

## THE DAN METHOD FOR CALCULATION OF VAPOUR-LIQUID EQUILIBRIA USING AN EQUATION OF STATE; FLASH CALCULATION

Josef P. NOVÁK<sup>a</sup>, Vlastimil RŮŽIČKA, jr.<sup>a</sup>, Anatol MALIJEVSKÝ<sup>a</sup>,  
Jaroslav MATOUŠ<sup>a</sup> and Jan LINEK<sup>b</sup>

<sup>a</sup> *Department of Physical Chemistry,  
Prague Institute of Chemical Technology, 166 28 Prague 6 and*

<sup>b</sup> *Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague 6*

Received February 10th, 1984

---

A modification of the computational technique for flash calculations using an equation of state has been developed. The procedure consists in the double application of the Newton-Raphson method (DAN) to the set of equilibrium conditions. The algorithm is designed to minimize the number of iterations. It is, therefore, especially useful in successive calculations, where a family of solutions at slightly changing conditions is desired.

---

Computations of phase equilibria in chemical engineering practice are devoted mainly to flash calculations, which include a broad variety of tasks. A typical task involves calculation of composition of two equilibrium phases at specified feed composition and two additional variables chosen among temperature, pressure and vapour to feed mole ratio. The conventional approach to the solution of such a problem issues from a first estimate of the equilibrium ratios. Mass balance equations arranged in a convenient criterion then give a value of the fractional vaporization. This in turn yields new estimates of the equilibrium phase composition and thus provides new values of the equilibrium ratios. This procedure is repeated until convergence is achieved<sup>1-3</sup>. The equilibrium ratio is usually assumed to be independent of composition within the iteration loop.

The method suggested in this work is a modification of the previously developed procedure<sup>4</sup>. It is based on solving the set of equilibrium conditions including the equality of fugacities and mass balance equations. It adopts the Newton-Raphson method, which in comparison with conventional procedures is applied twice. First, to solve the set of equilibrium conditions to obtain equilibrium quantities. Second, to determine the first estimate of the next equilibrium point. The method is thus called the DAN method to denote the Double Application of the Newton-Raphson method. Methods similar to that described here has been published lately by Asselineau and coworkers<sup>5</sup> and by Michelsen<sup>6</sup>. In the present approach density rather

than pressure is considered as independent variable. Most of the problems in finding densities of equilibrium phases are thus avoided. All partial derivatives that are required for the Newton–Raphson method are evaluated analytically using dimensionless quantities. This facilitates the application of any equation of state if an algorithm that provides dimensionless quantities is supplied.

As presented here, the procedure is applicable to equilibrium separation calculations in multicomponent systems where a feed stream is split into liquid and vapour stream. The extension to three phase systems is straightforward. A similar procedure has also been designed for bubble and dew point calculations<sup>7</sup>.

### THEORETICAL

Flash calculation by an equation of state is based on solving the following set of equilibrium conditions and mass balance equations

$$\begin{aligned} p &= p^L = p(T, d^L, x), \\ p &= p^V = p(T, d^V, y), \\ f_i^L &= f_i(T, d^L, x) = f_i^V = f_i(T, d^V, y), \\ (1 - \Phi) x_j + \Phi y_j &= w_j, \\ i &= 1, 2, \dots, N, \quad j = 1, 2, \dots, N - 1, \end{aligned} \quad (1)$$

where  $p$  denotes the pressure,  $T$  is the temperature,  $f_i$  is the fugacity of  $i$ -th component and  $d$  is the saturated density. The superscripts L and V indicate the liquid and vapour phases, respectively.  $x$  and  $y$  are vectors of  $N - 1$  independent mole fractions in the liquid and vapour phases, respectively [ $x = (x_1, x_2, \dots, x_{N-1})$ ,  $y = (y_1, y_2, \dots, y_{N-1})$ ].  $w$  is the vector of the feed composition mole fractions [ $w = (w_1, w_2, \dots, w_{N-1})$ ].  $\Phi$  is the vapour to feed mole ratio, also called fractional vaporization, defined by

$$\Phi = n^V / (n^L + n^V), \quad (2)$$

with  $n^L$  and  $n^V$  being the moles in liquid and vapour phases, respectively.  $n^L$  and  $n^V$  may also denote the flow rate quantities expressed in moles per time. Set (1) consists of  $2N + 1$  nonlinear equations which contain  $3N + 2$  variables  $T, p, \Phi, d^L, d^V, x, y, w$ . Therefore,  $N + 1$  variables have to be known in advance, before the remaining  $2N + 1$  unknown ones are calculated by solving the set of Eqs (1). According to the quantities specified, several problems may be considered. The discussion here is devoted to the three following problems encountered most frequently in chemical engineering practice. In all cases the feed composition is given. The additional quantities specified are the following: temperature and pressure; temperature and vapour to feed mole ratio; pressure and vapour to feed mole ratio.

A computational technique proposed here is based on the double application of the Newton–Raphson method to the first three equations of set (1). The Newton–Raphson method requires that partial derivatives of pressure and fugacity with respect to temperature, density and composition are available. These derivatives can easily be evaluated using the dimensionless quantities given in Appendix B of the paper by Novák and coworkers<sup>7</sup>.

A detailed description on the application of the suggested procedure to isothermal flash calculation with specified variables of temperature, pressure and feed composition is presented below. The other two problems mentioned above entail merely the modification of the set of equilibrium conditions. In general, the solution follows the same pattern as described for isothermal flash calculation.

By expanding the last equation of set (1) in a Taylor series and cancelling all but linear terms we get

$$(1 - \Phi) \Delta x_j + \Phi \Delta y_j + (y_j - x_j) \Delta \Phi = c_j, \quad j = 1, 2, \dots, N - 1, \quad (3)$$

where

$$c_j = w_j - (1 - \Phi) x_j - \Phi y_j, \quad j = 1, 2, \dots, N - 1. \quad (4)$$

Let us expand the vapour phase pressure in a Taylor series and cancel all but linear terms. If we substitute in the expansion for  $\Delta y_j$  expressed from Eq. (3), we obtain

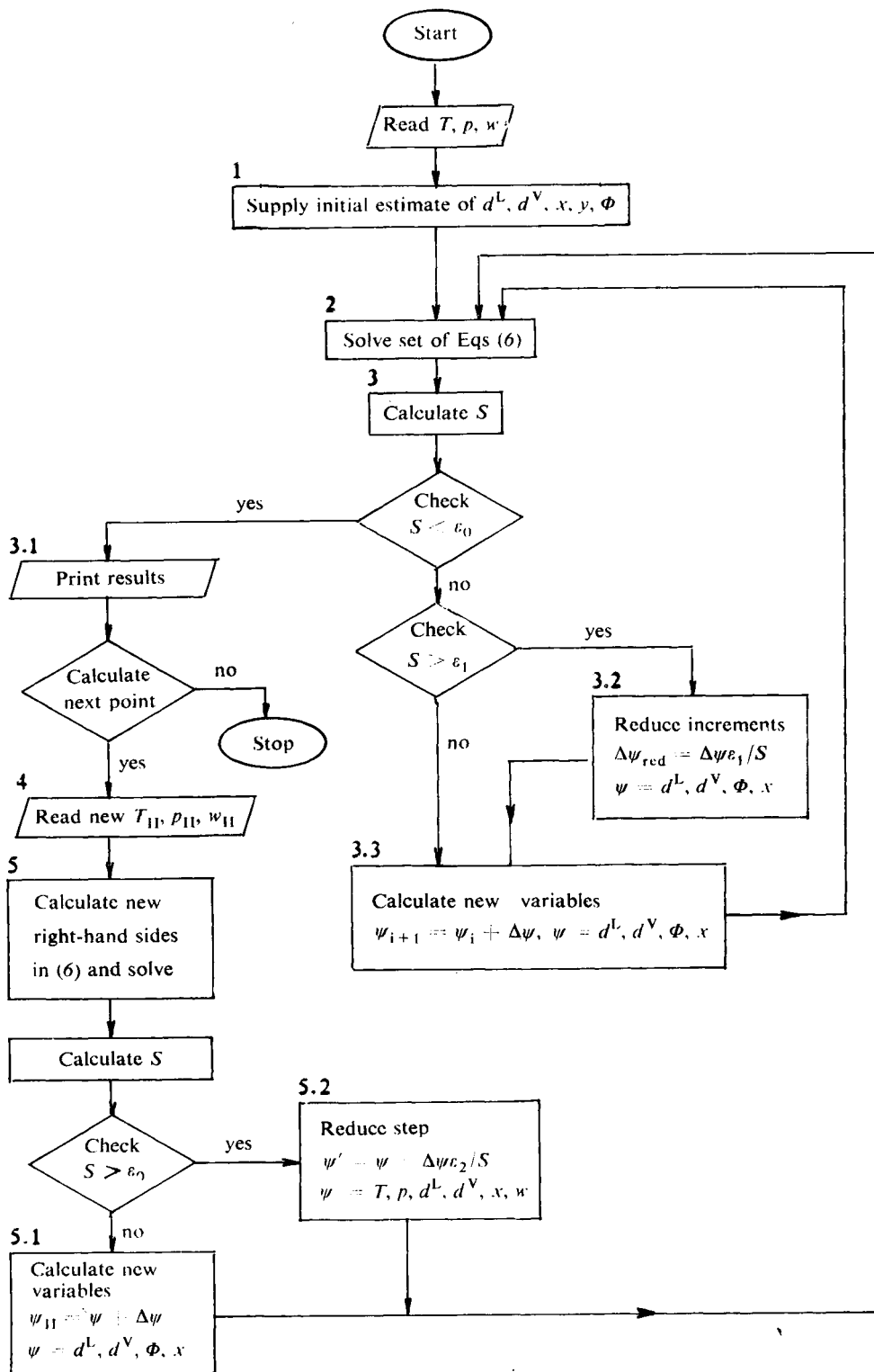
$$\begin{aligned} p^V &= p_0^V + (\partial p / \partial T)_0^V \Delta T + (\partial p / \partial d)_0^V \Delta d^V + \\ &+ \sum_{j=1}^{N-1} (\partial p / \partial y_j)_0^V (\Phi - 1) / \Phi \Delta x_j - \sum_{j=1}^{N-1} (\partial p / \partial y_j)_0^V (y_j - x_j) / \Phi \Delta \Phi + \\ &+ \sum_{j=1}^{N-1} (\partial p / \partial y_j)_0^V c_j / \Phi, \end{aligned} \quad (5)$$

where  $(\partial p / \partial T)_0^V$ ,  $(\partial p / \partial d)_0^V$ ,  $(\partial p / \partial y_j)_0^V$  are the derivatives of pressure determined at specified  $T$ ,  $d^V$ ,  $y$  with the composition of the vapour phase obtained from the last equation of set (1).

By expanding the fugacities of components in a similar way as described for pressure, the set of Eqs (1) becomes

$$\begin{aligned} (\partial p / \partial d)^L \Delta d^L + \sum_{j=1}^{N-1} (\partial p / \partial x_j)^L \Delta x_j &= p - p_0^L - (\partial p / \partial T)^L \Delta T, \\ (\partial p / \partial d)^V \Delta d^V + \sum_{j=1}^{N-1} (\partial p / \partial y_j)^V (\Phi - 1) / \Phi \Delta x_j - \\ - \sum_{j=1}^{N-1} (\partial p / \partial y_j)^V (y_j - x_j) / \Phi \Delta \Phi &= p - p_0^V - (\partial p / \partial T)^V \Delta T + \\ - \sum_{j=1}^{N-1} (\partial p / \partial y_j)^V c_j / \Phi, \\ (\partial f_i / \partial d)^L \Delta d^L - (\partial f_i / \partial d)^V \Delta d^V + \\ + \sum_{j=1}^{N-1} [(\partial f_i / \partial x_j)^L + (1 - \Phi) / \Phi \cdot (\partial f_i / \partial y_j)^V] \Delta x_j + \\ + \sum_{j=1}^{N-1} (\partial f_i / \partial y_j)^V (y_j - x_j) / \Phi \Delta \Phi &= \\ = (f_i)_0^V - (f_i)_0^L + [(\partial f_i / \partial T)^V - (\partial f_i / \partial T)^L] \Delta T + \sum_{j=1}^{N-1} (\partial f_i / \partial y_j)^V c_j / \Phi, \end{aligned} \quad (6)$$

$$i = 1, 2, \dots, N.$$



Thus the set of  $N + 2$  equations with  $N + 2$  unknowns  $d^V, d^L, \Phi, x$  is obtained. The flow diagram of the computational procedure is shown in Scheme 1 and entails the following steps:

1) for the given  $T, p$  and  $w$  a first estimate of variables  $d^L, d^V, x, y, \Phi$  must be supplied. This can be done by using, for example, Raoult's and Amagat's laws. Details are given in Appendix A.

2) Coefficients of the set of Eqs (6) are evaluated using values of  $d^L, d^V, y$  and  $\Phi$  determined in the preceding step. The increment  $\Delta T$  is equal to zero. By solving the set of Eqs (6) the increments  $\Delta d^L, \Delta d^V, \Delta x$  and  $\Delta \Phi$  are obtained.

3) Quantity  $S$  is calculated by

$$S = (\Delta d^V/d_{pc}^V)^2 + (\Delta d^L/d_{pc}^L)^2 + (\Delta \Phi)^2 + \sum_{j=1}^{N-1} (\Delta x_j)^2, \quad (7)$$

where pseudocritical densities  $d_{pc}^L$  and  $d_{pc}^V$  are given by

$$d_{pc}^L = \sum_{i=1}^N x_i(d_c)_i, \quad d_{pc}^V = \sum_{i=1}^N y_i(d_c)_i. \quad (8)$$

According to the size of  $S$ , three different cases may occur:

3. 1) If  $S$  is less than  $\varepsilon_0$ , the flash calculation is finished. A value of the convergence tolerance  $\varepsilon_0 = 10^{-7}$  is recommended as being sufficiently low in many cases where single precision is employed.

3. 2) If  $S$  exceeds a maximum step  $\varepsilon_1 \approx 0.1$  permitted in one iteration, values of calculated increments are reduced by

$$(\Delta \psi)_{red} = (\Delta \psi) \varepsilon_1 / S, \quad (9)$$

where  $\psi$  stands for  $d^L, d^V, \Phi$  and  $x$ . After reduction the calculation proceeds to step 3.3.

3. 3) If the relation  $\varepsilon_0 < S \leq \varepsilon_1$  is fulfilled, new values of variables are calculated

$$\psi_{i+1} = \psi_i + \Delta \psi, \quad (10)$$

where  $\psi$  is  $d^L, d^V, \Phi$  and  $x$ . A new value of the vapour phase composition is obtained from the last equation of set (1). The calculation then continues to step 2.

4) If it is desired to perform additional calculations at changed conditions of temperature, pressure and/or feed composition, the solution for given  $T, p, w$ , i.e. values of  $d^L, d^V, \Phi, x, y$  are utilized to obtain the first estimate of the next point characterized by  $T_{II}, p_{II}, w_{II}$ . The difference in temperature yields the increment  $\Delta T = T_{II} - T$ . Using this increment, adding the difference in pressure  $p_{II} - p$  to the first two equations of set (6) and calculating new  $c_j$  according to Eq. (4), the new right-hand sides of the set of Eqs (6) are evaluated. The coefficients on the left-hand sides are known from the last iteration step of the preceding point.

5) The solution of the set of Eqs (6) with the coefficients of the matrix obtained in step 4 gives new values of increments  $\Delta d^V, \Delta d^L, \Delta \Phi$  and  $\Delta x$ . Thus, a new value of  $S$  is determined. According to its size, two cases are considered:

SCHEME 1

Flow diagram for isothermal flash calculation (figures above boxes indicate the steps as described in text).

5. 1) If  $S$  is less or equal to a maximum step allowed along the equilibrium curve  $\varepsilon_2 \approx 0.1$ , the values of  $\psi_{11}$  given by

$$\psi_{11} = \psi + \Delta\psi \quad (11)$$

( $\psi = d^V, d^L, \Phi, x$ ) are used for the calculation of the equilibrium point specified by  $T_{11}, p_{11}$  and  $w_{11}$ . The calculation now returns to step 2.

5. 2) If  $S$  is greater than  $\varepsilon_2$  the next equilibrium point is too far from the preceding one. Then it is desirable to insert an intermediate step thus ensuring the calculation not to fail. In this case the intermediate point is calculated with the parameters

$$\psi' = \psi + \Delta\psi\varepsilon_2/S, \quad (12)$$

where  $\psi$  stands for  $T, p, d^L, d^V, x, w$ . Here the calculation is also returned to step 2.

## DISCUSSION

Finally, the applicability of the DAN method to isothermal flash calculation is presented. Vapour-liquid equilibrium data on the methane-ethane-propane-toluene-1-methylnaphthalene system by Li and coworkers<sup>8</sup> were chosen for illustration. The computations were performed using the Soave-Redlich-Kwong equation of state<sup>9</sup> with interaction parameters given by Li and coworkers<sup>8</sup>. The value of the convergence tolerance  $\varepsilon_0$  was set to  $1 \cdot 10^{-12}$ .

The mixture composition is as follows: methane 31 mol %, ethane 8 mol %, propane 6 mol %, toluene 33 mol %, 1-methylnaphthalene 22 mol %. In Table I, the number of Newton-Raphson iterations required to converge  $p, T$  specifications when proceeding from one equilibrium point to another is shown. The ability of the DAN method to find the solution even if the equilibrium point is rather far from the previously specified one is also illustrated in Table I. Convergence was obtained between two equilibrium points having the difference in pressure higher than one order of the magnitude.

The DAN method suggested here is very effective as it provides both the solution of the specified problem and a very qualified first estimate of the next equilibrium point. This enables to proceed from one equilibrium point to another one rather quickly and to achieve convergence within a few iterations. In successive computations, such as, for example, column calculations, the procedure offers a wide variety of applications. Its convergence efficiency does not depend on the number of variables, for example temperature, pressure or feed composition, that are changed when proceeding between equilibrium points.

The estimate of the next equilibrium point is obtained using a linear approximation of the path between two adjacent points. The procedure is therefore especially convenient for multicomponent mixtures as it leads to a set of linear equations only.

None of the variables to be calculated, for example liquid and vapour phase composition, vapour to feed mole ratio, liquid and vapour phase densities in isothermal flash calculations, is assumed to remain constant within the iteration loop. The convergence efficiency is thus enhanced in comparison with most conventional methods.

The procedure has been developed for use with a single equation of state. All partial derivatives which are necessary for the application of the Newton-Raphson method, are evaluated analytically employing the dimensionless quantities. Most of the computational problems due to the approximation of derivatives by finite differences may thus be avoided.

#### APPENDIX

##### Determination of Estimate of Equilibrium Quantities

The estimate of equilibrium quantities, *i.e.* vapour to feed mole ratio or temperature or pressure, composition of liquid and vapour equilibrium phases and liquid and vapour phase densities, is determined assuming the ideal solution (Raoult's law) and the ideal behaviour of the vapour phase (Dalton's law). The pure component vapour pressure and the vapour and liquid phase densities are estimated by using Eqs (A2) to (A6) given in Appendix A of the paper by Novák and coworkers<sup>7</sup>.

The following procedures are adopted for particular cases discussed in the paper.

TABLE I

Number of Newton-Raphson iterations required to converge  $p$ ,  $T$  specifications when proceeding from one equilibrium point to another one

Preceding point		Next point		No of iterations
$T$ , K	$p$ , MPa	$T$ , K	$p$ , MPa	
—	—	377.6	1.379	4 <sup>a</sup>
377.6	1.379	377.6	2.758	3
377.6	10.34	377.6	12.07	4
377.6	12.07	410.9	14.09	3
410.9	1.648	444.3	1.407	4
377.6	1.379	377.6	13.79	15 <sup>b</sup>
444.3	13.64	377.6	1.379	7 <sup>c</sup>

<sup>a</sup> Initial estimate obtained by Raoult's law; <sup>b</sup> two intermediate steps automatically supplied by the algorithm required ( $\epsilon_2 = 0.15$ ); (the  $(p, T)$  coordinates of the intermediate steps: (377.6 K, 3.539 MPa), (377.6 K, 7.726 MPa); <sup>c</sup> one intermediate step having the  $(p, T)$  coordinates (383.6 K, 2.472 MPa) required ( $\epsilon_2 = 0.15$ ).

1) *Flash calculation for specified T, p, w.* For a given temperature  $T$ , the ideal vapour-liquid equilibrium  $K$ -values are calculated by

$$K_i = p_i^0/p \quad i = 1, 2, \dots, N. \quad (A1)$$

The estimate of the vapour to feed mole ratio is obtained by solving the equation (see e.g. King<sup>1</sup>)

$$\sum_{i=1}^N \frac{w_i(K_i - 1)}{1 + \Phi(K_i - 1)} = 0. \quad (A2)$$

Applying the Newton-Raphson method, the  $(j + 1)$ -th approximation of  $\Phi$  is given by

$$\Phi_{j+1} = \Phi_j + \frac{\sum_{i=1}^N \frac{w_i(K_i - 1)}{1 + \Phi_j(K_i - 1)}}{\sum_{i=1}^N \frac{w_i(K_i - 1)^2}{[1 + \Phi_j(K_i - 1)]^2}}. \quad (A3)$$

The first guess of  $\Phi$  is set to 0.5. The equilibrium composition of the liquid and the vapour phases is found by using  $\Phi$  and  $K_i$  determined previously

$$x_i = w_i/[1 + \Phi(K_i - 1)], \quad (A4)$$

$$y_i = K_i x_i, \quad i = 1, 2, \dots, N. \quad (A5)$$

2) *Flash calculation for specified T,  $\Phi$ , w.* The estimate of pressure is found from Eq. (A2) which can be modified with the aid of Eq. (A1) to give

$$\sum_{i=1}^N \frac{w_i(p_i^0 - p)}{p + \Phi(p_i^0 - p)} = F = 0. \quad (A6)$$

For  $p_{j+1}$  then follows

$$p_{j+1} = p_j + \frac{F_j}{\sum_{i=1}^N \frac{w_i p_i^0}{[p_j + \Phi(p_i^0 - p_j)]^2}}, \quad (A7)$$

where  $F_j$  is the value of function  $F$  determined at the temperature  $T_j$ . The first approximation of pressure needed for the application of Eq. (A7) is calculated from

$$\ln p = \ln p_{pc} + 6.9(1 - T_{pc}/T). \quad (A8)$$

Pseudocritical temperature and pressure are evaluated by the Kay rule using the specified feed composition  $w$ . Composition of equilibrium phases is determined by Eqs (A4) and (A5) with equilibrium  $K$ -values calculated from the known vapour pressure and the estimated total pressure.

3) *Flash calculation for specified p,  $\Phi$ , w.* The estimate of temperature is found from (A6). Using the vapour pressure equation (Eq. (A2) in the work<sup>7</sup>), it follows for  $T_{j+1}$



$$\frac{1}{T_{j+1}} = \frac{1}{T_j} - \frac{F_j/p}{\sum_{i=1}^N \frac{w_i p_i^0 [-B/T_{ri}^2 + C/T_{ri} + 6DT_{ri}^5 + \omega_i(-F/T_{ri}^2 + G/T_{ri} + 6HT_{ri}^5)]}{T_{ci}[p + \Phi(p_i^0 - p)]^2_{T=T_j}}} \quad (49)$$

The first approximation of temperature is obtained from Eq. (48). The next steps are analogous to those described above for flash calculation at specified  $T$ ,  $\Phi$ ,  $w$ .

#### LIST OF SYMBOLS

$d$	molar density, $d = n/V$
$f$	fugacity
$K$	vapour-liquid equilibrium $K$ -value
$n$	number of moles
$N$	number of components
$p$	pressure
$p^0$	pure component vapour pressure
$R$	gas constant
$S$	quantity defined by Eq. (7)
$T$	temperature
$V$	volume
$V_m$	molar volume
$w$	vector of feed composition mole fractions
$x$	vector of liquid phase mole fractions
$y$	vector of vapour phase mole fractions
$\epsilon_0$	convergence tolerance
$\epsilon_1$	maximum step permitted in one iteration
$\epsilon_2$	maximum allowed step along the equilibrium curve
$\Phi$	vapour to feed mole ratio
$\omega$	acentric factor

#### Subscripts

c	critical property
i	i-th component in the $N$ component system
pc	pseudocritical property
r	reduced property

#### Superscripts

L	liquid phase
V	vapour phase

#### REFERENCES

1. King C. J.: *Separation Processes*. McGraw-Hill, New York 1980.
2. Prausnitz J. M., Anderson T. F., Grens E. A., Eckert C. A., Hsieh R., O'Connell J. P.: *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*. Prentice-Hall, Englewood Cliffs, New Jersey 1980.

3. Michelsen M. L.: Fluid Phase Equil. 9, 21 (1982).
4. Novák J., Šobr J.: *Příklady z technické fyzikální chemie. I. Stavové chování, termodynamické a transportní vlastnosti reálných tekutin*. Published by SNTL, Prague 1977, 1980.
5. Asselineau L., Bogdanic G., Vidal J.: Fluid Phase Equil. 3, 273 (1979).
6. Michelsen M. L.: Fluid Phase Equil. 4, 1 (1980).
7. Novák J. P., Růžička V., jr, Malijevský A., Matouš J., Linek J.: This Journal 50, 1 (1985).
8. Li Y.-H., Dillard K. H., Robinson R. L., jr: J. Chem. Eng. Data 26, 200 (1981).
9. Soave G.: Chem. Eng. Sci. 27, 1197 (1972).

Translated by the author (J. L.).