

## THE DAN METHOD FOR CALCULATION OF VAPOUR-LIQUID EQUILIBRIA USING AN EQUATION OF STATE; BUBBLE AND DEW POINT CALCULATIONS

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A modification of the computational technique for calculating bubble and dew points using an equation of state has been proposed. The procedure consists in the Double Application of the Newton-Raphson method (DAN) to the set of equilibrium conditions. The algorithm is very effective as it provides both values of equilibrium variables and a very qualified first estimate of the next equilibrium point. This enables to proceed along the phase envelope rather quickly and to achieve convergence within a few iterations except in the close vicinity of the critical point.

Calculation of vapour-liquid equilibria (VLE) using an equation of state is very effective as it uses the same thermodynamic model for both fluid phases. At elevated pressures and especially in the vicinity of the critical point this method provides practically the only possibility to determine the equilibrium quantities.

Several methods are employed to calculate VLE by an equation of state<sup>1-5</sup>. The already existing methods may be divided into two groups. The procedures which require only the evaluation of the fugacity of components belong to the first group and are represented for example by the method developed by Prausnitz and Chueh<sup>1</sup>. The second group comprises the methods which, except for the component fugacity, require also the derivatives of fugacity with respect to composition, temperature and pressure. The very elaborate procedure suggested by Michelsen<sup>5</sup> belongs to the latter group.

The formal simplicity is the greatest advantage of the first group methods. This is, however, compensated by the higher number of iterations required to obtain convergence of the problem. In some cases, the number of iterations may be as high as several hundred. Very frequently these methods fail in the vicinity of the critical point. In addition, the pressure is often considered to be an independent variable. Then it is necessary to decide whether the density determined for the specified temperature, pressure and estimated composition belongs to the liquid or to the vapour phases<sup>6-8</sup>.

The method suggested in this work is a modification of the previously developed procedure<sup>9</sup>. It adopts the Newton–Raphson method for calculating VLE and thus belongs to the second group. Methods similar to that described here have been published lately by Asselineau and coworkers<sup>10</sup> and by Michelsen<sup>5</sup>. Contrary to the above-mentioned papers, this work presents separately methods for calculating bubble and dew points (this paper) and flash calculation procedures (the second paper). Sets of equations for different special cases are explicitly given. 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.

This paper is devoted to the bubble point temperature and the dew point temperature and to the bubble point pressure and the dew point pressure calculations. Flash calculations are dealt with in the second paper. In these cases a composition of equilibrium phases for a given overall composition is usually sought. In addition, two more quantities, for example temperature and pressure, must also be specified.

The application of the Newton–Raphson method to the set of Eqs (1) is performed in two consecutive steps. First, to solve the equilibrium conditions to obtain the 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. 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<sup>11</sup> given in Appendix B.

## THEORETICAL

Calculation of vapour–liquid equilibria by an equation of state is based on solving the following set of equilibrium conditions

$$\begin{aligned} p &= p^V = p(T, d^V, y), \\ p &= p^L = p(T, d^L, x), \\ f_i &= f_i^V = f_i(T, d^V, y) = f_i^L = f_i(T, d^L, x), \quad i = 1, 2, \dots, N, \end{aligned} \quad (1)$$

where  $p$  denotes the pressure,  $T$  is the temperature,  $f_i$  is the fugacity of the  $i$ -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 the vapour phases, respectively [ $x = (x_1, x_2, \dots, x_{N-1})$ ,  $y = (y_1, y_2, \dots, y_{N-1})$ ]. In the  $N$ -component system this set of non-linear equations gives  $N + 2$  conditions for  $2(N + 1)$  variables  $T, p, d^V, d^L, x, y$ . Therefore,  $N$  variables must be specified before the remaining  $N + 2$  unknown ones are calculated by solving the set of Eqs (1).

Computation of VLE in the one-component system ( $N = 1$ ) is the simplest case of solving the set of Eqs (1). From the equality of pressure and fugacities the boiling point temperature or the saturation pressure is found for a given pressure or temperature. In multicomponent mixtures the set of Eqs (1) is usually solved for a given composition of the liquid (bubble point) or the vapour (dew point) phases. In addition, the system pressure or temperature must also be specified.

By expanding pressure and fugacities of components in a Taylor series and cancelling all but linear terms the set of Eqs (1) can be modified into the following form:

$$\begin{aligned}
 p &= p_0^L + (\partial p / \partial T)_0^L \Delta T + (\partial p / \partial d)_0^L \Delta d^L + \sum_{j=1}^{N-1} (\partial p / \partial x_j)_0^L \Delta x_j, \\
 p &= p_0^V + (\partial p / \partial T)_0^V \Delta T + (\partial p / \partial d)_0^V \Delta d^V + \\
 &\quad + \sum_{j=1}^{N-1} (\partial p / \partial y_j)_0^V \Delta y_j, \\
 f_i^V &= (f_i)_0^V + (\partial f_i / \partial T)_0^V \Delta T + (\partial f_i / \partial d)_0^V \Delta d^V + \\
 &\quad + \sum_{j=1}^{N-1} (\partial f_i / \partial y_j)_0^V \Delta y_j = \\
 &= (f_i)_0^L + (\partial f_i / \partial T)_0^L \Delta T + (\partial f_i / \partial d)_0^L \Delta d^L + \\
 &\quad + \sum_{j=1}^{N-1} (\partial f_i / \partial x_j)_0^L \Delta x_j, \quad i = 1, 2, \dots, N.
 \end{aligned} \tag{2}$$

Here the subscript 0 denotes the quantity which corresponds to values of variables  $T$ ,  $d^V$ ,  $d^L$ ,  $x$ ,  $y$ . The subscript 0 is in subsequent text omitted.

A detailed description on the application of the suggested procedure to the calculation of the bubble point pressure is presented below. The other problems, *i.e.* the calculation of the dew point pressure and the calculation of the bubble point temperature and dew point temperature are presented only briefly.

#### *Calculation of Bubble Point Pressure for Specified T and x*

The set of Eqs (2) can be rearranged in this case as follows:

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

$$\begin{aligned}
 & (\partial f_i / \partial d)^V \Delta d^V + \sum_{j=1}^{N-1} (\partial f_i / \partial y_j)^V \Delta y_j - (\partial f_i / \partial d)^L \Delta d^L = \\
 & = (f_i)_0^L - (f_i)_0^V + [(\partial f_i / \partial T)^L - (\partial f_i / \partial T)^V] \Delta T + \\
 & + \sum_{j=1}^{N-1} (\partial f_i / \partial x_j)^L \Delta x_j, \quad i = 1, 2, \dots, N.
 \end{aligned} \tag{3}$$

As the system pressure is not specified in this case, the first two equations of set (2) are joined into one equation.

Scheme 1 shows the flow diagram of the computational procedure which includes the following steps:

1) At the beginning a first estimate of the vapour and of the liquid phase densities  $d^V$  and  $d^L$  and of the vapour phase composition  $y$  must be supplied. This can be achieved by using, for example, Raoult's and Amagat's laws. Details are given in Appendix A.

2) Coefficients of the set of Eqs (3) are evaluated using values of  $d^V$ ,  $d^L$  and  $y$  determined in the preceding step. The increments  $\Delta T$  and  $\Delta x$  are equal to zero. By solving the set of Eqs (3) the increments  $\Delta d^V$ ,  $\Delta d^L$ ,  $\Delta y$  are obtained.

3) Quantity  $S$  is calculated by

$$S = (\Delta d^V / d_{pc}^V)^2 + (\Delta d^L / d_{pc}^L)^2 + \sum_{j=1}^{N-1} (\Delta y_j)^2, \tag{4}$$

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

$$d_{pc}^L = \sum_{i=1}^N x_i (d_c)_i, \quad d_{pc}^V = \sum_{i=1}^N y_i (d_c)_i. \tag{5}$$

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

3.1) If  $S$  is less than  $\varepsilon_0$ , a computation of the bubble point pressure is finished. Here  $\varepsilon_0$  is the chosen convergence tolerance. A value of  $\varepsilon_0$  of  $10^{-7}$  gives solutions that in single precision do not change significantly upon further reduction of  $\varepsilon_0$ .

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

$$(\Delta \psi)_{red} = \Delta \psi \varepsilon_1 / S, \tag{6}$$

where  $\psi$  stands for  $d^V$ ,  $d^L$  and  $y$ . This step-limiting often avoids a divergence of iterations. A value of  $\varepsilon_1$  of 0.1 is recommended. 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

$$\psi_{i+1} = \psi_i + \Delta\psi, \quad (7)$$

where  $\psi$  is  $d^V$ ,  $d^L$  and  $y$ . The calculation then continues to step 2.

4) If it is desired to proceed along the equilibrium curve, the solution for the given  $T$ ,  $x$ , i.e. the values of  $d^V$ ,  $d^L$  and  $y$  are utilized to obtain the first estimate of the next point characterized by  $T_{II}$  and  $x_{II}$ . Differences between temperatures and compositions yield the increments  $\Delta T = T_{II} - T$  and  $\Delta x = x_{II} - x$ . Using these increments the right-hand sides of the set of Eqs (3) are evaluated. The coefficients on the left-hand side are known from the last iteration step of the preceding point.

5) The solution of Eqs (3) with the coefficients of the matrix obtained in step 4 gives new values of increments  $\Delta d^V$ ,  $\Delta d^L$  and  $\Delta y$ . Thus, a new value of  $S$  is determined. According to its size, two cases are considered:

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

$$\psi_{II} = \psi + \Delta\psi \quad (8)$$

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

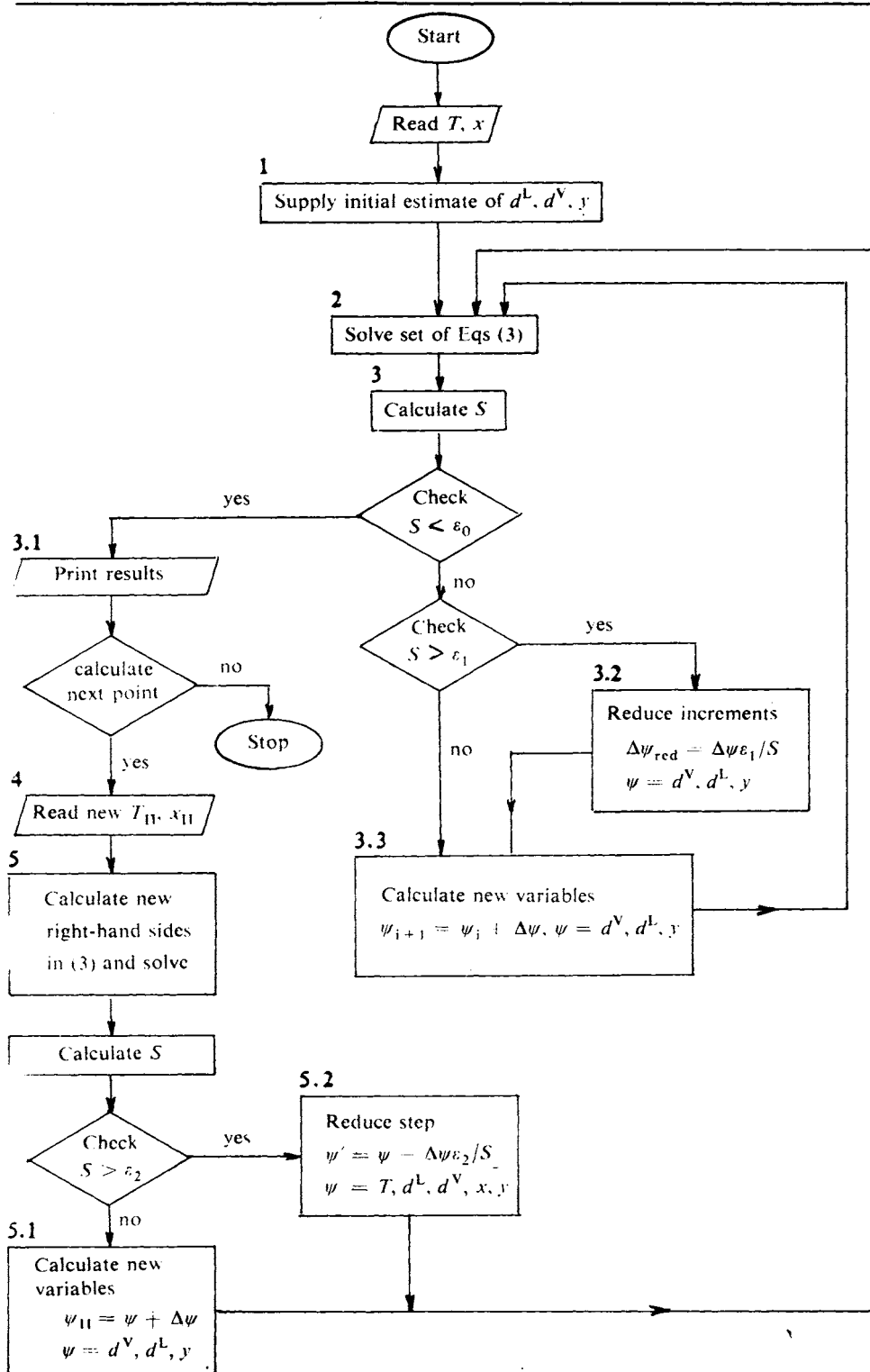
5.2) If  $S$  is greater than  $\varepsilon_2$ , the next equilibrium point is too far from the preceding one. Then it is desirable to insert an intermediate step thus ensuring the calculation not to fail. In this case the intermediate point is calculated with parameters

$$\psi' = \psi + \Delta\psi \varepsilon_2 / S, \quad (9)$$

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

#### *Calculation of Dew Point Pressure at Specified T and y*

It can easily be seen that in this case the set of equilibrium conditions differs from set (3) by designation of phases only. Therefore, for the determination of the dew point pressure, the procedure for calculating the bubble point pressure described above may be employed by interchanging densities and compositions of both phases in Eqs (3). The only difference is in determining the first approximation. Details are given in Appendix A.



### Calculation of Bubble Point Temperature at Specified $p$ and $x$

The set of Eqs (2) can be modified in this case into the form

$$\begin{aligned}
 & -[\partial p/\partial(1/T)]^L \Delta(1/T) - (\partial p/\partial d)^L \Delta d^L = p_0^L - p + \\
 & + \sum_{j=1}^{N-1} (\partial p/\partial x_j)^L \Delta x_j, \\
 & [\partial p/\partial(1/T)]^V \Delta(1/T) + (\partial p/\partial d)^V \Delta d^V + \sum_{j=1}^{N-1} (\partial p/\partial y_j)^V \Delta y_j = \\
 & = p - p_0^V, \\
 & \{[\partial f_i/\partial(1/T)]^V - [\partial f_i/\partial(1/T)]^L\} \Delta(1/T) + (\partial f_i/\partial d)^V \Delta d^V + \\
 & + \sum_{j=1}^{N-1} (\partial f_i/\partial y_j)^V \Delta y_j - (\partial f_i/\partial d)^L \Delta d^L = \\
 & = (f_i)_0^L - (f_i)_0^V + \sum_{j=1}^{N-1} (\partial f_i/\partial x_j)^L \Delta x_j, \quad i = 1, 2, \dots, N,
 \end{aligned} \tag{10}$$

where

$$\Delta(1/T) = (1/T_{i+1}) - (1/T_i). \tag{11}$$

To enhance convergence it is more convenient to consider the dependence of pressure and fugacities on the reciprocal temperature rather than on temperature. The order of the magnitude of the increments for unknowns  $\Delta T$ ,  $\Delta d^L$ ,  $\Delta d^V$  and  $\Delta y_j$  ( $j = 1, 2, \dots, N - 1$ ) is thus brought much closer.

The computational procedure is similar to that designed for calculating the bubble point pressure. Quantity  $S$  is now defined by

$$S = (\Delta T/T_{pc})^2 + (\Delta d^V/d_{pc}^V)^2 + (\Delta d^L/d_{pc}^L)^2 + \sum_{j=1}^{N-1} (\Delta y_j)^2, \tag{12}$$

where  $T_{pc}$  is the pseudocritical temperature given by

$$T_{pc} = \sum_{i=1}^N x_i T_{ci}. \tag{13}$$

The procedure then proceeds in the same manner as described for calculating the bubble point pressure.

#### SCHEME 1

Flow diagram for bubble point pressure calculation (figures above boxes indicate the steps as described in text)

The procedure developed for calculating the bubble point temperature can also be applied for computing the dew point temperature after interchanging the densities and compositions of phases.

## DISCUSSION

Calculation of the phase envelope by the procedure suggested in this work is very effective. This effectiveness is due to a qualified first estimate obtained on the basis of calculation of the preceding equilibrium point. In spite of this fact it may happen that the computation fails. Let us omit the failure due to a bad first estimate obtained on the basis of Raoult's and Amagat's laws. When the computation starts from a real equilibrium point, the reasons which may lead to failure of the calculation are as follows: *a)* the value of  $\varepsilon_2$  is too high; *b)* a wrong alternative of the computation of phase envelope is chosen; *c)* the thermodynamic instability in the two phase region. *Too high value of  $\varepsilon_2$ .* A value of  $\varepsilon_2$  of 0.1 is recommended. If the temperature is considerably lower than the critical temperatures of all components a higher value of  $\varepsilon_2$  may be used. In the critical region it is necessary to choose  $\varepsilon_2 < 0.1$ , especially if it is desired to approach a vicinity of the critical point.

*Wrong alternative.* It is always possible to find a solution for a given problem, if the temperature is lower than the critical temperatures of all components. In some cases, however, such solutions may not exist or multiple solutions may occur.

Let us suppose that in a binary system depicted in Fig. 1 quantities corresponding to point A (i.e.  $T, p_A, y_1, d^V$ ) and to point A' (i.e.  $T, p_A, x_1, d^L$ ) are known. Let us further assume that it is desired to calculate the equilibrium points B and B' at an equal

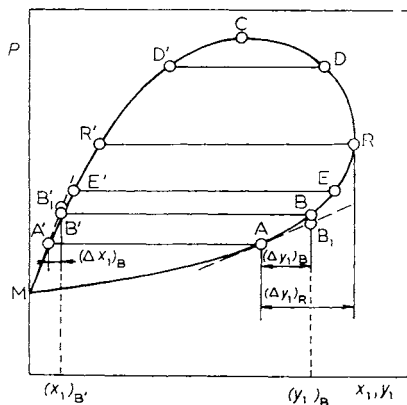


FIG. 1

Phase envelope including the retrograde region in a binary system



temperature, at the liquid and vapour phase compositions  $(x_1)_B$  and  $(y_1)_B$ . If the equilibrium curve is approximated by a straight line, points  $B_1$  and  $B'_1$  are used as a first estimate. Starting from point A the increment in the composition of the vapour phase must not exceed the value  $(\Delta y_1)_R$ . This means that it is not possible to find a dew point for a composition  $y_1 > (y_1)_R$  owing to the fact that for this composition the solution of the set of Eqs (3) does not exist.

Starting from equilibrium point A, only the part of the equilibrium curve which is restricted by points  $RR'$ , i.e. the dew point curve given by  $M-A-B-E-R$  and the bubble point curve given by points  $M-A'-B'-E'-R'$ , can be reached when the procedure for calculation of the dew point pressure was applied. As a result of this procedure, the total pressure and the liquid phase composition are obtained for the given temperature and the vapour phase composition. Thus both equilibrium points lying on the bubble and the dew point curve, e.g. E and  $E'$ , are determined simultaneously. Starting from equilibrium point D, only the part of the equilibrium curve which is given by points  $R'-D'-C-D-R$  can be calculated using the dew point pressure procedure. This indicates that the dew point pressure procedure does not enable to construct the whole phase envelope.

However, employing the bubble point pressure procedure we can proceed along the whole bubble point curve starting from equilibrium point  $A'$ . As this procedure yields also the vapour phase composition, the whole phase envelope may thus be constructed.

It is worth mentioning here that the procedure suggested in this work cannot be used if the critical point is desired. Choosing sufficiently small increments in mole fractions when proceeding along the equilibrium curve, i.e. choosing a small value of  $\varepsilon_2$ , it is possible to reach the close vicinity of the critical point. Therefore, the critical point can be found from the equilibrium curve calculation by extrapolation.

*Thermodynamic instability* in the two phase region is illustrated on the example of calculation of the bubble point pressure in a binary system. All relations derived here can be extended to multicomponent systems, too. The same conclusions are also valid for the bubble point temperature, the dew point temperature and the dew point pressure calculations.

The determinant of the set of Eqs (3) is given by

$$D_s = \begin{vmatrix} (\partial p / \partial d)^V & (\partial p / \partial y_1)^V & -(\partial p / \partial d)^L \\ (\partial f_1 / \partial d)^V & (\partial f_1 / \partial y_1)^V & -(\partial f_1 / \partial d)^L \\ (\partial f_2 / \partial d)^V & (\partial f_2 / \partial y_1)^V & -(\partial f_2 / \partial d)^L \end{vmatrix}. \quad (14)$$

To rearrange Eq. (14) the following relations are utilized

$$-(\partial p / \partial d)^V / (RT) + \sum_{i=1}^2 y_i (\partial f_i / \partial d)^V d^V / f_i^V = 0, \quad (15)$$

$$-(\partial p / \partial y_j)^V / (RT) + \sum_{i=1}^2 y_i (\partial f_i / \partial y_j)^V d^V / f_i^V = 0. \quad (16)$$

For determinant (14) then follows

$$D_s = \frac{f_1^V f_2^V}{y_2 d^V} \begin{vmatrix} (\partial p / \partial d)^V & (\partial p / \partial y_1)^V & -(\partial p / \partial d)^L \\ \left( \frac{\partial \ln f_1}{\partial d} \right)^V & \left( \frac{\partial \ln f_1}{\partial y_1} \right)^V & -\frac{(\partial f_1 / \partial d)^L}{(f_1)^V} \\ 0 & 0 & C \end{vmatrix}, \quad (17)$$

where

$$C = (\partial p / \partial d)^L / (RT) - d^V \sum_{i=1}^2 y_i (\partial f_i / \partial d)^L / f_i^V. \quad (19)$$

Eq. (17) can be modified to obtain

$$D_s = \frac{f_1^V f_2^V}{y_2 d^V} D_a^V C, \quad (19)$$

where

$$D_a^V = \begin{vmatrix} (\partial p / \partial d)^V & (\partial p / \partial y_1)^V \\ (\partial \ln f_1 / \partial d)^V & (\partial \ln f_1 / \partial y_1)^V \end{vmatrix}. \quad (20)$$

We call  $D_a^V$  the determinant of stability in the vapour phase. It follows from the existing conditions of thermodynamic stability<sup>12-15</sup> in the vapour phase that  $D_a^V$  must be positive in homogeneous and metastable regions. On the spinodal curve which represents the boundary between the metastable and the unstable region determinant  $D_a^V$  equals zero. The same is valid for the liquid phase.

It is obvious that points lying on the spinodal curve cannot be utilized while solving the set of Eqs (3). Crossing the spinodal curve the sign of determinant  $D_a^V$  changes and so does the sign of determinant  $D_s$  as the value of quantity  $C$  is positive. This causes the change of the sign of increments  $\Delta d^V$ ,  $\Delta d^L$  and  $\Delta y_1$ . It may happen that after crossing the spinodal curve a trivial solution  $x = y$ ,  $d^L = d^V$  is found. This difficulty may be overcome by checking the thermodynamic stability in both phases. The thermodynamic stability also guarantees that the equilibrium quantities, viz. compositions and densities will remain in proper phases in all iteration steps.

The reasons that may lead to thermodynamic instability are as follows: 1) inaccurate first estimate of equilibrium quantities especially of the liquid phase density; 2) too high value of step  $\varepsilon_2$  along the equilibrium curve especially in the presence of concave regions on the equilibrium curve; 3) the vicinity of the critical point; 4) the originally two phase system consisting of the liquid and the vapour phases splits into two or more liquid phases at conditions specified.

Complete check of thermodynamic stability in both phases in all iteration steps would result in mainly multicomponent systems in a considerable increase of computer time requirements. We have observed that in many cases it is sufficient to perform the complete check, which entails the calculation of determinants  $D_a^V$  and  $D_a^L$ , only at the end of the calculation when the convergence was achieved.

To illustrate the application of the DAN method several examples are here presented. They include the construction of the phase envelope in binary two phase systems consisting of the liquid and the vapour phases. Multicomponent systems and systems which split into two liquid phases will be dealt with in a separate paper.

The discussion is devoted to the following cases: 1) retrograde region; 2) vicinity of the mixture critical point; 3) azeotropic mixtures. In all cases the Soave-Redlich-Kwong<sup>16</sup> equation of state was adopted. A value of the convergence tolerance  $\varepsilon_0 = 1 \cdot 10^{-12}$  was employed and computations were performed in double precision.

Two isotherms in the system methane-propane which include the retrograde region are shown in Fig. 2. In isothermal calculations with the step along the equilibrium curve  $|\Delta x_1| = 0.05$  the number of iterations was 4 in the whole concentration region except in the vicinity of the critical point. Changing the temperature from 275 K to 300 K required 5 iterations.

In the system methane-propane and in similar systems with one of the components being at a supercritical temperature, some difficulties may arise in obtaining the first estimate of equilibrium quantities. Two possibilities are outlined which guarantee a qualified initial guess and thus lead to convergence of the iteration procedure. First, it is possible to start from a temperature below the critical temperature of all components in the mixture. Once the solution is found the temperature can be raised

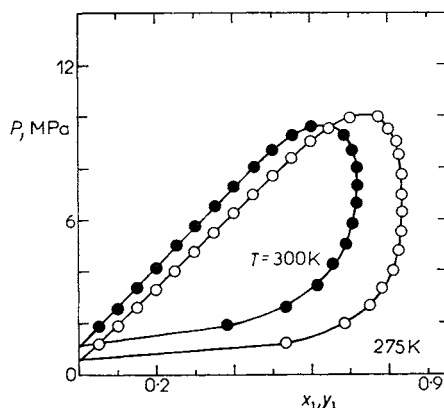


FIG. 2

Phase envelopes in the system methane(1) + propane(2). Up to 4 iterations required to construct the equilibrium points

stepwise gradually up to the desired value. Second, we can start at the given temperature from the mixture rich in a component that is at a subcritical temperature and which, in multicomponent systems, predominates. Saturated liquid and vapour phase densities of the pure component may be employed as a first estimate. These can be determined from Table I.

The behaviour in the vicinity of the critical point of the mixture is shown in Fig. 3. In this case the algorithm was slightly modified. At the beginning of the calculation the increment in the composition is firmly chosen, *e.g.*  $\Delta x_1 = 0.05$ . Approaching the vicinity of the critical point this step becomes too high. This may result in the substantial increase of the number of iterations or may lead to the failure of the calculation. As the number of iterations exceeds a chosen value, *e.g.* 10 or 15, the step along the equilibrium curve  $\Delta x_1$  is decreased five to ten times. Following the procedure repeatedly enables to approach a close proximity of the critical point.

In Fig. 3 the critical region of the system carbon dioxide–propane is shown. The critical point is located by the bubble and the dew points. The difference in the liquid and the vapour phase mole fractions is 0.0008, densities in both phases differ by 0.5%. The number of iterations in the last step was 15.

An example of an azeotropic mixture is given in Fig. 4. In the system ethane–carbon dioxide, the number of iterations did not increase even in a close proximity of the

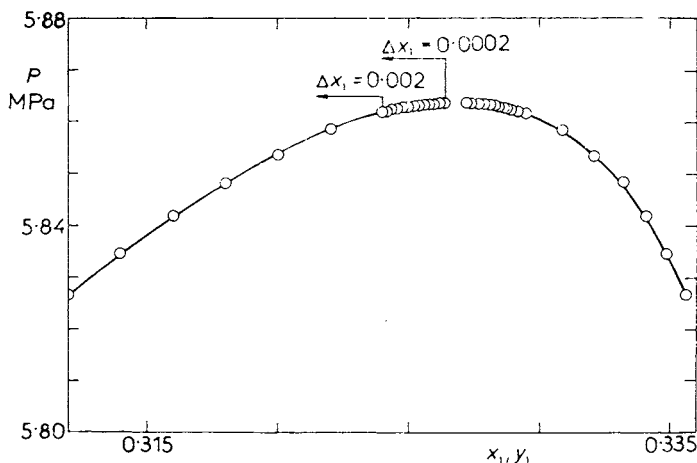


FIG. 3

Critical region of the phase envelope in the system carbon dioxide(1) + propane(2) at temperature 350 K. Critical point location:  $x_1 = 0.326400$ ,  $y_1 = 0.327206$ ,  $d^L = 5.2697 \cdot 10^{-3} \text{ mol/cm}^3$ ,  $d^V = 5.2455 \cdot 10^{-3} \text{ mol/cm}^3$ . Interaction parameters  $k_a = 0.16$ ,  $k_b = 0.03$  taken from Eveleine and Moore<sup>17</sup>

TABLE I  
Saturated liquid and vapour phase densities of pure components calculated by the Soave-Redlich-Kwong equation of state

$T_r^a$	$\omega = 0$				$\omega = 0.20$				$\omega = 0.60$				$\omega = 1.00$			
	$d_r^{Nb}$	$d_r^L$	$p_r^{0c}$	$d_r^V$	$d_r^L$	$p_r^0$	$d_r^V$	$d_r^L$	$d_r^V$	$d_r^L$	$p_r^0$	$d_r^V$	$d_r^L$	$d_r^V$	$d_r^L$	$p_r^0$
0.90	0.304	1.97	0.545	0.261	2.07	0.490	0.198	2.22	0.399	2.33	0.156	0.331	2.33	0.156	0.331	0.331
0.85	0.202	2.21	0.383	0.162	2.32	0.322	0.109	2.49	0.231	2.61	0.076	0.169	2.61	0.076	0.169	0.169
0.80	0.134	2.40	0.259	0.092E-2	2.52	0.201	5.73E-2	2.70	0.123	2.82	3.47E-2	7.8E-2	2.82	3.47E-2	7.8E-2	7.8E-2
0.75	8.58E-2 <sup>a</sup>	2.57	0.166	5.83E-2	2.69	0.117	2.81E-2	2.87	5.9E-2	3.00	1.42E-2	3.1E-2	3.00	1.42E-2	3.1E-2	3.1E-2
0.70	5.27E-2	2.72	0.100	3.21E-2	2.84	6.3E-2	1.23E-2	3.02	2.5E-2	3.14	4.92E-3	1.0E-2	3.14	4.92E-3	1.0E-2	1.0E-2
0.65	3.04E-2	2.85	5.6E-2	1.62E-2	2.97	3.0E-2	4.66E-3	3.14	9.0E-3	3.25	1.37E-3	2.7E-3	3.25	1.37E-3	2.7E-3	2.7E-3
0.60	1.61E-2	2.97	2.8E-2	7.24E-2	3.09	1.3E-2	1.43E-3	3.25	2.6E-3	3.35	2.81E-4	5.1E-4	3.35	2.81E-4	5.1E-4	5.1E-4
0.55	7.55E-3	3.08	1.2E-2	2.73E-3	3.19	4.5E-3	3.33E-4	3.34	5.5E-4	3.44	3.87E-5	6.4E-5	3.44	3.87E-5	6.4E-5	6.4E-5
0.50	3.01E-3	3.19	4.5E-3	8.19E-4	3.29	1.2E-3	5.28E-5	3.42	7.9E-5	3.51	3.11E-6	4.7E-6	3.51	3.11E-6	4.7E-6	4.7E-6
0.45	9.53E-4	3.28	1.3E-3	1.78E-4	3.37	2.4E-4	4.95E-6	3.50	6.7E-6	3.57	1.19E-7	1.6E-7	3.57	1.19E-7	1.6E-7	1.6E-7
0.40	2.17E-4	3.36	2.6E-4	2.44E-5	3.45	2.9E-5	2.21E-7	3.56	2.6E-7	3.62	1.59E-9	1.9E-9	3.62	1.59E-9	1.9E-9	1.9E-9
0.35	3.04E-5	3.44	3.2E-5	1.71E-6	3.52	1.8E-6	3.35E-9	3.61	3.5E-9	3.67	4.6E-12	4.8E-12	3.67	4.6E-12	4.8E-12	4.8E-12
0.30	2.03E-6	3.52	1.8E-6	4.31E-8	3.58	3.9E-8	9.5E-12	3.66	8.5E-12	3.71	1.2E-15	1.1E-15	3.71	1.2E-15	1.1E-15	1.1E-15
0.25	4.06E-8	3.58	3.0E-8	2.0E-10	3.64	1.5E-10	1.7E-15	3.71	1.3E-15	3.74	6.4E-21	4.8E-21	3.74	6.4E-21	4.8E-21	4.8E-21

<sup>a</sup>  $T_r = T/T_c$ ; <sup>b</sup>  $d_r = d/d_c = 1/3(RT_c/p_c) \cdot d$ ; <sup>c</sup>  $p_r^0 = p^0/p_c$ ; <sup>d</sup>  $8.58E-2 = 8.58 \cdot 10^{-2}$ .

azeotropic point and was within 2 to 3 for increment  $\Delta x_1 = 0.05$ . It should be noted, however, that the coordinates of the azeotropic point cannot be determined using the algorithm here suggested. As the tracing of the phase envelope requires preliminary specification of the composition of one of the phases, the azeotropic point is usually crossed. Applying the modification as described above for the critical point location, the azeotropic point may also be found by extrapolation.

The procedure developed is most efficient in successive calculations, *e.g.* where a tracing of the phase envelope is desired. The effectiveness is mainly due to the fact that the results of the calculation of the preceding equilibrium point are completely utilized in obtaining the estimate of the next equilibrium point. The tracing technique consists in the linear approximation of the equilibrium curve. It is, therefore, especially convenient for multicomponent mixtures where it leads to a set of linear equations.

The problems arising from poor initial estimates which may result in trivial solutions are avoided. At conditions where an initial estimate obtained, for example, by Raoult's and Amagat's laws does not guarantee a convergency even with step-limiting, the calculation may be started at more favourable conditions. Once a solution of an equilibrium point is found it is possible to proceed along the equilibrium curve rather quickly.

The algorithm is developed for use with a single equation of state. The partial derivatives needed in the application of the Newton-Raphson method may be evaluated analytically employing dimensionless quantities. At the same time dimensionless quantities can also be used to calculate all thermodynamic properties.

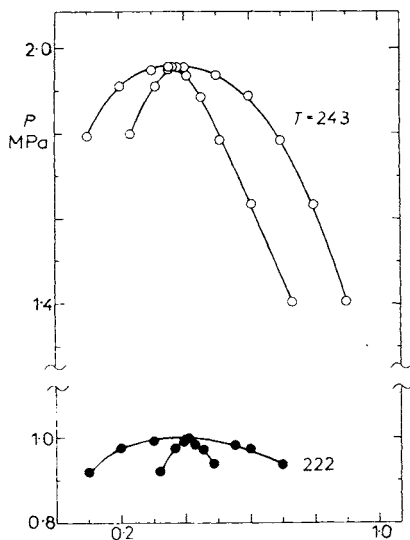


FIG. 4

Phase envelopes in the system ethane(1) + carbon dioxide(2). Up to 3 iterations required to construct the equilibrium points including a close proximity of the azeotropic point. Interaction parameters  $k_a = 0.19$ ,  $k_b = 0$  taken from Eveleine and Moore<sup>17</sup>

## APPENDIX A

## Determination of Estimate of Equilibrium Quantities

The estimate of equilibrium quantities, *i.e.* temperature or pressure, liquid and vapour phase densities and composition of liquid or vapour phase, is determined assuming the ideal solution (Raoult's law) and the ideal behaviour of the vapour phase (Dalton's law)

$$py_i = x_i p_i^0, \quad i = 1, 2, \dots, N. \quad (A1)$$

The pure component vapour pressure  $p_i^0$  is calculated from the Lee and Kesler<sup>18</sup> generalized corresponding states equation

$$\ln(p_i^0/p_{ci}) = A + B/T_{ri} + C \ln(T_{ri}) + D T_{ri}^6 + \omega_i(E + F/T_{ri} + G \ln(T_{ri}) + H T_{ri}^6), \quad (A2)$$

where  $T_{ri}$  is the reduced temperature,  $T/T_{ci}$ , and  $\omega_i$  is the acentric factor. The values of the generalized constants are:  $A = 5.92714$ ,  $B = -6.09648$ ,  $C = -1.28862$ ,  $D = 0.169347$ ,  $E = -15.2518$ ,  $F = -15.6875$ ,  $G = -13.4721$ ,  $H = 0.43577$ .

The vapour phase density is determined from the ideal gas equation of state

$$d^V = p/(RT). \quad (A3)$$

The liquid phase density is estimated by generalized Amagat's law<sup>19</sup>

$$1/d^L = V_m^L = \sum_{i=1}^N x_i V_{mi}, \quad (A4)$$

where  $V_{mi}$  is the molar volume of component  $i$  calculated by the Rackett equation<sup>20</sup>

$$V_{mi} = V_{ci} z_{ci}^{(1-T_r)^{2/7}}, \quad (A5)$$

where  $V_{ci}$  is the critical molar volume and  $z_{ci}$  the critical compressibility factor of component  $i$ . The molar volumes  $V_{mi}$  of all components are evaluated at the same pseudoreduced temperature of mixture  $T_r = T/T_{pc}$  with pseudocritical temperature calculated by the Kay rule

$$T_{pc} = \sum_{i=1}^N x_i T_{ci}. \quad (A6)$$

In some cases the density of the liquid phase determined by Eq. (A4) and used in an equation of state may lead to serious errors in calculated pressure. Therefore, if it is desirable to improve the estimate of the liquid phase density, this can be done by solving the equation of state for a given pressure to calculate the liquid density.

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

1) *Calculation of bubble point pressure (specified variables T, x)*

The system pressure is estimated using Raoult's law

$$p = \sum_{i=1}^N x_i p_i^0. \quad (A7)$$

The vapour phase composition is calculated from Eq. (A1).

2) *Calculation of dew point pressure (specified variables T, y)*

The system pressure is estimated by

$$p = \left( \sum_{i=1}^N y_i / p_i^0 \right)^{-1}. \quad (A8)$$

The liquid phase composition is obtained from Eq. (A1).

3) *Calculation of bubble point temperature (specified variables p, x)*

The temperature is determined by solving Eq. (A7). Applying the Newton-Raphson method the  $(j+1)$ -th approximation of temperature is given by

$$\begin{aligned} \ln p &= \ln p_j + [\partial \ln p / \partial (1/T)]_{T=T_j} (1/T_{j+1} - 1/T_j) = \\ &= \ln p_j - (T_j^2 / p_j) (\partial p / \partial T)_{T=T_j} (1/T_{j+1} - 1/T_j), \end{aligned} \quad (A9)$$

where  $p_j$  is the pressure calculated by Eq. (A7) using the pure component vapour pressures determined at the temperature  $T_j$ . Employing the vapour pressure Eq. (A2) the derivative  $(\partial p / \partial T)$  is given by

$$\begin{aligned} (\partial p / \partial T)_{T=T_j} &= \sum_{i=1}^N x_i p_i^0 (\partial \ln p_i^0 / \partial T)_{T=T_j} = \\ &= \sum_{i=1}^N \frac{x_i p_i^0}{T_{ci}} \left[ -\frac{B}{T_{ri}^2} + \frac{C}{T_{ri}} + 6D T_{ri}^5 + \omega_i \left( -\frac{F}{T_{ri}^2} + \frac{G}{T_{ri}} + 6H T_{ri}^5 \right) \right]. \end{aligned} \quad (A10)$$

For  $T_{j+1}$  then follows

$$\frac{1}{T_{j+1}} = \frac{1}{T_j} + \frac{p_j \ln (p_j / p)}{\sum_{i=1}^N x_i p_i^0 [-(B + \omega_i F) T_{ci} + (C + \omega_i G) T + 6(D + \omega_i H) T \cdot T_{ri}^6]_{T=T_j}}. \quad (A11)$$

The first estimate of temperature needed for solving Eq. (A11) is determined from the equation

$$\ln p = \ln p_{pc} + 6.9(1 - T_{pc}/T), \quad (A12)$$

where  $p_{pc}$  and  $T_{pc}$  are the pseudocritical pressure and temperature calculated by the Kay rule (Eq. (A6)) using the liquid phase mole fraction  $x$ .

4) *Calculation of dew point temperature (specified variables p, y)*

In this case the temperature is estimated by solving the Eq. (A8). Derivative  $(\partial p / \partial T)$  is given by

$$\begin{aligned} (\partial p / \partial T)_{T=T_j} &= \left[ \left( \sum_{i=1}^N y_i / p_i^0 \right)^{-2} \cdot \sum_{i=1}^N y_i / p_i^0 (\partial \ln p_i^0 / \partial T) \right]_{T=T_j} = \\ &= p_j^2 \sum_{i=1}^N \frac{y_i}{p_i^0 T_{ci}} \left[ -\frac{B}{T_{ri}^2} + \frac{C}{T_{ri}} + 6D T_{ri}^5 + \omega_i \left( -\frac{F}{T_{ri}^2} + \frac{G}{T_{ri}} + 6H T_{ri}^5 \right) \right]. \end{aligned} \quad (A13)$$



For  $T_{j+1}$  then follows

$$\frac{1}{T_{j+1}} = \frac{1}{T_j} + \frac{\ln(p_j/p)}{p_j \sum_{i=1}^N y_i/p_i^0 [-(B + \omega_i F) T_{ci} + (C + \omega_i G) T + 6(D + \omega_i H) T \cdot T_{ri}^6]_{T=T_j}} \quad (A14)$$

The next steps are analogous to those described above for the bubble point temperature. Pseudo-critical temperature and pressure are calculated using the vapour phase mole fraction  $y$ .

## APPENDIX B

### Dimensionless Quantities

#### Basic relations

Equation of state:

$$z = pV/(nRT) = z(T, d, x)$$

a) Defined dimensionless quantities

$$Q_d = z + d(\partial z / \partial d)_{T,x}$$

$$Q_T = z + T(\partial z / \partial T)_{d,x}$$

$$Q = \int_0^d (z - 1) d \ln d$$

$$Q_U = T(\partial Q_F / \partial T)_{d,x}$$

$$Q_C = T^2(\partial^2 Q_F / \partial T^2)_{d,x}$$

$$\tilde{z}_i = z + (\partial z / \partial x_i)_{T,d,x_{k \neq i}} - \sum_{j=1}^{N-1} x_j (\partial z / \partial x_j)_{T,d,x_{k \neq j}}$$

$$Q_{F,i} = \int_0^d (\tilde{z}_i - 1) d \ln d =$$

$$= Q_F + (\partial Q_F / \partial x_i)_{T,d,x_{k \neq i}} - \sum_{j=1}^{N-1} x_j (\partial Q_F / \partial x_j)_{T,d,x_{k \neq j}}$$

$$Q_{U,i} = T(\partial Q_{F,i} / \partial T)_{d,x}$$

$$Q_{C,i} = T^2(\partial^2 Q_{F,i} / \partial T^2)_{d,x}$$

$$Q_{F,i,j} = (\partial Q_{F,i} / \partial x_j)_{T,d,x_{k \neq i}}$$

$$i = 1, 2, \dots, N; \quad j = 1, 2, \dots, N - 1$$

b) Dependence of equation of state parameters on composition

$$\begin{aligned}
 B &= \sum_{i=1}^N \sum_{j=1}^N x_i x_j B_{ij}, \quad B_{ij} = B_{ji} \\
 \bar{B}_i &= B + (\partial B / \partial x_i)_{x_{k \neq i}} - \sum_{j=1}^{N-1} x_j (\partial B / \partial x_j)_{x_{k \neq j}} = \\
 &= -B + 2 \sum_{j=1}^N x_j B_{ij}, \quad i = 1, 2, \dots, N \\
 (\partial B / \partial x_j)_{x_{k \neq j}} &= \bar{B}_j - \bar{B}_N, \quad j = 1, 2, \dots, N-1 \\
 (\partial \bar{B}_i / \partial x_j)_{x_{k \neq j}} &= \bar{B}_N - \bar{B}_j + 2(B_{ij} - B_{iN}), \\
 &\quad i = 1, 2, \dots, N; \quad j = 1, 2, \dots, N-1
 \end{aligned}$$

c) Calculation of thermodynamic functions using dimensionless quantities

$$\begin{aligned}
 U &= U^0 - RTQ_U \\
 H &= H^0 - RT(Q_U + 1 - z) \\
 S &= S^0 - R[\ln(p/p_{st}) - \ln z + Q_F + Q_U] \\
 A &= A^0 + RT[\ln(p/p_{st}) - \ln z + Q_F] \\
 G &= G^0 + RT[\ln(p/p_{st}) - \ln z + Q_F + z - 1] \\
 \ln v &= \ln(f/p) = -\ln z + Q_F + z - 1 \\
 C_v &= C_v^0 - R(2Q_U + Q_C) \\
 C_p &= C_p^0 - R(1 + 2Q_U + Q_C - Q_T^2/Q_d) \\
 \mu_{JT} &= (Q_T - Q_d)/(C_p Q_d) \\
 w_{ad}^2 &= (RT/M)(C_p/C_v) Q_d \\
 T\alpha_p &= (\partial \ln V / \partial \ln T)_{p,x} = Q_T/Q_d \\
 p\beta_T &= -(\partial \ln V / \partial \ln p)_{T,x} = z/Q_d
 \end{aligned}$$

Partial molar quantities ( $i = 1, 2, \dots, N$ )

$$\begin{aligned}
 \bar{V}_i &= [1 + (\tilde{z}_i - z)/Q_d]/d \\
 \bar{U}_i &= U_i^0 - RT[Q_{U,i} - (Q_T - z)(\tilde{z}_i - z)/Q_d] \\
 \bar{H}_i &= H_i^0 + RT[-Q_{U,i} + z - 1 + (\tilde{z}_i - z)Q_T/Q_d] \\
 \bar{S}_i &= S_i^0 - R[\ln(x_i RTd/p_{st}) - Q_{U,i} + Q_{F,i} + (z - \tilde{z}_i)Q_T/Q_d] \\
 \bar{A}_i &= A_i^0 + RT[\ln(x_i RTd/p_{st}) + Q_{F,i} - z(\tilde{z}_i - z)/Q_d] \\
 \bar{G}_i &= G_i^0 + RT[\ln(x_i RTd/p_{st}) + Q_{F,i} + z - 1]
 \end{aligned}$$

$$\ln v_i = \ln [f_i/(px_i)] = -\ln z + Q_{F,i} + z - 1$$

$$\bar{C}_{v,i} = C_{v,i}^0 + R[-2Q_{U,i} - Q_{C,i} + T(\partial Q_T/\partial T)_{d,x}(\bar{z}_i - z)/Q_d]$$

d) Calculation of pressure, fugacity and their derivatives with respect to temperature, density and composition

$$p = zRTd$$

$$(\partial p/\partial T)_{d,x} = RdQ_T$$

$$(\partial p/\partial d)_{T,x} = RTQ_d$$

$$(\partial p/\partial x_j)_{T,d,x_{k \neq j}} = RTd(\bar{z}_j - \bar{z}_N)$$

$$f = RTd \exp(Q_F + z - 1) \quad (\text{pure component})$$

$$(\partial f/\partial T)_{d,x} = f(1 - z + Q_T + Q_U)/T \quad (\text{pure component})$$

$$(\partial f/\partial d)_{T,x} = fQ_d/d \quad (\text{pure component})$$

$$f_i = x_i RTd \exp(Q_{F,i} + z - 1)$$

$$(\partial f_i/\partial d)_{T,x} = f_i(\bar{z}_i - z + Q_d)/d$$

$$(\partial f_i/\partial T)_{d,x} = f_i(1 - z + Q_T + Q_{U,i})/T$$

$$(\partial f_i/\partial x_j)_{T,d,x_{k \neq j}} = f_i[\bar{z}_i - \bar{z}_N + (\delta_{ij} - \delta_{iN})/x_i + Q_{F,i,j}]$$

$$i = 1, 2, \dots, N; \quad j = 1, 2, \dots, N - 1$$

$$(\delta_{ij} = 1 \quad \text{for } i = j, \quad \delta_{ij} = 0 \quad \text{for } i \neq j)$$

Calculation of Dimensionless Quantities using the Soave-Redlich-Kwong equation of state

$$z = 1/(1 - bd) - ad/[RT(1 + bd)]$$

$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij}, \quad b_{ii} = 0.08644 RT_{ci}/p_{ci}$$

$$b_{ij} = (1 - k_{bij})(b_{ii} + b_{jj})/2 \quad k_{bij} = k_{bji}$$

$$a = A - BT^{1/2} + CT$$

$$A = \sum_{i=1}^N \sum_{j=1}^N x_i x_j A_{ij}, \quad B = \sum_{i=1}^N \sum_{j=1}^N x_i x_j B_{ij}$$

$$C = \sum_{i=1}^N \sum_{j=1}^N x_i x_j C_{ij}$$

$$a_{ii} = 0.42747 R^2 T_{ci}^2/p_{ci}, \quad m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$$

$$s_{ij} = (1 - k_{aij})(a_{ii}a_{jj})^{1/2}, \quad k_{aij} = k_{aji}$$

$$A_{ij} = s_{ij}(1 + m_i)(1 + m_j)$$

$$B_{ij} = s_{ij}[(1 + m_i)m_j T_{cj}^{-1/2} + (1 + m_j)m_i T_{ci}^{-1/2}]$$

$$\begin{aligned}
C_{ij} &= s_{ij} m_i m_j (T_{ci} T_{cj})^{-1/2} \\
\bar{a}_i &= \bar{A}_i - \bar{B}_i T^{1/2} + \bar{C}_i T \\
a_{ij} &= A_{ij} - B_{ij} T^{1/2} + C_{ij} T \\
Q_d &= 1/(1 - bd)^2 - ad(2 + bd)/[RT(1 + bd)^2] \\
Q_T &= 1/(1 - bd) - d[CT - 0.5BT^{1/2}]/[RT(1 + bd)] \\
Q_F &= -\ln(1 - bd) - [a/(RTb)] \ln(1 + bd) \\
Q_U &= [A - 0.5BT^{1/2}]/(RTb) \ln(1 + bd) \\
Q_C &= -[(2A - 0.75BT^{1/2})/(RTb)] \ln(1 + bd) \\
\bar{z}_i &= [1 + d(\bar{b}_i - 2b)]/(1 - bd)^2 - \bar{a}_i d/[RT(1 + bd)] + \\
&\quad + d^2 a(\bar{b}_i - b)/[RT(1 + bd)^2] \\
Q_{F,i} &= -\ln(1 - bd) + (\bar{b}_i - b) d/(1 - bd) - \\
&\quad - [\bar{a}_i/(RTb)] \ln(1 + bd) + [a(\bar{b}_i - b)/(RTb^2)] \cdot \\
&\quad \cdot [\ln(1 + bd) - bd/(1 + bd)] \\
Q_{U,i} &= (bRT)^{-1} \{(\bar{A}_i - 0.5\bar{B}_i T^{1/2}) \ln(1 + bd) + \\
&\quad + (\bar{b}_i/b - 1)(0.5BT^{1/2} - A) [\ln(1 + bd) - bd/(1 + bd)]\} \\
Q_{F,i,j} &= [d/(1 - bd)] \{2(b_{ij} - b_{iN}) - \\
&\quad - (\bar{b}_j - \bar{b}_N) [1 - (\bar{b}_i - b) d/(1 - bd)]\} + \\
&\quad + (RTb^3)^{-1} \{(\bar{b}_j - \bar{b}_N) (\bar{a}_i b - 2a\bar{b}_i) + b\bar{b}_i(\bar{a}_j - \bar{a}_N) + \\
&\quad + 2b[a(b_{ij} - b_{iN}) - b(a_{ij} - a_{iN})]\} \ln(1 + bd) + \\
&\quad + d\{(\bar{b}_j - \bar{b}_N) (2a\bar{b}_i - \bar{a}_i b) - \\
&\quad - b(\bar{b}_i - b) (\bar{a}_j - \bar{a}_N) - 2ab(b_{ij} - b_{iN}) + \\
&\quad + a(b_i - b) bd(b_j - b_N)/(1 + bd)\}/[RTb^2(1 + bd)]
\end{aligned}$$

## LIST OF SYMBOLS

$A$	Helmholtz energy
$C_p$	molar heat capacity at constant pressure
$C_v$	molar heat capacity at constant volume
$d$	molar density, $d = n/V$
$D$	determinant
$f$	fugacity
$G$	molar Gibbs energy
$H$	molar enthalpy
$M$	molar mass
$n$	number of moles

$N$	number of components
$p$	pressure
$p^0$	pure component vapour pressure
$p_{st}$	standard pressure
$R$	gas constant
$S$	molar entropy
$S$	quantity defined by Eq. (4) or (12)
$T$	temperature
$U$	molar internal energy
$V$	volume
$V_m$	molar volume
$w_{ad}$	adiabatic velocity of sound
$x$	vector of liquid phase mole fractions
$y$	vector of vapour phase mole fractions
$z$	compressibility factor
$\alpha_p$	thermal expansion
$\beta_T$	isothermal compressibility
$\delta_{ij}$	Kronecker delta
$\varepsilon_0$	convergence tolerance
$\varepsilon_1$	maximum step permitted in one iteration
$\varepsilon_2$	maximum allowed step along the equilibrium curve
$\mu_{JT}$	Joule-Thompson coefficient
$\nu$	fugacity coefficient
$\omega$	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
$^\circ$	molar thermodynamic quantity in the ideal gas state at temperature $T$ and standard pressure $p_{st}$
$V$	vapour phase

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Complete check of thermodynamic stability in both phases in all iteration steps would result in mainly multicomponent systems in a considerable increase of computer time requirements. We have observed that in many cases it is sufficient to perform the complete check, which entails the calculation of determinants  $D_a^V$  and  $D_a^L$ , only at the end of the calculation when the convergence was achieved.

To illustrate the application of the DAN method several examples are here presented. They include the construction of the phase envelope in binary two phase systems consisting of the liquid and the vapour phases. Multicomponent systems and systems which split into two liquid phases will be dealt with in a separate paper.

The discussion is devoted to the following cases: 1) retrograde region; 2) vicinity of the mixture critical point; 3) azeotropic mixtures. In all cases the Soave-Redlich-Kwong<sup>16</sup> equation of state was adopted. A value of the convergence tolerance  $\varepsilon_0 = 1 \cdot 10^{-12}$  was employed and computations were performed in double precision.

Two isotherms in the system methane-propane which include the retrograde region are shown in Fig. 2. In isothermal calculations with the step along the equilibrium curve  $|\Delta x_1| = 0.05$  the number of iterations was 4 in the whole concentration region except in the vicinity of the critical point. Changing the temperature from 275 K to 300 K required 5 iterations.

In the system methane-propane and in similar systems with one of the components being at a supercritical temperature, some difficulties may arise in obtaining the first estimate of equilibrium quantities. Two possibilities are outlined which guarantee a qualified initial guess and thus lead to convergence of the iteration procedure. First, it is possible to start from a temperature below the critical temperature of all components in the mixture. Once the solution is found the temperature can be raised

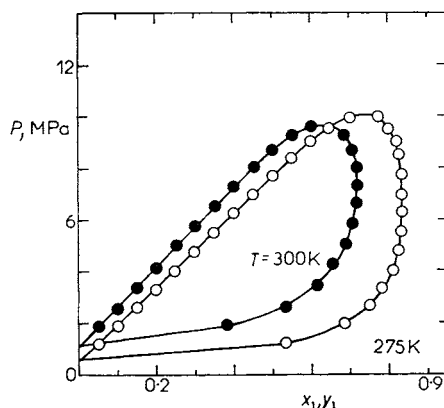


FIG. 2

Phase envelopes in the system methane(1) + propane(2). Up to 4 iterations required to construct the equilibrium points