however, provide the necessary relations for a direct determination. At the temperature maximum

$$\left(\frac{dT}{dP} \right)_{P_{\text{spec}}} = 0, \quad \text{yielding} \quad \frac{\partial Q}{\partial P} = 0, \quad \text{or} \quad (19)$$

$$f_{N+2} = \sum_i y_i \left\{ \frac{\partial \ln \phi_i(\mathbf{y})}{\partial P} - \frac{\partial \ln \phi_i(\mathbf{z})}{\partial P} \right\} = 0 \quad (20)$$

which together with eqns. (1 and 2) enables us to determine the $N+2$

unknown (y, T, P). Similarly at the pressure maximum, eqn. (20) with temperature derivatives replacing the pressure derivatives, is used.

Newton–Raphson solution is straightforward, since essentially no new derivatives are needed. Composition derivatives of f_{N+2} are given by

$$\begin{aligned} \frac{\partial f_{N+2}}{\partial y_j} &= \frac{\partial \ln \phi_j(\mathbf{y})}{\partial P} - \frac{\partial \ln \phi_j(\mathbf{z})}{\partial P} + \frac{\partial}{\partial P} \left(\sum_i y_i \frac{\partial \ln \phi_i(\mathbf{y})}{\partial y_j} \right) \\ &= \frac{\partial \ln \phi_j(\mathbf{y})}{\partial P} - \frac{\partial \ln \phi_j(\mathbf{z})}{\partial P} \end{aligned} \quad (21)$$

since the last term is identically zero by virtue of the Gibbs–Duhem equation.

Derivatives of f_{N+2} with respect to T and P lead to second derivatives of the type $\partial^2 \ln \phi_i / \partial P^2$ and $\partial^2 \ln \phi_i / \partial P \partial T$. These terms are most conveniently evaluated numerically, and a single calculation at a perturbed pressure is sufficient, i.e.

$$\frac{\partial^2 \ln \phi_i}{\partial P^2} = \frac{1}{\epsilon} \left\{ \left(\frac{\partial \ln \phi_i}{\partial P} \right)_{P+\epsilon} - \left(\frac{\partial \ln \phi_i}{\partial P} \right)_P \right\} \quad (22)$$

$$\frac{\partial^2 \ln \phi_i}{\partial P \partial T} = \frac{1}{\epsilon} \left\{ \left(\frac{\partial \ln \phi_i}{\partial T} \right)_{P+\epsilon} - \left(\frac{\partial \ln \phi_i}{\partial T} \right)_P \right\} \quad (23)$$

Apart from these only the “usual” first derivatives of fugacity coefficients with respect to composition, temperature and pressure are required.

A direct substitution procedure similar to that used for conventional saturation point calculations is also a possibility. At the current value of y the Newton correction in T and P to satisfy the two equations

$$Q_2 = \frac{\partial Q_2}{\partial P} = 0 \quad (24)$$

is determined, and y is subsequently reevaluated from eqns. (11) and (14).

Since, in particular, the pressure maximum is frequently close to the critical point, convergence of this procedure can be slow, and divergence can occur for direct substitution as well as for the Newton–Raphson method, unless the initial estimates are close.

IMPROVED ESTIMATES

One manner of improving the approximate calculation of the phase boundary is to take into account explicitly that the equilibrium phase composition changes with changing pressure. Rather than taking $\hat{y} = y^*(P_{\text{spec}})$ one could use

$$\hat{y}(P) = y^*(P_{\text{spec}}) + \frac{d}{dP}(y)_{P_{\text{spec}}}(P - P_{\text{spec}}) \quad (25)$$

With eqn. (25), the error in \hat{y} is proportional to ΔP^2 , and hence the error in T determined from Q_1 or Q_2 is proportional to ΔP^4 . This greatly increases the accuracy of the predictions and the range within which they yield meaningful results.

To calculate the pressure derivative of \mathbf{y} , we note that given a solution $\mathbf{x} = \mathbf{x}^*$ to a set of nonlinear equations

$$\mathbf{f}(\mathbf{x}) = \mathbf{0} \quad (26)$$

the derivative \mathbf{x}_α of this solution with respect to a parameter of the problem is the solution to the set of *linear* equations

$$\mathbf{J}\mathbf{x}_\alpha + \mathbf{f}_\alpha = \mathbf{0} \quad (27)$$

where \mathbf{J} is the Jacobian of \mathbf{f} , $J_{ij} = \partial f_i / \partial x_j$, and \mathbf{f}_α is the derivative of \mathbf{f} with respect to α , both evaluated at $\mathbf{x} = \mathbf{x}^*$.

In our case \mathbf{f} is the set of $N + 1$ eqns. (1 and 2) with $\mathbf{x}^T = (y_1, y_2, \dots, y_N, T)$, and α is the specified pressure. If the Newton–Raphson method is used for solving the saturation point eqns. (1 and 2), \mathbf{J} is available, and only calculation of the pressure derivatives of \mathbf{f} are required, i.e.

$$\frac{\partial f_i}{\partial P} = \frac{\partial \ln \phi_i(\mathbf{y})}{\partial P} - \frac{\partial \ln \phi_i(\mathbf{z})}{\partial P} \quad i = 1, 2, \dots, N \quad (28)$$

and

$$\frac{\partial f_{N+1}}{\partial P} = 0 \quad (29)$$

The saturation point calculation at $P = 60$ atm with $\hat{\mathbf{y}} = \mathbf{y}^*(P = 50 \text{ atm})$ using $Q_2(T, P) = 0$ is in error by 0.43 K (Table 1). Compensating for the change in $\hat{\mathbf{y}}$ by means of eqn. (25) reduces this error to 2×10^{-4} K.

The refined estimates using a linear extrapolation for $\hat{\mathbf{y}}$ can also be used for providing approximate values for the pressure and temperature maximum. To determine the temperature maximum we use as a basis a dew point calculation at $P_{\text{spec}} = 30$ atm. The phase boundary obtained combining eqn. (25) with $Q_2(T, P) = 0$ is shown in Table 2.

The correct maximum temperature is $T = 255.76$ K (at $P = 70.06$ atm), and the error of the prediction ($T_{\text{max}} = 255.62$ K) is a modest 0.14 K even though the prediction is based on a much lower pressure. To avoid negative \hat{y}_i in the extrapolation, eqn. (25), $\ln \hat{y}_i$ rather than the \hat{y}_i are extrapolated.

A similar approximate calculation of the pressure maximum, where $\hat{\mathbf{y}}$ is taken to vary linearly with temperature, is shown in Table 3. The extrapolation is based on a bubble point pressure calculation at $T_{\text{spec}} = 220$ K, with $P = 65.00$ atm.

The true pressure maximum is $P = 86.81$ atm at $T = 247.04$ K, and we observe that a decent approximation ($P = 85.8$ atm) is obtained based on

TABLE 2

Approximate phase boundary calculation from $P_{\text{spec}} = 30$ atm using extrapolated composition of equilibrium phase

P (atm)	T (K)	Error (K)
30	243.00	0
35	246.09	0
40	248.65	0
45	250.77	3×10^{-3}
50	250.49	1×10^{-2}
55	253.83	3×10^{-2}
60	254.87	5×10^{-1}
65	255.43	8×10^{-2}
70	255.62	0.13
75	255.30	0.18

extrapolation from a temperature about 30 K lower. The error may appear large compared to that for the maximal temperature, but it is worthwhile noticing that the maximum pressure is on the dew branch of the phase boundary, while the extrapolation originates from the bubble branch (the critical point being at $T = 232.2$ K). Hence the approximate phase boundary calculation is capable of passing the critical point.

The use of the methods presented here require periodic readjustment by means of a complete saturation point calculation if the complete phase boundary is desired, and in most cases probably 4–5 points will be sufficient for a quite accurate determination. The approximate phase compositions used for the extrapolation and the fact that resulting (T, P) pairs are known to be located in the two-phase region significantly reduce the probability of divergence or convergence to a trivial solution during calculation of high pressure saturation points.

TABLE 3

Approximate phase boundary calculation from $T_{\text{spec}} = 220$ K using extrapolated composition of equilibrium phase

T (K)	P (atm)	Error (atm)
220	65.00	0
225	70.47	2×10^{-3}
230	75.66	4×10^{-2}
235	80.20	0.23
240	83.88	0.39
245	85.78	0.78
247	85.75	1.06
250	84.02	2.1

An interesting possibility is to include the critical point as an anchor point for the phase boundary construction. An efficient method for location of the critical point has recently been developed (Michelsen, 1984), and this method provides as a byproduct the sensitivities needed for accurate extrapolation.

CONCLUSION

Suggestions are given for conducting simplified saturation point calculations, where only a single equation is solved. These simplified calculations may be of sufficient accuracy or they may be of value as initial estimates for a complete calculation. Whether the present methods are competitive with a stepwise construction of the entire phase boundary as suggested earlier (Michelsen, 1980) remains to be seen.

LIST OF SYMBOLS

e	error
f	deviation function, eqns. (1–3)
<i>i, j</i>	component indices
J	Jacobian matrix
<i>k</i>	iteration counter
<i>N</i>	number of components in mixture
<i>P</i>	pressure
Q_1	saturation point function, eqn. (3)
Q_2	saturation point function, eqn. (7)
S	Jacobian matrix, eqn. (15)
<i>T</i>	temperature
\hat{T}	estimate of saturation temperature
v	deviation vector, eqn. (6)
x	vector of independent variables
y, y*	equilibrium phase compositions
\hat{y}	estimate of equilibrium phase composition
Y	vector defined in eqn. (11)
z	feed composition

Greek symbols

α	parameter of thermodynamic model
ϵ	small quantity
λ	eigenvalue
ϕ_i	fugacity coefficient, component <i>i</i>

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