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# Calculation of Critical Points from Cubic Two-Constant Equations of State

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Evaluation of critical points for multicomponent mixtures based on an equation of state has attracted considerable attention in recent years. The first general procedure for direct determination of critical temperature and pressure was developed by Peng and Robinson (1977), who used a criterion based on the Gibbs free energy, while a later method by Heidemann and Khalil (1979) is based on the Helmholtz free energy. Indirect methods, where the critical point is found from a phase envelope construction, have also been suggested (Assilineau et al, 1979, Michelsen, 1980).

The direct methods result in two complex non-linear equations. The method of Heidemann and Khalil is far superior, since it requires a computational effort proportional to $n^3$ ($n$ being the number of components) as compared to $n^5$ in the procedure of Peng and Robinson. The partial derivatives required using the Helmholtz free energy are much more rapidly evaluated than those using the Gibbs free energy.

The present paper describes a computational modification of the method of Heidemann and Khalil, applicable to simple, two-constant Cubic Equations of State such as the SRK-equation (Soave, 1972) and the PR-equation (Peng and Robinson, 1976). This modification reduces the computing time by a factor of 5-10.

For systems where the unlike binary interaction parameters may be calculated from the pure-component parameters using the geometric mean values, a further simplification is given, whereby computing times are reduced to a few milliseconds, almost irrespective of the number of components.

### Method of Heidemann and Khalil

Using a Taylor series expansion of the Helmholtz free energy, Heidemann and Khalil derived the following criterion: At the critical point a mixture of total composition $\mathbf{N}$ must satisfy

$$\mathbf{Q}\mathbf{\Delta N} = 0, \quad \mathbf{\Delta N}^T\mathbf{\Delta N} = 1 \tag{1}$$

and

$$C = \sum_i\sum_j\sum_K \Delta N_i \Delta N_j \Delta N_K \left(\frac{\partial^3 A}{\partial N_i \partial N_j \partial N_K}\right)_{T,V} = 0 \tag{2}$$

where $A$ is the Helmholtz' free energy, and

$$Q_{ij} = \left(\frac{\partial^2 A}{\partial N_i \partial N_j}\right)_{T,V} = RT\left(\frac{\partial \ln f_i}{\partial N_j}\right)_{T,V} \tag{3}$$

To evaluate $T_c$ and $v_c$ nested iterations were used. Newton iteration at a fixed value of $v$ is used to determine a temperature where the set of homogeneous equations (1) have a nontrivial solution. The elements $\Delta N_i$ are calculated, and evaluation of the cubic form $C$ is used to correct $v$ in an outer loop. For simple cubic equations of state the evaluation of $C$ requires essentially only one or two double summations, and for general equations numerical evaluation as described in (Michelsen, 1980) is inexpensive. The computationally expensive part is that of solving (1). The solution technique suggested in the following takes advantage of the specific temperature dependence in the SRK- and PR-equations of state.

### Two-Constant Cubic Equations of State

We shall consider Cubic Equations of State of the form

$$P = \frac{RT}{v - b} - \frac{a}{(v + \delta_1 b)(v + \delta_2 b)} \tag{4}$$

where the mixture constants $a$ and $b$ are given by the mixing rules

$$a = \sum_i\sum_j y_i y_j a_{ij} \tag{5}$$

$$b = \sum_i y_i b_i \tag{6}$$

$$a_{ij} = (a_{ii}a_{jj})^{\frac{1}{2}}(1 - k_{ij}) \tag{7}$$

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The pure component constants are found from

$$a_{ii} = \Omega_a R^2 Tc_i^2/Pc_i[1 + m_i(1 - (T/Tc_i)^{\frac{1}{2}})]^2 \tag{8}$$

$$m_i = m(\omega_i)$$

$$b_i = \Omega_b RTc_i/Pc_i \tag{9}$$

The constants $\Omega_a$ and $\Omega_b$ are determined applying eq. (4) at the critical point for a pure component.
For the SRK-equation of state

$$\delta_1 = 1,\ \delta_2 = 0,\ \Omega_a = 0.42748,\ \Omega_b = 0.08664 \tag{10}$$

$$m(\omega_i) = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \tag{11}$$

and for the Peng-Robinson equation

$$\delta_1 = 1 + \sqrt{2},\ \delta_2 = 1 - \sqrt{2},$$

$$\Omega_a = 0.45724,\ \Omega_b = 0.07780 \tag{12}$$

and

$$m(\omega_i) = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \tag{13}$$

The elements $Q_{ij}$ are evaluated from

$$\begin{aligned} n_T Q_{ij} &= n_T RT\left(\frac{\partial \ln f_i}{\partial N_j}\right)_{T,V} \\ &= RT\left\{\frac{\delta_{ij}}{y_i} + (\beta_i + \beta_j)F_1 + \beta_i\beta_j F_1^2\right\} \\ &\quad + \frac{a}{b}\{\beta_i\beta_j F_3 - a_{ij}/a\ F_5 + (\beta_i\beta_j - \alpha_i\beta_j - \alpha_j\beta_i)F_6\} \end{aligned} \tag{14}$$

where

$$\beta_i = \frac{b_i}{b},\ \alpha_i = \frac{1}{a}\sum_j y_j a_{ij} \tag{15}$$

and where $F_1 - F_8$ given in Appendix A are simple functions of the dimensionless volume $\kappa = v/b$.

From the temperature dependence of $a_{ii}$ it is evident that all elements of $Q_{ij}$ are second degree polynomials in $\lambda = T^{\frac{1}{2}}$, that is

$$\mathbf{Q} = \mathbf{Q}_0(\kappa) + \lambda\mathbf{Q}_1(\kappa) + \lambda^2\mathbf{Q}_2(\kappa) \tag{16}$$

Hence, to solve for $T$ and $\mathbf{\Delta N}$ at a given value of $\kappa$ is equivalent to solving the generalized algebraic eigenvalue problem

$$(\mathbf{Q}_0 + \lambda\mathbf{Q}_1 + \lambda^2\mathbf{Q}_2)\mathbf{\Delta N} = 0 \tag{17}$$

Since we are interested in only one eigenvalue/eigenvector pair (that corresponding to the largest temperature root) the inverse iteration technique described in (Wilkinson, 1965, Chap. IX, sect. 61) is very attractive. A trial value of $\lambda$ is chosen, and triangular decomposition of $\mathbf{Q}(\kappa, \lambda)$ is performed. Each subsequent iteration requires only inexpensive matrix-vector multiplications. The convergence is linear, with a rate inversely proportional to the error in our trial value of $\lambda$.

Treating equation (1) as the eigenvalue problem of equation (17) is the principal departure from the procedure of Heidemann and Khalil (1979) which we propose.
The cubic form $C$ can for a given $\mathbf{\Delta N}$ be evaluated from

$$\begin{aligned} n_T^2 C &= RT\left\{-\sum_i \Delta N_i^3/y_i^2 + 3\overline{N}(\overline{\beta}F_1)^2 + 2(\overline{\beta}F_1)^3\right\} \\ &\quad + \frac{a}{b}\{3\overline{\beta}^2(2\overline{\alpha} - \overline{\beta})(F_3 + F_6) - 2\overline{\beta}^3F_4 - 3\overline{\beta}\overline{\alpha}F_6\} \end{aligned} \tag{18}$$

where

$$\overline{N} = \sum_i \Delta N_i,\ \overline{\beta} = \sum_i \Delta N_i\beta_i \tag{19}$$

$$\overline{\alpha} = \sum_i \Delta N_i\alpha_i,\ \text{and } \overline{a} = \frac{1}{a}\sum_i\sum_j \Delta N_i\Delta N_j a_{ij} \tag{20}$$

The simplicity of evaluating (18) once $\lambda$ and $\mathbf{\Delta N}$ have been found, will be obvious.

At a critical point, in addition to equation (17), we must also have $n_T^2C = 0$. A new procedure is proposed here for satisfying these equations.

Let the eigenvalue and eigenvector corresponding to our initial choice of $\kappa$, $\kappa = \kappa_1$ be $(\lambda_1, \mathbf{\Delta N}_1)$. The vector is normalized, $(\mathbf{\Delta N}_1)^T(\mathbf{\Delta N}_1) = 1$, and the cubic form $C_1 = C(\lambda_1, \mathbf{\Delta N}_1)$ is evaluated.

An increment in $\kappa$ is chosen, $\kappa_2 = \kappa_1 + \Delta\kappa$, and as initial estimates for $\lambda_2$ and $\mathbf{\Delta N}_2$ are chosen

$$\lambda_2 = \lambda_1 + \left(\frac{d\lambda}{d\kappa}\right)\Delta\kappa,\ \mathbf{\Delta N}_2 = \mathbf{\Delta N}_1 \tag{21}$$

where $\left(\frac{d\lambda}{d\kappa}\right)$ is evaluated from

$$\frac{d\lambda}{d\kappa} = -(\mathbf{\Delta N}^T\mathbf{Q}_\kappa\mathbf{\Delta N})/(\mathbf{\Delta N}^T\mathbf{Q}_\lambda\mathbf{\Delta N}) \tag{22}$$

with

$$\mathbf{Q}_\kappa = \frac{\partial}{\partial\kappa}(\mathbf{Q}) \text{ and } \mathbf{Q}_\lambda = \frac{\partial}{\partial\lambda}(\mathbf{Q})$$

Evaluation of $C_2$ then permits adjustment of $\kappa$ for subsequent iterations by inverse interpolation. Following the recommendations of Heidemann and Khalil, $C$ is replaced by $C^* = C(\kappa - 1)^2$, and the iteration scheme becomes

$$\kappa_{k+1} = \kappa_k + \frac{C_k^*}{C_{k-1}^* - C_k^*}(\kappa_k - \kappa_{k-1}) \tag{23}$$

To avoid discrete jumps in $\mathbf{\Delta N}$ the additional requirement

$$(\mathbf{\Delta N}_k)^T\mathbf{\Delta N}_1 > 0 \tag{24}$$

is imposed in the normalization of $\mathbf{\Delta N}_k$.
As initial estimates are used

$$\kappa_1 = 3.5;\ \lambda_1^2 = 1.3\sum_i y_iTc_i;\ \mathbf{\Delta N}_1 = \mathbf{N} \tag{25}$$

Normally 5-7 iterations in $\kappa$ are required. At $\kappa_1$ about 4-6 iterations are necessary to determine $\lambda_1$, while all subsequent inner iterations usually converge in 1 or 2 steps, since an excellent initial estimate of $\lambda$ and $\mathbf{\Delta N}$ is available.

The total computing time for the 32 systems investigated by Peng and Robinson (1977) is 0.4 sec. (IBM 3033, FORTG compiler), ranging from 0.006 sec. for 3 components to about 0.07 sec. for 12 components.

## Systems with Zero Interaction Coefficients

The method described above can be directly extended to an equation of state with two interaction deviation parameters, as described in (Heidemann and Khalil, 1979). Here we shall describe an alternative development which can be used for systems where all $k_{ij}$ are equal to zero. Such systems are of importance since the assumption $k_{ij} = 0$ is frequently used for mixtures of pure hydrocarbons.
Provided all $k_{ij}$ are equal to zero, we obtain

$$a_{ij} = (a_{ii}a_{jj})^{\frac{1}{2}} = \alpha_i\alpha_j a \tag{26}$$

Equation (1) can be written

$$S_i = \sum_j Q_{ij}\Delta N_j = 0,\ i = 1, 2, \ldots, n \tag{27}$$

or, using (13), (14), (18), and (19)

$$\begin{aligned} RT\left(\frac{\Delta N_i}{y_i} + (\beta_i\overline{N} + \overline{\beta})F_1 + \beta_i\overline{\beta}F_2\right) + \frac{a}{b}\{\beta_i\overline{\beta}_iF_3 \\ + (\beta_i\overline{\beta} - \alpha_i\overline{\beta} - \beta_i\overline{\beta})F_6 - \alpha_i\overline{\alpha}F_5\} = 0 \end{aligned} \tag{28}$$

From (27) the following set of conditions must also hold

$$\sum_i y_i S_i = 0;\ \sum y_i \beta_i S_i = 0;\ \sum y_i \alpha_i S_i = 0 \qquad (29)$$

Substitution of (27) results in a homogeneous set of only 3 equations in $(\overline{N}, \overline{\alpha}, \overline{\beta})$. Elimination of $\overline{N}$ yields after some rearrangement the following form

$$\begin{pmatrix} D_1 & D_2 \\ D_3 & D_4 \end{pmatrix} \begin{pmatrix} \overline{\beta} \\ \overline{\alpha} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \qquad (30)$$

where

$$S_{\beta\beta} = \sum_i y_i \beta_i^2,\ S_{\alpha\beta} = \sum_i y_i \alpha_i \beta_i,\ S_{\alpha\alpha} = \sum_i y_i \alpha_i^2 \qquad (31)$$

$$D_1 = RT(1 + F_1) + \frac{a}{b}\{S_{\beta\beta}F_8 + (S_{\beta\beta} - S_{\alpha\beta})F_6\} \qquad (32)$$

$$D_2 = \frac{a}{b}\{S_{\beta\beta}F_7 + (S_{\beta\beta} - S_{\alpha\beta})F_5\} \qquad (33)$$

$$D_3 = RT\,F_1 + \frac{a}{b}\{S_{\alpha\beta}F_8 + (S_{\alpha\beta} - S_{\alpha\alpha})F_6\} \qquad (34)$$

$$D_4 = RT + \frac{a}{b}\{S_{\alpha\beta}F_7 + (S_{\alpha\beta} - S_{\alpha\alpha})F_5\} \qquad (35)$$

The temperature root is found from

$$D_1 D_4 - D_2 D_3 = 0 \qquad (36)$$

Since $D_1$, $D_2$, $D_3$, and $D_4$ are all second degree polynomials, in $\lambda = T^{\frac{1}{2}}$ we get 4 and only 4 nonzero roots. Solving (36) and using for normalization $\underline{\alpha} = 1$ yields

$$\overline{\beta} = -D_2/D_1 \qquad (37)$$

$$RT\overline{N} + \frac{a}{b}F_7\overline{\alpha} + (RTF_1 + \frac{a}{b}F_8)\overline{\beta} = 0 \qquad (38)$$

The individual $\Delta N_i$ can be recovered from (28), and all terms needed for evaluation of $C$ are available, since for $k_{ij} = 0$, $\overline{a} = \overline{\alpha}^2 = 1$.

Computing times using this extremely simple result are of the order 2-4 millisec, almost independent of the number of components in the mixture.

For systems with $k_{ij} \neq 0$ critical properties calculated using the $k_{ij} = 0$ assumption often deviate only slightly from those found using actual $k_{ij}$-values and serve as excellent initial estimates for the complete calculation. Hereby total computing times can be reduced approximately by a factor of 2.

### Conclusion and Suggestions

The development of rapid and accurate procedures for calculation of critical points is of value for general phase equilibrium calculations, since convergence is often difficult to obtain in the critical region. The ability to locate the critical region in advance will greatly help selecting the proper computational strategy.

The reduction in dimensionality in the case when all binary interaction coefficients are zero can also be utilized in phase equilibrium calculations for multicomponent systems. Using $a$ and $b$ as variables rather than using phase compositions reduces the number of independent variables to three for phase envelope calculations and for flash calculations at specified $T$ and $P$, irrespective of the number of components. Computational methods based on this simplification are currently being investigated.

### APPENDIX: Volume functions $F_1(\kappa) - F_8(\kappa)$, $\kappa = v/b$:

$$F_1 = 1/(\kappa - 1)$$

$$F_2 = 2\{(\delta_1/(\kappa + \delta_1)) - (\delta_2/(\kappa + \delta_2))\}/(\delta_1 - \delta_2)$$

$$F_3 = \{(\delta_1/(\kappa + \delta_1))^2 - (\delta_2/(\kappa + \delta_2))^2\}/(\delta_1 - \delta_2)$$

$$F_4 = \{(\delta_1/(\kappa + \delta_1))^3 - (\delta_2/(\kappa + \delta_2))^3\}/(\delta_1 - \delta_2)$$

$$F_5 = 2\ln\{(\kappa + \delta_1)/(\kappa + \delta_2)\}/(\delta_1 - \delta_2)$$

$$F_6 = F_2 - F_5$$

$$F_7 = -F_2/(1 + F_1)$$

$$F_8 = F_3/(1 + F_1)$$

## NOTATION

$A$ = Helmholtz free energy
$a$, $b$ = Parameters in equation of state
$C$ = Cubic form, eq. 2
$D_1 - D_4$ = See eqs. 32-34
$F_1 - F_9$ = Volume functions, see Appendix
$f_i$ = Fugacity of component $i$
$k_{ij}$ = Binary interaction coefficient
$\underline{N}$ = Component vector
$N_i$ = Number of moles of $i$'th component
$m$ = Parameter in equation of state
$n$ = Number of components in mixture
$n_T$ = Total number of moles in mixture
$P$ = Pressure
$\underline{\underline{Q}}$ = Matrix of partial derivatives
$R$ = Gas constant
$S_i$ = See eq. 27
$T$ = Absolute temperature
$V$ = Total volume
$v$ = Molar volume
$y_i$ = Mole fraction, component $i$

### Subscripts

$c$ = Critical property
$i$, $j$, $k$ = Component numbers

### Greek Letters

$\alpha_i$ = See eq. 15
$\beta_i$ = See eq. 15
$\delta_1$, $\delta_2$ = Constants in equation of state
$\kappa$ = Dimensionless volume, $\kappa = v/b$
$\lambda$ = $T^{\frac{1}{2}}$
$\Omega_a$, $\Omega_b$ = Constants in equation of state
$\omega$ = Acentric factor

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