**ChE** *classroom*

# COMPUTING PHASE EQUILIBRIA

## *How Gibbs Energy Considerations Reduce the Role of Rachford-Rice Analysis*

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The two-phase liquid-vapor phase equilibrium flash problem for a molar (F=1) n-component system can be written as 2n equations in 2n unknowns (L, V, $\{x_i\}$, $\{y_i\}$) for specified values of temperature T, pressure P, and feed composition $\{z_i\}$

$$Lx_i + Vy_i = z_i \qquad i = 1, \ldots, n \tag{1}$$

$$\hat{f}_{il}\left(T, P, \{x_i\}\right) = \hat{f}_{ig}\left(T, P, \{y_i\}\right) \qquad i = 1, \ldots, n \tag{2a}$$

This problem is often expressed in terms of vaporization ratios $K_i$ ("K-values"), which are formally a ratio of fugacity coefficients

$$K_i\left(P, T, \{x_i\}, \{y_i\}\right) \equiv \frac{y_i}{x_i} = \frac{\hat{\phi}_{il}\left(T, P, \{x_i\}\right)}{\hat{\phi}_{ig}\left(T, P, \{y_i\}\right)} \tag{3}$$

The equilibrium Eqs. (2a) are then

$$y_i = K_i\left(P, T, \{x_i\}, \{y_i\}\right)x_i \qquad i = 1, \ldots, n \tag{2b}$$

The Rachford-Rice approach[1] to the calculation of phase equilibria is well known, both pedagogically and practically. It starts from the problem descriptions Eqs. (1) and (2b), where the set $\{K_i\}$ have fixed values at the time of solution

$$Lx_i + Vy_i = z_i \qquad i = 1, \ldots, n \tag{1}$$

$$y_i = K_i x_i \qquad i = 1, \ldots, n \tag{2c}$$

Combination of these equations leads to a single equation for a function F(L)

$$F(L) = \sum_{i=1}^{n} \frac{z_i\left(1 - K_i\right)}{\left[K_i + \left(1 - K_i\right)L\right]} = 0 \tag{4}$$

F(L) can be numerically solved for L, which in turn will analytically yield the remaining variables V, $\{x_i\}$, and $\{y_i\}$. The function F(L) is monotonically decreasing in the variable L. Therefore it is often emphasized that evaluating F(L) at L = 0 and L = 1 readily identifies whether there is a solution to Eq. (4) for L between L = 0 and 1. This will be the case if F(0) • F(1) < 0 or, equivalently, F(0) > 0 and F(1) < 0. Thus, examination of the values of F(0) and F(1) reveal if there will be two phases (0 < L < 1) *for the particular set of* $\{K_i\}$. This view is sometimes exercised in undergraduate chemical engineering courses[2] where simple versions of $\{K_i\}$ are used, such as the DePriester nomograph[3] or the Wilson suggestion[4]

$$\ell n\, K_i = 5.37\left(1 - \frac{1}{T_R}\right)\left(1 + \omega\right) - \ell n\, P_R \tag{5}$$

where $T_R$ is the reduced temperature, $P_R$ is the reduced pressure, and $\omega$ is the acentric factor. The Wilson suggestion is based on the assumption of Raoult's Law, using a simple vapor pressure correlation constructed from critical point and acentric factor information. In both the DePriester nomograph and the Wilson suggestion, $K_i = K_i(P,T)$, *i.e.*, there is no composition dependence. Consequently, for a specified flash calculation, the values $\{K_i\}$ would be fixed in Eqs. (2c).

Rudimentary correlations such as the DePriester nomograph and the Wilson suggestion are primarily intended to be *initiations* of more sophisticated descriptions. The DePriester nomographs initiate the DePriester charts, whose K-values are based on the Benedict-Webb-Rubin equation-of-state

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(EOS) for natural gas systems and are composition dependent (like their somewhat more difficult-to-use precursor, the Kellogg Equilibrium Charts[5])

$$K_i = K_i\left(P, T, \{x_i\}, \{y_i\}\right) \qquad (6)$$

The Wilson suggestion has been used to initiate phase equilibrium computations using modern cubic EOSs such as the Soave-Redlich-Kwong EOS[6] or the Peng-Robinson EOS,[7] whose K-values are also composition-dependent. Use of a simple composition-independent K-value correlation in Eqs. (1) and (2c) often yields qualitatively sensible values for $\{x_i\}$ and $\{y_i\}$, which can then be used to initiate solution of the more general composition-dependent problem. In physical terms, what the composition-independent K-values lack is a measure of how the phase equilibrium of a species i is affected by the background of the other species in the mixture $\{x_j\}_{j\neq i}$. Theories such as the SRKEOS and the PREOS are designed to provide this measure.

Implementation of the Rachford-Rice method to solve for vapor-liquid phase equilibria typically involves carrying out an iterative solution technique whereby initialization of $\{x_i\}$ and $\{y_i\}$ is accomplished using a composition-independent K-value correlation. This compositional information is used to update the K-values via Eq. (3). Then the problem for L is solved again, yielding further updated values of $\{x_i\}$ and $\{y_i\}$, which in turn update (again) the K-values (Eq. 3), etc. The procedure is repeated until satisfactory convergence of L (and $\{x_i\}$ and $\{y_i\}$) is achieved. Essentially, the iterative procedure is one of successive substitution, although solution of Eq. (4) for L can easily be carried out using a second-order technique such as Newton-Raphson. The procedure satisfactorily converges in a few iterations (typically less than ten), as in many phase equilibrium problems the background effect on the $\{K_i\}$ is secondary. Of course, if desired, the iterative procedure can be executed as a Newton-Raphson problem in its entirety.

Whether there actually is a solution to Eqs. (1) and (2c) in the domain $0 < L < 1$ is not generally crucial when using an approximate K-value correlation. It has been demonstrated that one does not need an answer for L in the domain $0 < L < 1$ at the point of initiation in order to progress with the solution of a vapor-liquid problem. Whitson and Michelsen[8] have shown that computations that yield L outside the two-phase domain will still yield useful compositional data $\{x_i\}$ and $\{y_i\}$ for updating $\{K_i\}$. In this "negative flash" case, the pivot point $\{z_i\}$ of the lever principle (>ßøP1) is collinear with, but not between, $\{x_i\}$ and $\{y_i\}$.

It is advantageous to know ahead of time, however, whether or not the full composition-dependent K-value flash problem will produce a realistic two-phase solution in the domain $0 < L < 1$. A negative indication means that one should not undertake the two-phase computation. A positive indication, of course, means the two-phase computation should be performed, and more importantly, if the two-phase computation fails to converge, it should not be abandoned; rather, it should be redone with a "better" initiation. Gibbs energy analysis can provide an unambiguous indication of whether or not a two-phase calculation should be carried out. Furthermore, information garnered from Gibbs energy analysis can often provide a subsequent two-phase computation initiation superior to that provided by a composition-independent K-value initiation scheme.

## GIBBS ENERGY ANALYSIS

For an n-component mixture, the Gibbs energy is a function of temperature, pressure, and composition, with $\{x_i\}$ being used here as a general composition

$$G\left(P, T, \{x_i\}\right) = \sum_{i=1}^{n} x_i \mu_i\left(T, P, \{x_i\}\right) \qquad (7)$$

For an EOS such as the SRKEOS or the PREOS, this function is homogeneous, meaning it represents every fluid phase of the mixture. A common tangent (hyper)plane to this (hyper)surface at two points identifies two phases in equilibrium

$$\mu_{il}\left(T, P, \{x_i\}\right) = \mu_{ig}\left(T, P, \{y_i\}\right) \qquad i = 1, \ldots, n \qquad (8)$$

Equation (8) is formally equivalent to Eq. (2a).

Given a system at T and P, a tangent plane can be constructed to the Gibbs surface at a feed composition $\{z_i\}$. If the tangent plane does not intersect the Gibbs surface anywhere, then the system is single-phase, with composition $\{z_i\}$. If the tangent plane intersects the surface somewhere, the system is two (or more) phases.[9] These indications are based on the Gibbs minimum principle version of the Second Law. Since the Gibbs surface is constructed using the same composition-dependent formalism (*e.g.,* SRKEOS or PREOS) as the phase equilibrium problem of interest, the indication for whether or not to continue to do a two-phase computation is unambiguous. Figure 1 schematically demonstrates this concept. For a feed F1, the tangent plane does not intersect the Gibbs surface (excluding the point of tangency); for feed F2 it does. An appropriate flash calculation thus should be performed for feed F2. ("Appropriate" here is interpreted to be vapor-liquid; in reality, for some mixtures the phase equilibria could be more complex.)

To exploit this geometry, one must of course establish if the tangent plane, such as the one at F1, intersects the Gibbs surface, the determination of which may be challenging. Ensuring success with this calculation has been the subject of many studies. Suffice it to say, *not* finding an intersection could simply mean that the search failed. Michelsen[10] advised locating *stationary points,* compositions at which there are extrema of the vertical distance D between the Gibbs surface and the tangent plane. D would be positive when the plane is below the surface and negative when the plane is above the surface (see Figure 1). A caveat is in order here: failure to find a stationary point with $D < 0$ for a given feed stream could mean that the search for the stationary point failed, as opposed to establishing unequivocally that it does not exist. This would be analogous to computationally failing to find an intersection(s).

When searching for stationary points, it can be helpful to recognize that the existence of equilibrium phases is generally associated with the existence of stationary points at nearby compositions. For example, if $D = 0$ at an extremum, then the tangent plane is common to both the feed and the stationary point. The stationary point is an infinitesimal phase in equilibrium with the phase at the feed composition, as with a bubble point or a dew point scenario.[11] Consequently, stationary-point searches are often initiated with rudimentary K-value correlations such as the above Wilson suggestion. The thermodynamics and mathematics to be dealt with when searching for stationary points are presented in Appendix A. Compared to a flash calculation, a stationary point is mathematically simpler to perform and converges more reliably. This is because only a single composition vector (that of the stationary point) is sought vis-á-vis two composition vectors $\{x_i\}$ and $\{y_i\}$ in a vapor-liquid calculation.

Successful execution of the Gibbs analysis provides the assurance to undertake the phase equilibrium computation. An added dividend to performing the stationary point calculation is that the stationary point composition information can serve as an improved initiation for the equilibrium computation. We will now demonstrate 1) the generation of stationary point information for determining whether a vapor-liquid equilibrium computation should be performed, and 2) the use of that information for initiation of the vapor-liquid equilibrium computation.

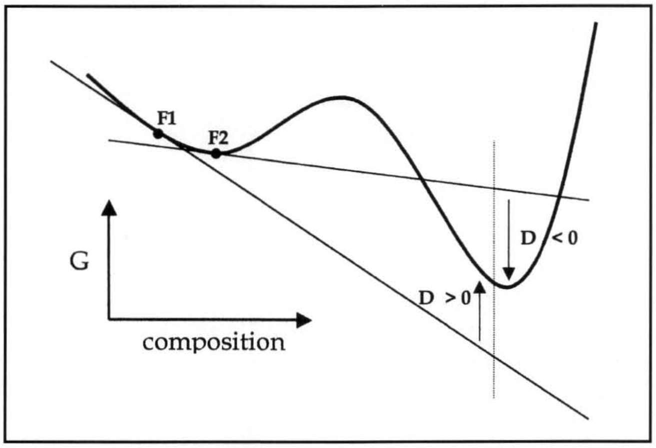

**Figure 1.** *Schematic diagram of Gibbs surface at fixed T and P, with tangent lines at a single-phase system point (F1) and a two-phase system point (F2). The vertical dashed line locates the stationary point corresponding to point F1, for which $D > 0$.*

## EXAMPLE

The importance of employing the Gibbs stability analysis before solving a phase-equilibrium flash calculation can be readily illustrated. Consider a molar feed mixture of 77-mole % methane, 10-mole % ethane, 8-mole % propane, and 5-mole % n-butane at 225 K, to be flashed isothermally at pressures ranging from 0.47 to 83 bars. The SRKEOS is used to model the phase equilibria. Figure 2a and 2b compare the liquid phase fractions L computed from the SRKEOS result and the Wilson suggestion. There is fairly close agreement in the low-pressure (near the dew point, where $L = 0$) region, as shown in Figure 2b, which magnifies the flash results in the vicinity of 1.8 bars. As the pressure is increased beyond 50 bars, the disparity between the SRK and the Wilson results grows, which might be expected considering that the basis of Wilson's suggestion is Raoult's Law. The SRK bubble point ($L = 1$) occurs at about 71 bars; for the Wilson suggestion, it occurs at about 82 bars. Between 71 and 82 bars, the Wilson

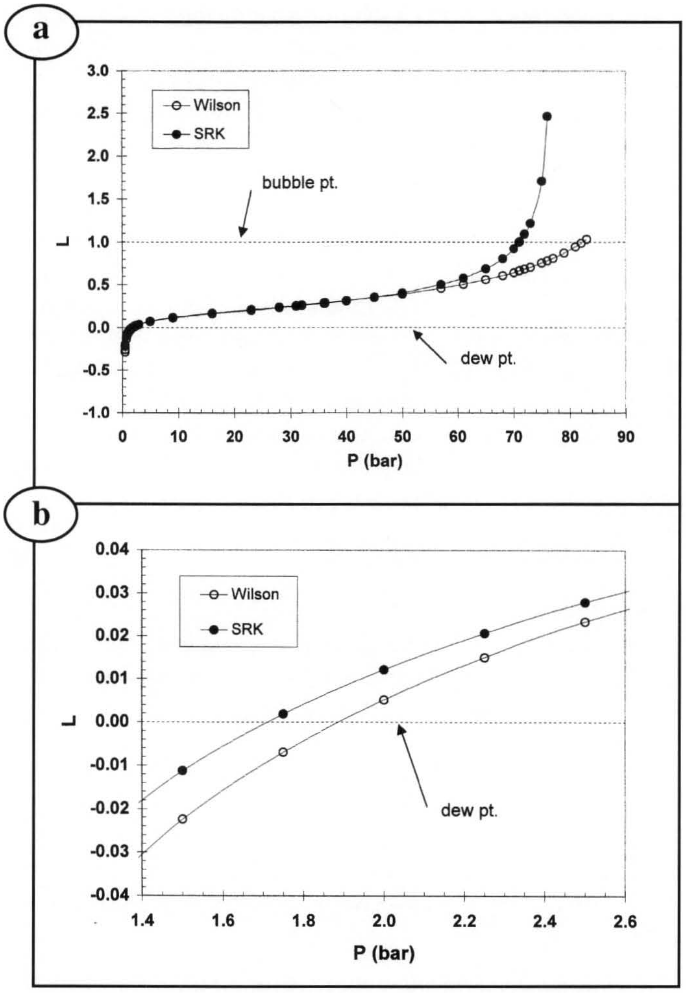

**Figure 2 (a).** *Liquid mole fraction L as a function of pressure at 225 K for a 77-mole % $CH_4$, 10-mole % $C_2H_6$, 8-mole % $C_3H_8$, 5-mole % n-$C_4H_{10}$ mixture. The filled circles are SRKEOS results and the open circles are Wilson results.* **(b)** *Magnification of the dew-point region of Figure 2a.*

calculation (used as a flash problem initiation, say), indicates that a two-phase SRK calculation should follow, whereas the SRK result is a single-liquid phase.

Performance of an SRK stationary-point calculation prior to a flash calculation will correctly indicate if a subsequent two-phase SRK flash calculation should be performed. Figure 3 illustrates how the chÛtance D between the Gibbs surface and the plane tangent to the feed composition varies as a function of pressure at 225 K for this quaternary mixture. When $D > 0$, the system will be one phase according to the SRKEOS; when $D < 0$, the system will be two phases, the description of which would be obtained (from the same SRKEOS). The two points $D = 0$ denote the bubble and dew point boundaries of the SRK two-phase region.

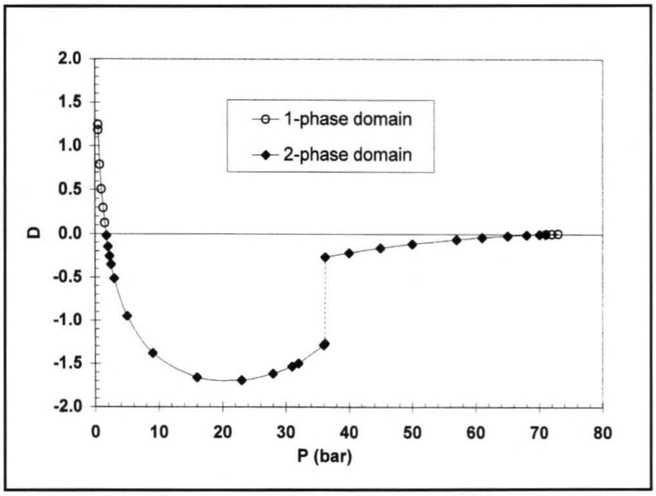

***Figure 3.*** *Distance D as a function of pressure at 225 K for a 77-mole %* $Ch_4$*, 10-mole %* $C_2H_6$*, 8-mole %* $C_3H_8$*, 5-mole % n-*$C_4H_{10}$ *mixture.*

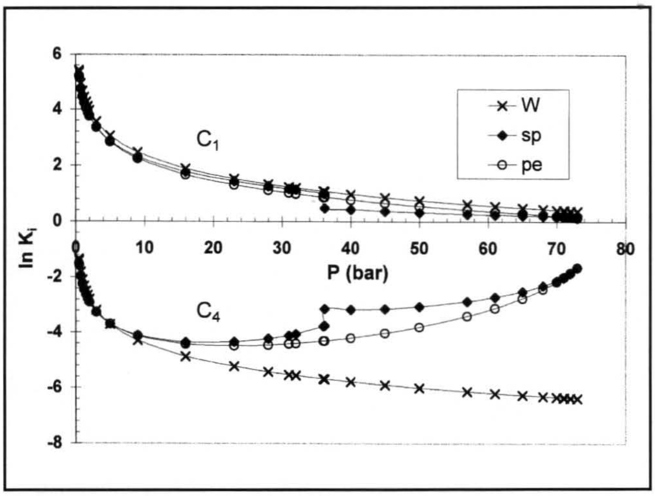

***Figure 4.*** *Natural logarithm of K-values as a function of pressure at 225K for a 77-mole %* $CH_4$*, 10-mole %* $C_2H_6$*, 8-mole %* $C_3H_8$*, 5-mole % n-*$C_4H_{10}$ *mixture. The curves represent the phase-equilibrium results (**pe**), the stationary point results (**sp**), and the Wilson (**W**) for methane (*$C_1$*) and n-butane (*$C_4$*).*

The discontinuity in the stationary point D-curve at a pressure of about 36 bars is caused by the SRKEOS having volume root multiplicity, with its corresponding change of the most stable root from vapor-like to liquid-like.

It is well understood that closeness of initial K-value guesses to the flash-problem final (converged) K-values positively impacts the chance of success of a two-phase flash calculation. In addition to indicating if the flash problem will be a two-phase computation result, Gibbs stationary-point analysis can provide superior K-value estimates that can be used to initiate the two-phase flash computation. These K-values initiations can be used in place of those provided by a rudimentry composition-independent theory. Figure 4 plots K-values for the components methane and n-butane as a function of pressure for the above quaternary system at 225 K. For methane, the Gibbs stationary point result and the Wilson suggestion have comparable K-values, but for n-butane the Gibbs stationary-point result provides a much better initiation (*i.e.,* closer to the actual K-value of the converged flash problem). The authors' experience is that stationary-point results provide superior K-values for heavier, less volatile species in the context of popular thermodynamic models such as the SRKEOS and the PREOS. This is especially true at moderately high pressures. Corresponding to Figure 3, there is a discontinuity in the stationary point K-values in Figure 4.

## CONCLUSIONS

An iterative vapor-liquid equilibrium calculation for a feed mixture $\{z_i\}$ flashed at temperature T and pressure P often employs a simple composition-independent correlation for K-values for initiation. Such correlations can give a misleading indication of whether or not there will actually be two phases when subsequently using a more sophisticated composition-dependent theory of fluid-phase equilibria (such as the Soave-Redlich-Kwong EOS). Gibbs energy analysis, specifically stationary-point analysis of the EOS Gibbs surface, can provide an unambiguous indication of whether there will be two phases in such composition-dependent theories. Additionally, information obtained from stationary point analysis offers K-value initiation of the vapor-liquid equilibrium problem that is superior to that provided by simple composition-independent correlations.

## NOMENCLATURE

| | |
|---|---|
| D | distance between Gibbs surface and tangent plane to Gibbs surface |
| $\hat{f}$ | fugacity |
| G | extensive Gibbs energy |
| K | vaporization ratio (K-value) |
| L | mole fraction of liquid phase |
| P | pressure |
| $\hat{\phi}$ | fugacity coefficient |
| T | temperature |

| | |
|---|---|
| V | mole fraction of vapor phase |
| $\mu$ | chemical potential |
| $\omega$ | acentric factor |
| x | mole fraction of liquid |
| y | mole fraction of vapor |
| z | mole fraction of feed |

Subscripts

| | |
|---|---|
| g | vapor |
| i,j | species |
| l | liquid |
| R | reduced |

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## APPENDIX: STATIONARY POINT FORMALISM

Let the Gibbs energy of an n-component system at temperature $T = T_o$ and pressure $P = P_o$ be represented by Eq. (7)

$$G(\{x_i\}) = \sum_{i=1}^{n} x_i \mu_i(\{x_i\}) \qquad (7)$$

where the independent composition variables will be chosen as $\{x_i\}$, i = 1,2,...n-1, with

$$x_n = 1 - \sum_{i=1}^{n-1} x_i \qquad (A1)$$

The tangent plane at a specified compositon $\{z_i\}$ can be expressed as

$$T(\{x_i\}) = \sum_{i=1}^{n-1} \left[\mu_i(\{z_i\}) - \mu_n(\{z_i\})\right](x_i - z_i) + G(\{z_i\}) \qquad (A2)$$

The distance between the Gibbs surface and the tangent plane to point $(\{z_i\})$ is expressible as

$$F(\{x_i\}) = G(\{x_i\}) - T(\{x_i\}) \qquad (A3)$$

A stationary point is the extremum of this function F in composition space; the composition of the stationary point can be found from the equations

$$\frac{\partial F(\{x_i\})}{\partial x_i} = 0 \qquad i = 1,\ldots,n-1 \qquad (A4)$$

which are expressible as

$$\mu_i(\{x_i\}) - \mu_n(\{x_i\}) - \mu_i(\{z_i\}) - \mu_n(\{z_i\}) = 0$$

$$i = 1,\ldots,n-1 \qquad (A5)$$

or

$$\mu_i(\{x_i\}) - \mu_i(\{z_i\}) = \mu_n(\{x_i\}) - \mu_n(\{z_i\}) = D$$

$$i = 1,\ldots,n-1 \qquad (A6)$$

where D is distance of separation of the parallel tangent plane to points $\{x_i\}$ and $\{z_i\}$. Equivalently, the distance D is the difference between the tangent plane intercepts at the n-1 compositional vertices. A single value of D indicates that point $\{x_i\}$ is a stationary point with respect to point $\{z_i\}$.

Solution for the composition $\{x_i\}$ is typically sought using the fugacity formalism in Eqs. (A6)

$$\hat{\phi}_i(\{x_i\}) x_i = \hat{\phi}_i(\{z_i\}) z_i e^{\frac{D}{RT}} \qquad i = 1,\ldots n-1 \qquad (A7)$$

Michelsen[10] has suggested employing a K-ratio approach when solving Eqs. (A7),

$$\left(\frac{Y_i}{z_i}\right) = \tilde{K}_i = \left(\frac{x_i e^{-\frac{D}{RT}}}{z_i}\right) = \left(\frac{\hat{\phi}_i(\{z_i\})}{\hat{\phi}(\{x_i\})}\right) \qquad i = 1,\ldots n-1 \qquad (A8)$$

This approach produces an analogy to the saturation calculation where the "phase" composition $\{z_i\}$ is known and the other "phase" composition $\{Y_i\}$ is sought. It should be noted that

$$Y_i = x_i e^{-\frac{D}{RT}} \qquad (A9)$$

and

$$\sum_{i=1}^{n} Y_i = e^{-\frac{D}{RT}} \qquad (A10)$$

Therefore, for the case of D = 0, one has solved the saturation-point problem,[11] identifying the infinitesimal phase $\{x_i\}$ in equilibrium with the finite phase $\{z_i\}$.

The goal of solving the stationary-point problem in principle is to find if there is a stationary point with $D < 0$ for the feed of composition $(\{z_i\})$, in which case the feed is not a stable single phase at $(T_o, P_o)$. A phase equilibrium computation is thus mandated to determine how the feed splits. As pointed out in the earlier discussion of Gibbs energy analysis, failure to find a stationary point with $D < 0$ may indicate an unsuccessful search for an existing stationary point of that nature. ❐