THE NEGATIVE FLASH

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ABSTRACT

This paper describes a procedure for calculating vapor-liquid equilibrium
for systems that physically exist as a single phase, but still yield non-negative
equilibrium compositions that satisfy the material balance and equal fugacity
constraints of the P-T flash. Theoretical and practical consequences of the
"negative flash" are discussed. For example, it is shown that the negative flash
corresponds to a saddle point in the Gibbs energy surface. It is also shown that
the limits of pressure and temperature where the negative flash ceases to converge
to a non-trivial solution defines the well-known convergence pressure envelope of
the mixture. Finally, it is suggested that the continuity of properties across
phase boundaries, as calculated by the negative flash, makes the method attractive
for algorithms that nest a standard P-T flash inside an outer loop (e.g., an
isenthalpic flash or a three-phase dewpoint).

INTRODUCTION

Calculation of vapor-liquid equilibrium (VLE) based on an equation of state
(EOS) is the basic tool for determining the compositions and properties of
coexisting phases in thermodynamic equilibrium. Typically, the total composition
and conditions of pressure and temperature are known, thereby reducing the problem

to solving for the unknown vapor and liquid compositions and the relative amounts of each phase.

The usual approach to solving the VLE problem is to require that the chemical potential (expressed in terms of fugacity) be equal for each component in each phase,

$$f_{Li} = f_{Vi} \tag{1}$$

where $f_{Li}=F(x,p,T)$ and $f_{Vi}=F(y,p,T)$.

A component material balance must also be satisfied,

$$z_i n = y_i n_V + x_i n_L \tag{2}$$

where the overall material balance requires that

$$n = n_V + n_L \tag{3}$$

Introducing $\beta=n_V/n$, Eq. 2 can be written in the familiar form

$$z_i = y_i \beta + x_i (1-\beta) \tag{4}$$

where β is the vapor mole fraction. The equilibrium mole fractions must also sum to unity,

$$\sum_{i=1}^{N} x_i = \sum_{i=1}^{N} y_i = 1 \tag{5}$$

The most straight-forward calculation procedure to solve for y_i, x_i, and β is trial-and-error by successive substitution. Eqs. 4 and 5 can be satisfied by solving the so-called Rachford-Rice (1952) relation,

$$h(\beta) = \sum_{i=1}^{N} (y_i - x_i) = 0 \tag{6}$$

Combining Eqs. 4 and 6, and using the definition for equilibrium ratios $K_i=y_i/x_i$, this relation can be expressed

$$h(\beta) = \sum_{i=1}^{N} \frac{z_i(K_i-1)}{1 + \beta(K_i-1)} = 0 \tag{7}$$

The function $h(\beta)$ decreases monotonically and has the form shown in Fig. 1, where asymptotes occur at values of $\beta=1/(1-K_i)$. Solutions to Eq. 7 occur between all asymptotes, although the solution β between asymptotes $\beta_{min}=1/(1-K_{max})$ and $\beta_{max}=1/(1-K_{min})$ is the only one which yields all non-negative phase compositions y_i and x_i. It can be shown that $\beta_{min}<0<1<\beta_{max}$ when $K_{min}<1$ and $K_{max}>1$.

Having solved Eq. 7 for the correct β ($\beta_{min}<\beta<\beta_{max}$) within an acceptable tolerance, the phase compositions are calculated from

$$x_i = \frac{z_i}{1 + \beta(K_i-1)} \tag{8}$$

$$y_i = \frac{z_i K_i}{1 + \beta(K_i-1)} = x_i K_i \tag{9}$$

Fugacities are then calculated from an EOS using these compositions, and an error

function is computed, e.g.,

$$E = \sum_{i=1}^{N}(f_{Li}/f_{Vi}-1)^2 \tag{10}$$

to check if the equal-fugacity constraint is satisfied within an acceptable tolerance. If the tolerance is not met, new K-values are estimated using, for example, the successive substitution approach

$$K_i^{new} = K_i^{old}(\frac{f_{Li}}{f_{Vi}}) \tag{11}$$

The rate of convergence may be accelerated using methods such as the General Dominant Eigenvalue Method (GDEM) (Crowe and Nishio, 1975), a Newton method (Fussel and Yanosik, 1978), or some combination (Michelsen, 1982b).

When the fugacity tolerance is satisfied, the flash calculation is complete. Michelsen (1982a) discusses how to check if the two-phase solution is stable by searching for additional phases that may reduce the mixture Gibbs energy. Also, if the two-phase solution is trivial, where K-values approach unity and the equilibrium phases are identical with the feed, a two-phase stability test can be made to confirm the VLE calculation results.
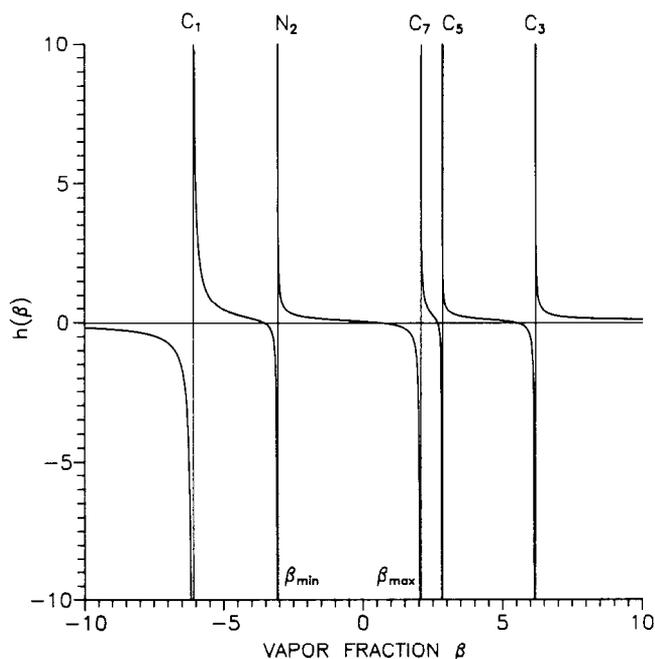
Fig. 1. Rachford-Rice function $h(\beta)$ for a five-component mixture, showing the solution β where $\beta_{min}<\beta<\beta_{max}$ ensures non-negative phase compositions.

THE NEGATIVE FLASH PROCEDURE

During the iterative flash procedure, if the solution of $h(\beta)$ yields $\beta<0$ or $\beta>1$, most published methods suggest that the β satisfying Eq. 7 be discarded and a "physically acceptable" value be used instead. For example, if $\beta<0$, it is suggested to use $\beta=0$, $x_i=z_i$, and y_i calculated from Eq. 9 (and subsequently normalized). Likewise, if $\beta>1$, it is suggested to use $\beta=1$, $y_i=z_i$, and x_i calculated by normalizing values from Eq. 8.

The proposed flash procedure consists of always using the β calculated from Eq. 7 during the iterative flash procedure, where $\beta_{min}<\beta<\beta_{max}$, even though β may be outside the range 0 to 1. Because this β always yields positive molar compositions ($y_i>0$ and $x_i>0$), there is no reason to impose the "physically acceptable" limits of 0 to 1. There are, however, several reasons for using β even when it exceeds these limits. For example, when the flash calculation converges to a non-trivial solution with $\beta<0$ or $\beta>1$ (what we refer to as a "negative flash"), the feed can be assumed stable (single phase), at least with the same certainty that a traditional stability test provides. Also, most flash algorithms should perform better near phase boundaries because the discontinuity imposed by limiting β from 0 to 1 is removed. Other applications of the negative flash are covered later in the paper.

To our knowledge, this modification of the traditional flash algorithm was first mentioned by Li and Nghiem (1982), although they incorrectly suggest that β "can take any value," where in fact it must be limited to the range $\beta_{min}<\beta<\beta_{max}$. Neoschil and Chambrette (1978), in an unpublished paper in 1978, also suggest the idea of allowing β to exceed the physical limits of 0 to 1 for a flash algorithm using convergence pressure K-values.

Although this modification to the flash calculation is seemingly trivial, several important consequences of the method lead to theoretical and practical results which are now presented.

Interpreting the Negative Flash

Fig. 2 shows a P-T phase diagram for a binary containing 50 mol-% ethane and 50 mol-% butane, calculated using the Peng-Robinson (1976) EOS. The figure also shows the region within which the negative flash exists. This region encloses the phase envelope of the binary, and is bound by the vapor pressure curves for the two components. Finally, we have marked the region within which the parallel tangent condition (stability analysis) has a nontrivial solution.
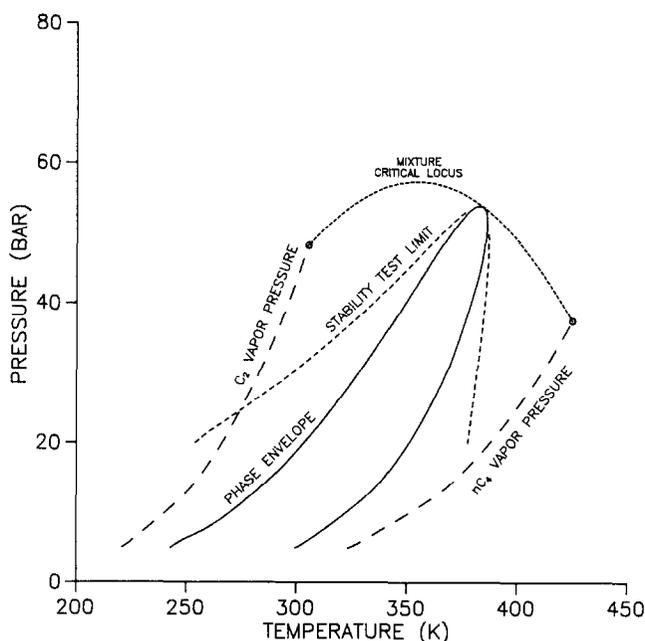
Fig. 2. C_2-nC_4 binary showing vapor pressure curves of C_2 and nC_4; phase envelope and stability test limit for a 50-50 binary mixture; and the binary critical locus determined by solving the negative flash for the 50-50 mixture as $\beta \to \pm\infty$. Calculations with the PR EOS.

In fact, the bounding envelope within which the negative flash exists for a binary corresponds to the loci of critical points for all mixtures of the two components. For a specific mixture, $\beta \to -\infty$ along the bounding envelope at temperatures less than the mixture's critical temperature, and $\beta \to +\infty$ at temperatures greater than the mixture's critical temperature.

At the limiting conditions where $\beta \to \pm\infty$, K-values approach unity and the equilibrium compositions become identical, corresponding to a composition z_c that has its critical point at the prevailing pressure and temperature. The critical compositions z_c along the $\beta = \pm\infty$ envelope are not equal to the feed composition except when the system temperature equals the critical temperature of the feed. For a binary system, any single mixture composition can be used to determine the entire convergence pressure envelope by tracking pressure and temperature conditions where the negative flash yields $\beta \to \pm\infty$. We will refer to the locus of these points as the convergence pressure envelope, where the properties of

convergence pressure are interestingly the same as discussed by Rzasa, et al. (1952), Rowe (1967), and others.

The negative flash for multicomponent mixtures is illustrated for a ternary system in Fig. 3 and Table 1. We can easily show that all compositions z located on the tie line BD will separate into vapor composition y at B and liquid composition x at D, with $0 \leq \beta \leq 1$. Using the negative flash procedure it is easily confirmed that y and x can be determined by flashing any mixture along the line AE, where AB and DE are extensions of the "physical" tie line. The limits A and E are defined by β_{min} and β_{max}, points where one of the component mole fractions approaches zero.

THEORETICAL ASPECTS OF THE NEGATIVE FLASH
General Discussion

The interpretation of a negative flash is perhaps easiest to describe for binary and ternary systems. Consider the (reduced) excess Gibbs energy curve in Fig. 4 (50% ethane, 50% n-butane at 390K and 40 bar using the Peng-Robinson EOS), where g^E, defined as

$$g^E = z_1 \ln\left(\frac{f_1}{f_{1pure}}\right) + (1-z_1)\ln\left(\frac{f_2}{f_{2pure}}\right) \tag{12}$$
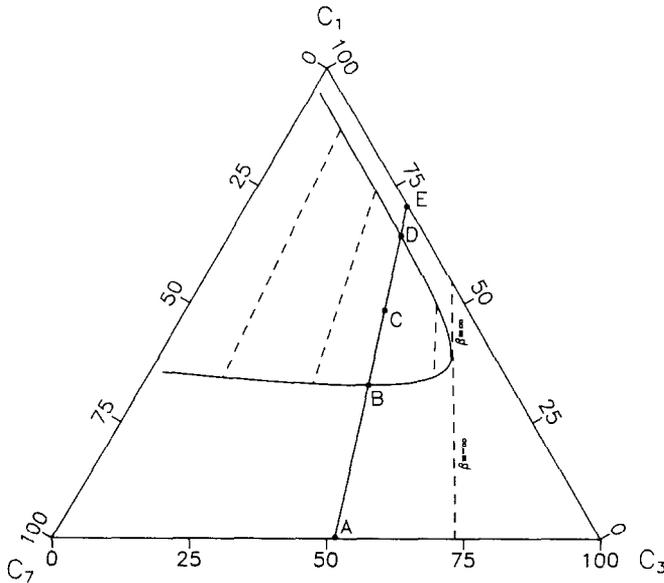
Fig. 3. C_1-C_3-nC_7 ternary diagram calculated by the SRK EOS at 373K and 100 bar.

TABLE 1

Conditions along the equilibrium tie-line A-E for the ternary shown in Fig. 3; calculated from the SRK EOS at 373 K and 100 bar.

Point	β_{mix}	Mixture Compositions (%) $z_i = \beta_{mix}y_i + (1-\beta_{mix})x_i$			Comments
		C_1	C_3	nC_7	
A	-1.03318	0.315	51.436	48.250	$\beta_{mix} \approx \beta_{min}$
B	0	32.837	41.205	25.958	$z_i = x_i$
C	0.5	48.576	36.254	15.170	two-phase mixture
D	1	64.315	31.302	4.383	$z_i = y_i$
E	1.193135	70.394	29.390	0.216	$\beta_{mix} \approx \beta_{max}$
		1.9586	0.7597	0.1688	$K_i = y_i/x_i$

is plotted versus mole fraction z_1. For any mixture with composition z in the range $x \leq z \leq y$, two phases will form with compositions, x and y, these compositions having a common tangent to the g^E curve. The Gibbs energy change associated with the phase split equals the vertical distance from the g^E curve to the common tangent.

Mixtures with composition $x_I \leq z \leq y_I$ are intrinsically unstable, where x_I and y_I are the inflection points on the g^E curve. The Gibbs energy for such mixtures can be decreased by a phase split with infinitesimal change in composition; this condition of instability is verified by the condition $(\partial^2 g^E/\partial z^2) < 0$.

Compositions in the range $x < z < x_I$ and $y_I \leq z < y$ are metastable. Such mixtures form two phases, but the instability is not revealed by the local properties of the g^E surface. Verification of instability thus requires a global search, e.g. by means of the tangent plane criterion, as suggested by Baker, et al. (1982). The mixture of composition z is stable if and only if the tangent to the energy surface at z does not intersect the energy surface.

Michelsen (1982a) suggests a check of stability by minimizing the distance from the energy surface to the tangent plane at z. Minima of the tangent plane distance are located at compositions y_s where the local tangent plane is parallel to that at z. The system is stable if the tangent at y_s is above the tangent at z (i.e. a positive tangent plane distance); the system is unstable if the tangent of y_s is below the tangent at z (a negative tangent plane distance).

ETHANE MOLE FRACTION
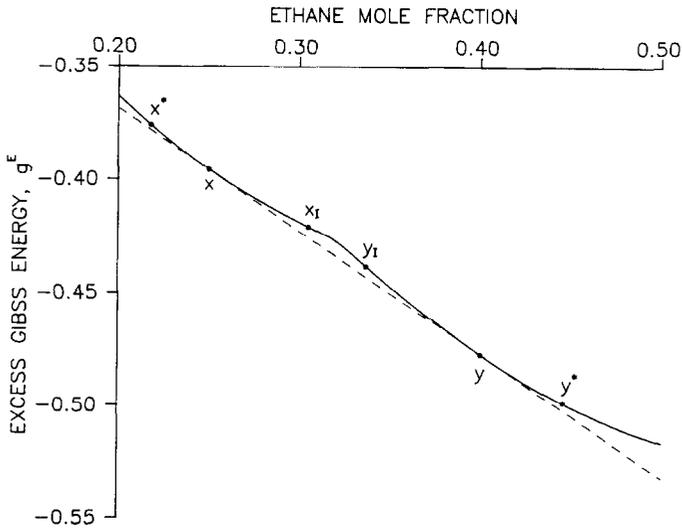
Fig. 4. Excess Gibbs energy diagram versus C_2 mole fraction for the C_2-nC_4 binary, calculated by the PR EOS at 390K and 40 bar. Indicated are: equilibrium compositions, y and x; intrinsic instability compositions y_I and x_I; and limiting compositions for non-trivial stability solution, y^* and x^*.

We observe that parallel tangents can be located for any composition in the interval $x^* \leq z \leq y^*$, where x^* and y^* are the compositions at which the tangent is parallel to the tangents at the inflection points y_I and x_I, respectively. Of course, only compositions in the range $x \leq z \leq y$ are unstable, having a negative tangent plane distance.

A traditional flash calculation attempts to split the feed in vapor and liquid phase fractions β and $1-\beta$, respectively, where $0 \leq \beta \leq 1$. For our binary mixture, the solution to this flash exists for any feed in the interval $x \leq z \leq y$. The criteria for a negative flash are identical to those for the conventional flash, except that the constraint on β is removed. For a binary, the solution is found for any composition $0 < z < 1$, with $z < x$ corresponding to $\beta < 0$ and $z > y$ corresponding to $\beta > 1$.

For the g^E diagram of the ethane-butane mixture shown in Fig. 4, the composition of the equilibrium phase (ethane mole fraction) is $x=0.250$ and $y=0.399$; the inflection points are located at $x_I=0.305$ and $y_I=0.337$; and the

limits between which parallel tangents can be located are $x^*=0.218$ and $y^*=0.446$.

Gibbs Energy Analysis

The change in Gibbs energy associated with forming β moles of composition y and $(1-\beta)$ moles of composition x from one mole of composition z is given by

$$\Delta g = \beta g_y + (1-\beta)g_x - g_z \tag{13}$$

where g_y, g_x, and g_z are the molar Gibbs energies of the vapor, liquid, and feed, respectively. At equilibrium, Δg is at a minimum. The Hessian matrix of $\Delta g/RT$ is given by

$$H_{ij} = \frac{1}{RT}\left(\frac{\partial^2 \Delta g}{\partial n_i \partial n_j}\right) = \frac{1}{\beta(1-\beta)}(E_{ij}+U_{ij}) \tag{14}$$

where the independent variables n_i denote molar amounts in one of the phases.

The matrix $\underline{E}$ is the ideal part of the Hessian,

$$E_{ij} = \left(\frac{z_i}{x_i y_i}\right)\delta_{ij} - 1 \tag{15}$$

with $\delta_{ij}=0$ for $i \neq j$ and $\delta_{ij}=1$ for $i=j$. $\underline{U}$ is the nonideal part of the Hessian,

$$\underline{U} = \beta\underline{\Psi}_x + (1-\beta)\underline{\Psi}_y \tag{16}$$

with

$$\Psi_{ij} = n_T\left(\frac{\partial \ln \phi_i}{\partial n_j}\right) \tag{17}$$

for each phase, where ϕ_i is the fugacity coefficient and $n_T = \Sigma_k n_k$.

Formally, we can use the same definition of Δg for the negative flash. However, the solution to the negative flash does not correspond to a minimum in Δg, as it does for a physical flash. It is, for example, readily verified that the Hessian matrix for an ideal mixture ($U_{ij}=0$) has exactly one positive eigenvalue and $N-1$ negative eigenvalues for an N-component mixture with β outside the range 0 to 1. The solution of the negative flash is therefore a saddle point of the Gibbs energy, as illustrated in Fig. 5a for the C_2-nC_4 (50-50) binary at 390K and 40 bar. As a consequence, minimization methods (e.g., Trangenstein, 1985) must be used cautiously to solve the negative flash.

Using the equilibrium compositions from the 50-50 feed in Fig. 5a, feed compositions for $\beta=1$ and $\beta=0.5$ were computed, and their Gibbs energy surfaces are shown in Figs. 5b and 5c, respectively. For the dewpoint feed, a line of $\Delta g=0$ occurs for the compositions with $\beta=1$, having equilibrium compositions located at the point where the surface turns into a saddle point. For the $\beta=0.5$ feed, the equilibrium condition is clearly at the minimum of the Gibbs energy surface. [Note that every point on the Gibbs energy surface shown in Figs. 5 represents a different β value, as determined by the $h(\beta)$ function for the particular set of compositions (i.e., K-values).]
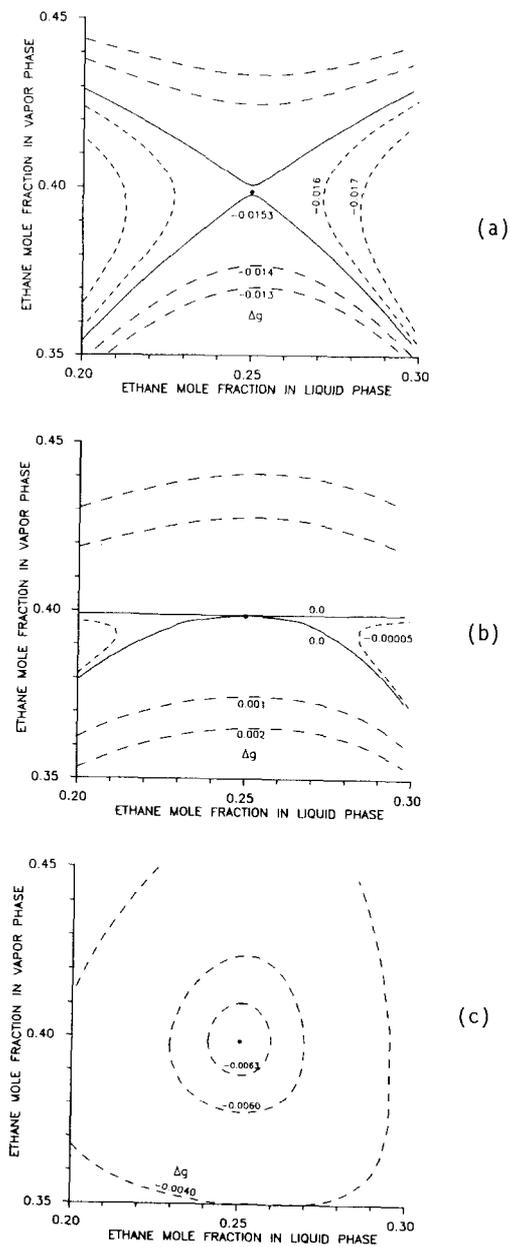
Fig. 5. Change in Gibbs energy contours for the C_2-nC_4 binary calculated with the PR EOS at 390K and 40 bar: (a) solution with $\beta=1.674$ illustrating saddle point, (b) solution with $\beta=1$ (dew point), and (c) solution with $\beta=0.5$.

Convergence of Successive Substitution

Michelsen (1982b) shows that for the two-phase P-T flash converging to a physical β, successive substitution can only converge to a stationary point which is a minimum of Δg. A similar result does not hold for the negative flash because Michelsen's observation is based on $\underline{E}$ being positive definite, which is not true for the negative flash.

The rate of convergence for the negative flash is, as for the conventional flash, determined by the eigenvalues of the matrix

$$\underline{M} = -\underline{E}^{-1}\underline{U} \tag{18}$$

evaluated at the solution. In brief, the magnitude of the largest eigenvalue of $\underline{M}$ equals the reduction factor in error, and convergence requires that all eigenvalues of $\underline{M}$ be smaller than unity in magnitude. In practice we observe that close to the phase boundary the rate of convergence for the negative flash corresponds to that for the conventional flash. As we proceed into the one-phase region, the dominant eigenvalues increase, and finally, as we approach the limit of existence for the negative flash (characterized by the two equilibrium phases becoming critical) two eigenvalues approach unity just as in the conventional flash near a critical point. The variation of the successive substitution eigenvalues with temperature is shown in Fig. 6 for the C_2-nC_4 50-50 mixture at 40 bar.

Acceleration of Successive Substitution

Several acceleration methods have been used with success to promote the rate of convergence of successive substitution (e.g., Mehra, 1982; Michelsen, 1982b; and Nghiem et al., 1983). In the conventional flash, acceleration can be performed without jeopardizing the robustness of the basic procedure by enforcing a reduction of the Gibbs energy at every iteration. An unfortunate acceleration step leading to an increase in Gibbs energy can be discarded or modified until a reduction is achieved. If the initial K-value estimates are based on stability analysis, Gibbs energy of mixing during the flash calculation must always be below that for the single phase and the enforcement of Gibbs energy reduction prevents convergence to the trivial solution.

For the negative flash the situation is less fortunate. The Gibbs energy no longer serves as a guide for checking the acceleration step, and also the trivial solution is potentially a point of attraction for the equations. We can therefore expect the negative flash to be more sensitive to the quality of the initial K-value estimates, and the application of acceleration increases the risk of arriving at the undesired trivial solution.
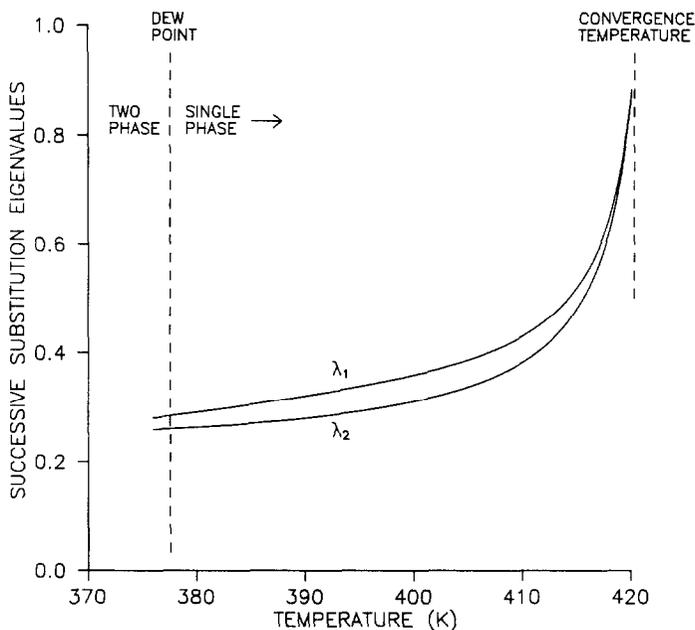
Fig. 6. The two dominant successive substitution eigenvalues for the 50-50 C_2-nC_4 binary mixture as a function of temperature in the single-phase region at 40 bar, calculated by the PR EOS.

In most calculations we have made, the Wilson (Wilson, 1968) K-value estimates are adequate, and acceleration is unproblematic. When problems are encountered (as indicated by convergence to the trivial solution where a nontrivial solution does in fact exist) they normally occur far removed from the phase boundary. Fig. 7 and Table 2 show results for a seven-component mixture at 230 K, where the SRK EOS (Soave, 1972) predicts a dewpoint pressure of about 80 bar. Using Wilson K-values as initial estimates, direct substitution with or without acceleration converges to a trivial solution at pressures in the single-phase region from about 102 bar to the convergence pressure of 123 bar (see Fig. 8).

Fig. 9 shows the rate of convergence of direct substitution for a set of feeds having the same final equilibrium composition but different β values. Initial K-values from the Wilson relation are the same for each feed, but the composition path towards the solution varies for each feed, as does the shape of the Gibbs energy surface. It is obviously not straight forward to quantify the expected difficulty of a flash calculation merely by it's location relative to the phase and convergence pressure envelopes.

TABLE 2

Seven-component system calculated using the SRK EOS at 230 K.

Component	Feed Composition	Equilibrium at 100 bar[a]			Critical Composition[b]
		y_i	x_i	K_i	
N_2	1.40	1.3552	0.6007	2.2558	1.063
C_1	94.30	93.1781	74.3031	1.2540	86.805
C_2	2.70	2.8342	5.0926	0.5565	3.450
nC_3	0.74	0.8469	2.6456	0.3201	1.271
nC_4	0.49	0.6636	3.5850	0.1851	1.276
nC_5	0.27	0.5271	4.8528	0.1086	1.397
nC_6	0.10	0.5948	8.9201	0.0667	4.735

a. β=1.0594 for feed composition.
b. At convergence pressure of 122.9 bar.
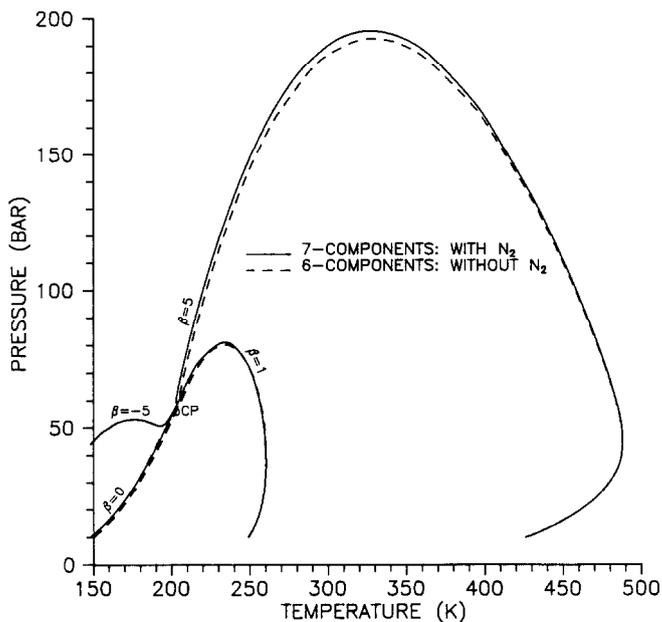
Fig. 7. The phase and approximate convergence pressure (β=±5) envelopes for multicomponent systems calculated by the SRK EOS. Solid lines for feed composition in Table 2, and dashed lines for same composition without nitrogen (normalized). Note: dashed line with β=-5 happens to lie almost coincident with the β=0 solid line.
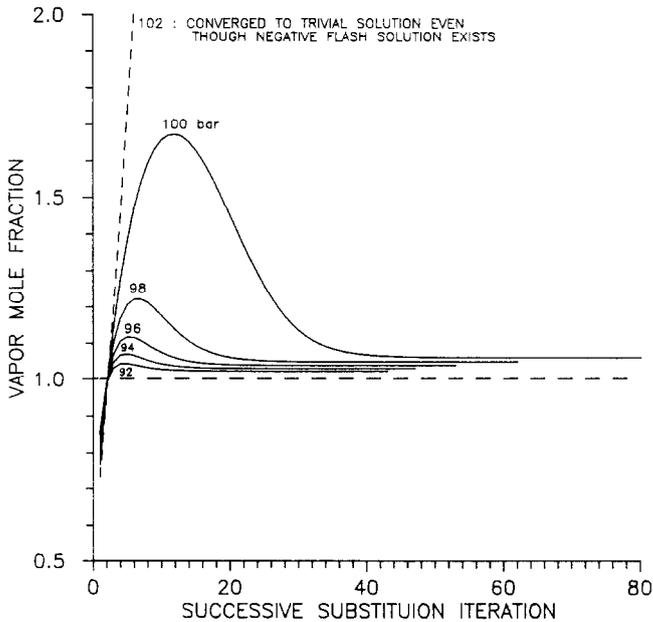
Fig. 8. Pure successive substitution convergence performance of the 7-component feed in Table 2 calculated by the SRK EOS at 230K.

The importance of initial K-values should not be exaggerated, however, because as many as several hundred flash calculations can be calculated using the combination of stability analysis and safeguarded flash calculation within a few minutes of CPU on most microcomputers, and in less than a second on supercomputers. The real need for good initial K-values to avoid using stability analysis prior to each flash, is when many thousands of flash calculations are required, as for example in reservoir simulation.

However, in such simulations the VLE characteristics between neighboring grid cells, and from one time step to another are very similar. In these cases accurate initial K-value estimates should always be available, and Newton-type methods can safely be employed (Young 1987).

Table 3 illustrates the use of converged K-values from one condition to initialize a difficult flash calculation at a different but "nearby" condition. A series of flash calculations are made with the SRK EOS at 230 K, with the first pressure at 80 bar, just below the dewpoint pressure. Wilson K-values are used to initialize the first flash calculation, and thereafter converged K-values are

$$z_i = y_i\beta_{mix} + x_i(1-\beta_{mix})$$

$\beta_{mix} = 0$: B.P. MIXTURE
$\beta_{mix} = 1$: D.P. MIXTURE
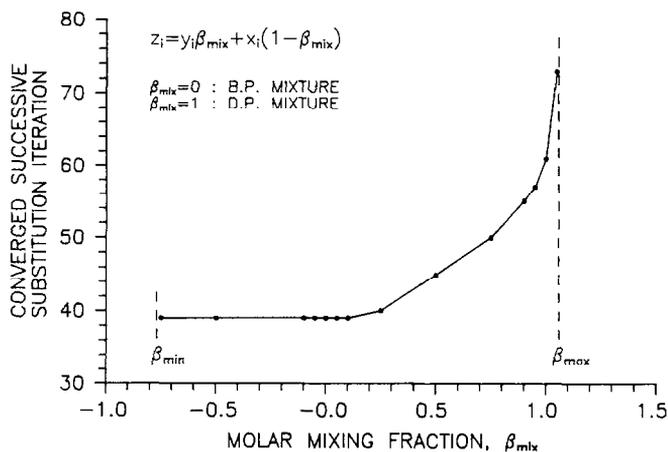
Fig. 9. Rate of convergence for pure successive substitution for a series of feeds related to the feed in Table 2, where each feed has the same equilibrium compositions but different β values at 230K and 100 bar using the SRK EOS.

TABLE 3

Effect of K-value estimates on negative flash convergence using SSI/GDEM for the seven-component mixture in Table 2 (230 K).

Order of Flash Calculation	Pressure (bar)	Total SSI/GDEM Iterations	Converged Flash Results		
			β	$K_{max}(N_2)$	$K_{min}(C_6)$
1[a]	80	11	0.9972	3.535	0.0119
2	100	12	1.0594	2.256	0.0667
3	120	21	1.7969	1.290	0.4519
4	122.5	26[b]	6.1209	1.058	0.8398
5	120	31	1.7969	1.290	0.4519
6	100	21	1.0594	2.256	0.0667
7	80	11	0.9972	3.535	0.0119

a. Wilson K-value estimates; $K_{max}(N_2)=5.339$, $K_{min}(C_6)=8.53(10^{-5})$, and initial $\beta=0.384$. Otherwise, K-value estimates are taken as the final K-values from the previous flash calculation.
b. One promotion rejected because K-values following the promotion were "upside down."

used to initialize the next flash calculation at a different pressure. The series of flash calculations are conducted in the order of pressures 80, 100, 120, 122.5, 120, 100, and 80 bar. Recall that the negative flash converged to the trivial solution for pressures greater than 102 bar when Wilson K-values were used to initialize the flash.

It is seen that all the flash calculations converge without problems, even for the near-critical condition at 122.5 bar. Interestingly, problems are not encountered when using the near-unity K-values from this flash as initial estimates for the flash at 120 bar (though 10 iterations more are required to converge this flash than using initial K-values from the converged flash at 100 bar).

In summary, an approach to the trivial solution for both the traditional flash and the negative flash is usually due to inadequate initial K-value estimates. In fact, stability analysis followed by flash calculation restricted by a monotonically decreasing Gibbs energy is the only certain method of finding a nontrivial solution to the traditional flash problem. This procedure is, however, expensive. As mentioned above, our experience shows that direct substitution with GDEM promotion using initial K-value estimates from the Wilson equation usually results in the correct solution for traditional and negative flash problems, even near the phase boundary. If a trivial solution is found, however, stability analysis is then used to confirm the result, and if the feed is unstable a new flash calculation is started using K-value estimates from the stability analysis.

Finally, we note that if β begins within the range 0 to 1, then goes outside the range and remains there for several iterations, there is little chance that β will return to and converge within the physical range 0 to 1. This observation may be helpful in reducing computing costs when it is acceptable to prematurely stop the negative flash calculation with a message that the feed is "very likely" single phase.

The Critical Region

We observe from Fig. 7 that the phase boundary and the limits of existence for parallel tangents and the negative flash all coincide at the critical point. In the immediate vicinity of the critical point these loci can be analyzed as described by Michelsen (1984). He found that the Gibbs energy surface in this region can be described in terms of characteristic parameters b, c, d, and d^*. At the critical point b and c are both zero, and d and d^*, which satisfy $d \geq d^* > 0$, can be assumed constant near the critical point. For binary mixtures, the tangent plane distance is approximated by

$$TPD(s) = bs^2 + cs^3 + d^*s^4 \tag{19}$$

where s is a measure of the distance in composition.

The existence of a parallel tangent plane requires that TPD(s) has a nontrivial (s≠0) minimum, i.e.,

$$\frac{d}{ds}(TPD) = 2bs + 3cs^2 + 4d^*s^3 = 0 \text{ for } s \neq 0 \tag{20}$$

yielding

$$b^* \leq \frac{9c^2}{32d^*} \tag{21}$$

In addition, Michelsen (1984) derives the following relation for the phase split β, formally valid in the entire range $-\infty < \beta < \infty$:

$$(1-2\beta)^{-2} = 1 + 2(d^*/d)(1-4bd^*/c^2) \tag{22}$$

The phase boundary ($\beta=0$) is thus located at

$$b = \frac{c^2}{4d^*} \tag{23}$$

and the limit for the negative flash at

$$b = \frac{3c^2}{8d^*}(1+\frac{d-d^*}{2d^*}) \tag{24}$$

If we consider variations along a line of constant and small c for a binary mixture ($d=d^*$), the relative location of the lines of interest are:

Spinodal Curve:	$b = 0$	(25a)
Phase Boundary:	$b = (8/32)(c^2/d^*)$	(25b)
Limit for Parallel Tangent:	$b = (9/32)(c^2/d^*)$	(25c)
Limit for Negative Flash:	$b = (12/32)(c^2/d^*)$	(25d)

The distance from the phase boundary to the limit for the negative flash is thus at least four times larger than the distance to the limit for parallel tangents. Although this result is only quantitatively correct in the critical region it does provide an indication about the general location of these limiting curves.

PRACTICAL APPLICATIONS OF THE NEGATIVE FLASH

One desirable feature of the negative flash is that derived properties of the mixture do not exhibit discontinuities at the phase boundary. This facilitates flash calculations for more general specifications based on "overiteration," i.e., satisfying the specifications by nested loops, where the P-T flash is used in the inner loop (e.g., Michelsen, 1982b and Agarwal, et al., 1988). While overiteration is often uneconomical compared with a more direct

approach, it does have the advantage of simple implementation and robustness, provided the basic P-T flash is adequately coded.

As an example, consider the P-H (isenthalpic) flash, using the secant method to correct the temperature in the outer loop. Rapid convergence can be expected when H(T) has continuous derivatives. Using the traditional P-T flash for the inner loop, H does not have a continuous derivative at the phase boundary, and specifications located close to the phase boundary are difficult to converge. In contrast, using the negative flash in the inner loop will yield continuous derivatives also in this region.

A more complex example is the calculation of the hydrocarbon dewpoint in the presence of liquid water. A three-phase flash permitting negative values of the hydrocarbon liquid fraction can be used advantageously, as shown in Fig. 10. The negative flash may in fact be valuable for several types of multiphase calculations where the phases are well defined.

The calculation of "thermodynamic" minimum miscibility pressure (MMP), a concept of interest in reservoir engineering, can also be improved using a variant of the negative flash. Briefly, this calculation aims at determining the pressure at which a specified composition (at fixed temperature) is located on the extension of a critical tie line. The MMP thus corresponds to a point on the boundary for the negative flash for the specified composition. Jensen and Michelsen (1987) describe a procedure for multicomponent mixtures by tracing a sequence of negative flash calculations at increasing pressures.

Based on the results in Table 3 and our general experience with the negative flash procedure, convergence to the nontrivial solution is almost certain if K-values from a flash at "nearby" conditions are used to initialize the calculation. This has important implications for application of the negative flash in compositional reservoir simulation. For example, it may be more efficient to complete a negative flash than a stability test in single-phase grid cells adjacent to two-phase grid cells. Also, the K-values from a negative flash should provide very good initial estimates for subsequent time steps where the single-phase cells are checked to see if they have gone two-phase.

In connection with this application of the negative flash, it is interesting to note the relative proximity of the convergence pressure envelope to the phase envelope away from the critical point. The applicability of the negative flash depends primarily on the extent of pressure-temperature space separating these two envelopes. The phase and convergence pressure envelopes will generally be close along the bubblepoint curve if low-solubility components such as nitrogen are not present. This is shown clearly in Fig. 7, where two very similar mixtures, one with a small amount of nitrogen and the other without nitrogen, have dramatically
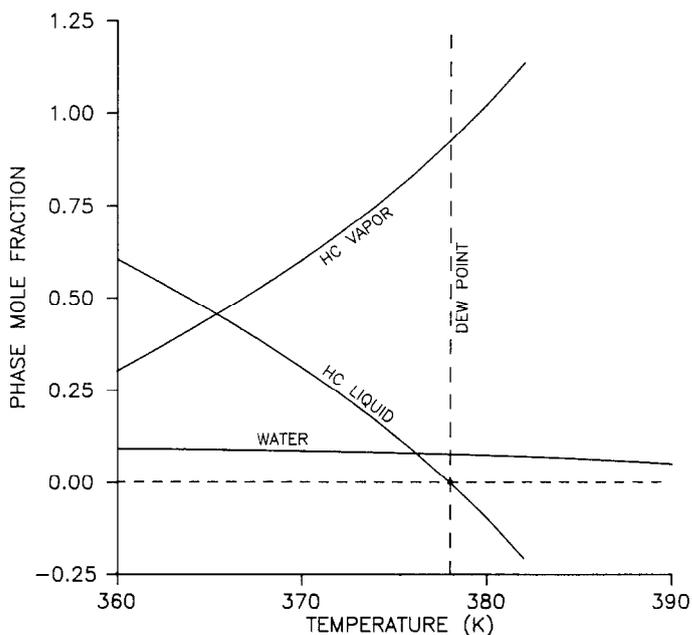
Fig. 10. Phase mole fractions for a gas condensate mixture in the presence of water, showing that the phase fractions (as all other properties) are continuous at the dew point.

different convergence pressure envelopes for $T<T_c$. On the other hand, the phase envelope and convergence pressure envelope for gas-like systems ($T>T_c$) will almost always have large separation because of heavy, low-volatility components. The negative flash is particularly robust in the large area of pressure and temperature (away from the retrograde region) where $\beta>1$, thereby making it useful for processes containing mainly gas-like mixtures (see Fig. 6).

Another application of the negative flash in compositional reservoir simulation is to indicate the phase type -- i.e., designating a single-phase grid cell as "oil" or "gas." This is required for assigning phase pressures, relative permeability, and other phase-related properties. If the converged flash gives $\beta\leq0$ the phase can be considered "oil," and if the converged flash gives $\beta\geq1$ the phase can be considered "gas." For conditions outside the convergence pressure envelope the negative flash converges to the trivial solution, and it is not possible to use negative flash results as a phase indicator.

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