

## Stability analysis for PE251 (Following the approach of Michelsen<sup>1</sup>)

The following discussion/analysis is derived for a closed system with an overall composition  $\underline{z}$  at constant temperature (T) and pressure (P).

We have formulated the two-phase PT-flash problem in terms of the iso-fugacity criterion

$$\hat{f}_i^v = \hat{f}_i^l, \quad i = 1, \dots, N_c \quad (1)$$

subject to the mass balance equations

$$z_i = x_i(1 - \beta) + y_i\beta, \quad i = 1, \dots, N_c \quad (2)$$

Eq. (1) can be rewritten in terms of the of fugacity coefficients

$$y_i \hat{\phi}_i^v P = x_i \hat{\phi}_i^l P, \quad i = 1, \dots, N_c \quad (3)$$

Equation (1) is a necessary condition for equilibrium but not a sufficient condition.

To see why this is true consider the case

$$z_i = x_i = y_i, \quad i = 1, \dots, N_c \quad (4)$$

This solution to Eq. (1) and (2) is known as the **trivial** solution and exists for any specification of the overall composition  $\underline{z}$ , T and P.

To arrive at a necessary and sufficient condition for the coexistence of vapor and liquid phases, the Gibbs tangent plane criterion is derived below:

The total Gibbs energy  $G_t$  for a mixture of composition  $\underline{z}$  is given by

$$G_t = G_z = G(\underline{z}) = \sum_{i=1}^{N_c} n_i \mu_i = n_t \sum_{i=1}^{N_c} z_i \mu_i \quad (5)$$

If we remove  $dn_i$  moles of component  $i$  from the original mixture to form a new phase  $\underline{w} = [w_1, w_2, \dots, w_{N_c}]$  the change in  $G_z$  is given by

$$dG_z = - \sum_{i=1}^{N_c} dn_i \mu_i(\underline{z}) \quad (6)$$

and the change in  $G_w$

$$dG_w = \sum_{i=1}^{N_c} dn_i \mu_i(\underline{w}) \quad (7)$$

From Eqs. (6) and (7) we can find the change in  $G_t$

$$dG_t = dG_z + dG_w = dn_t \sum_{i=1}^{N_c} w_i (\mu_i(\underline{w}) - \mu_i(\underline{z})) \quad (8)$$

The total Gibbs energy for a closed system at equilibrium will be the lowest possible energy state (global minimum) and hence the requirement for stability of the overall composition  $\underline{z}$  can be formulated as

$$dG_t \geq 0 \quad (9)$$

for any selection of a trial phase  $\underline{w}$ . Eq. (8) can hence be written as

$$TPD(\underline{w}) = \sum_{i=1}^{N_c} w_i (\mu_i(\underline{w}) - \mu_i(\underline{z})) \geq 0 \quad (10)$$

Eq. (10) is known as the tangent plane criterion of Gibbs and can be read as follows:

If the tangent plane distance, **TPD**, is positive throughout the entire  $N_c$  dimensional composition space (all possible  $\underline{w}$ ), a given overall composition  $\underline{z}$  will form a single phase only.

It can be proven that the **TPD** criterion is a necessary and sufficient condition for stability. The **TPD** criterion can be used to test if a given overall composition will remain single phased or split up on 2 or more phases. For the remainder of these notes, we assume that a maximum of 2 phases can coexist (VLE).

Eq.(10) can be rewritten in terms of fugacity coefficients by inserting

$$\mu_i(\underline{z}) = \mu_i^o + RT(\ln z_i + \ln \hat{\phi}_i^z + \ln P) \quad (11)$$

and

$$\mu_i(\underline{w}) = \mu_i^o + RT(\ln w_i + \ln \hat{\phi}_i^w + \ln P) \quad (12)$$

to arrive at

$$TPD(\underline{w}) = RT \sum_{i=1}^{N_c} w_i (\ln w_i + \ln \hat{\phi}_i^w - d_i) \geq 0 \quad (13)$$

with

$$d_i = \ln z_i + \ln \hat{\phi}_i^z \quad (14)$$

For convenience we introduce the reduced tangent plane distance ***tpd***(w)

$$tpd(\underline{w}) = \frac{TPD(\underline{w})}{RT} = \sum_{i=1}^{N_c} w_i (\ln w_i + \ln \hat{\phi}_i^w - d_i) \geq 0 \quad (15)$$

To test all possible trial phase compositions (w) would be an impossible task. However, if we can demonstrate that ***tpd*** is greater than or equal zero at all stationary points, the ***TPD*** condition can not be violated at any point in composition space and the mixture will form a single phase.

#### Locating the stationary points of ***tpd***:

Any stationary point of ***tpd*** must satisfy

$$\frac{\partial(tdp)}{\partial w_i} = 0, \quad i = 1, \dots, N_c \quad (16)$$

subject to the constraint

$$\sum_{i=1}^{N_c} w_i = 1 \quad (17)$$

Hence, locating the stationary points of ***tpd*** corresponds to performing a constrained optimization of Eq. (15). This can be done by formulating the Lagrange function

$$L(\underline{w}, \lambda) = tdp(\underline{w}) - \lambda \sum_{i=1}^{N_c} (w_i - 1) \quad (18)$$

and subsequently solve the non-linear set of equations

$$\frac{\partial L}{\partial w_i} = 0, \quad i = 1, \dots, N_c \quad (19)$$

$$\frac{\partial L}{\partial \lambda} = 1 - \sum_{i=1}^{N_c} w_i = 0 \quad (20)$$

A more convenient formulation of the **tpd** criterion allows us to locate the stationary points directly by unconstrained optimization. Michelsen<sup>1</sup> introduced the modified tangent plane function **tm** given by

$$tm(\underline{W}) = 1 + \sum_{i=1}^{N_c} W_i (\ln W_i + \ln \phi_i^w - d_i - 1) \quad (21)$$

Eq. (21) introduces a new set of variables  $W_i$  that is formally treated like a mole numbers.  $W_i$  is related to the mole fraction  $w_i$  through

$$w_i = \frac{W_i}{W_t} \quad , \quad W_t = \sum_{i=1}^{N_c} W_i \quad (22)$$

The functional form of Eq. (21) is not chosen arbitrary, as the **tm** will have exactly the same stationary points as **tpd**. Stationary points of **tm** can be located by solving

$$\frac{\partial tm}{\partial W_i} = 0, \quad i = 1, \dots, N_c \quad (23)$$

with the LHS of Eq. (23) given by

$$\frac{\partial tm}{\partial W_i} = \ln W_i + \ln \hat{\phi}_i^w - d_i - 1 + W_i \left( \frac{1}{W_i} + \frac{\partial \ln \hat{\phi}_i^w}{\partial W_i} \right) + \sum_{k \neq i}^{N_c} W_k \left( \frac{\partial \ln \hat{\phi}_k^w}{\partial W_i} \right) \quad (24)$$

By collecting terms in Eq. (24) and applying Euler's theorem of homogeneous functions, the term involving compositional derivatives of the fugacity coefficients disappear as

$$\sum_k^{N_c} W_k \left( \frac{\partial \ln \hat{\phi}_k^w}{\partial W_i} \right) = 0 \quad (25)$$

and Eq.(23) reduces to

$$h_i(\underline{W}) = \frac{\partial tm}{\partial W_i} = \ln W_i + \ln \hat{\phi}_i^w - d_i = 0 \quad , \quad i = 1, \dots, N_c \quad (26)$$

which is a set of non-linear equations in the unknowns  $W_i$ .

Eq. (26) can be solved by a Newton scheme by evaluating the Hessian matrix

$$H_{ij} = \frac{\partial h_i}{\partial W_j} \quad (27)$$

and solving the linear system

$$\underline{\underline{H}} \cdot \underline{\Delta W} + \underline{h} = \underline{0} \quad (28)$$

Given the correction vector ( $\underline{\Delta W}$ ) we can update the unknown variables from iteration  $k$  to  $k+1$  by

$$\underline{W}^{(k+1)} = \underline{W}^{(k)} + \underline{\Delta W} \quad (29)$$

The elements of the Hessian matrix require evaluation of the compositional derivatives of the fugacity coefficients

$$H_{ij} = \frac{\bar{\sigma}_{ij}}{W_i} + \frac{\partial \ln \hat{\phi}_i^w}{W_j} \quad (30)$$

If we assume that the second term on the RHS of Eq. (30) is small, corresponding to a weak dependence of the fugacity coefficient of component  $i$  with respect to component  $j$ , we can derive a successive substitution approach for locating the stationary points of Eq. (21).

$$H_{ij}^{ss} = \frac{\bar{\sigma}_{ij}}{W_i} \approx H_{ij} \quad (31)$$

$\underline{\underline{H}}^{ss}$  is a diagonal matrix and solving Eq. (28) reduces to updating each component separately (successive substitution):

$$H_i^{ss} \cdot \Delta W_i + h_i = 0, \quad i = 1, \dots, N_c \quad (32)$$

By inserting Eq. (31) and Eq. (26) into Eq. (32) we get

$$\frac{\Delta W_i}{W_i} + \ln W_i + \ln \hat{\phi}_i^w - d_i = 0, \quad i = 1, \dots, N_c \quad (33)$$

or

$$\Delta \ln W_i + \ln W_i + \ln \hat{\phi}_i^w - d_i = 0, \quad i = 1, \dots, N_c \quad (34)$$

Hence, to update  $\underline{W}$  from iteration  $k$  to  $k+1$  we use

$$\ln W_i^{(k+1)} = d_i - \ln \hat{\phi}_i^{(k)}, \quad i = 1, \dots, N_c \quad (35)$$

The convergence rate of the successive substitution will obviously depend on the accuracy of approximating  $H$  by  $H^{ss}$ . As for the phase split calculation by successive substitution, the convergence rate of the minimization can become very slow near critical points. But for calculations where speed is not an issue

(PE251), the above approach will converge and provide a simple approach for testing for phase stability.

At a stationary point, the value of **tm** is given by

$$tm^{sp} = 1 + \sum_{i=1}^{N_c} W_i(-1) = 1 - W_t \quad (36)$$

and **tpd<sup>sp</sup>** can be calculated from

$$tpd^{sp} = tm^{sp} + W_t - 1 - \ln W_t \quad (37)$$

Figure 1 demonstrate the shape of **tpd** for a equimolar binary mixture

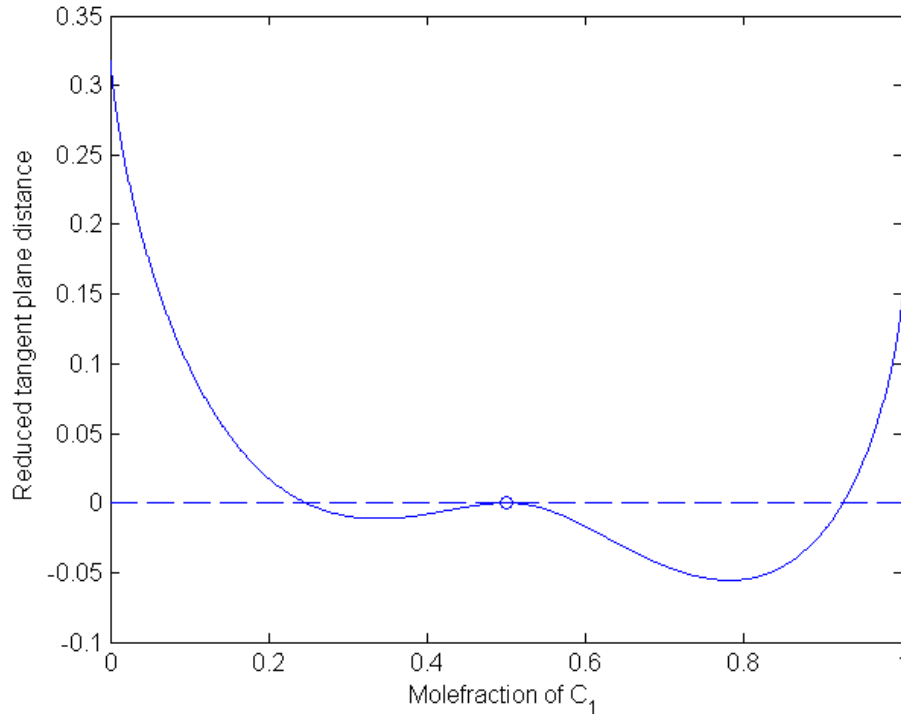


Figure 1: Reduced tangent plane distance for an **unstable** 50/50 mixture of C<sub>1</sub> and nC<sub>4</sub>

The **tpd** curve of Fig. 1 display two stationary points. One at a composition with a high fraction of the light component (vapor like phase) and one with a high mole fraction of the heavy component (liquid like phase). It is important to realize that even though a given mixture have more than one stationary point, locating a single stationary point with a negative **tpd** will establish that the overall

composition is unstable and will split up in two phases. Accordingly, we can initialize our search for stationary points of ***tpd*** by:

- a) guessing on a vapor like trial phase
- b) guessing on a liquid like trial phase

This is referred to as the double-sided stability test.

### Generation of initial estimates

In general, a new phase (**w**) can consist of any combination of the components in the original mixture (**z**). However, for VLE calculations we know that a vapor like phase will be rich in the more volatile components and a liquid like phase will be rich in the least volatile components of the mixture. Hence, to generate initial estimates for the location of stationary points of Eq. (21) we can use the Wilson equation:

$$\ln K_i = \ln \frac{P_c}{P} + \left( 5.37 * (1 + \omega_i) \left( 1 - \frac{T_c}{T} \right) \right) \quad (38)$$

Initial estimates for vapor and liquid are generated as

$$W_i = z_i K_i \quad (39)$$

for vapor like trial phases and

$$W_i = \frac{z_i}{K_i} \quad (40)$$

for liquid like trial phases.

### Possible solutions

As for the phase split calculation, the trivial solution is also a stationary point of Eq. (21) corresponding to ***tpd*** = 0 (stable overall composition **z**). Figure 2 demonstrates a ***tpd*** curve for the binary system where only one non-trivial stationary point exists. At the conditions (T,P) of figure 2, initializing the search with a vapor like trial phase will converge to the trivial solution whereas an initial,

liquid like, estimate will converge to a non-trivial stationary point with negative ***tpd*** (hence unstable). Figure 3 demonstrates the opposite example.

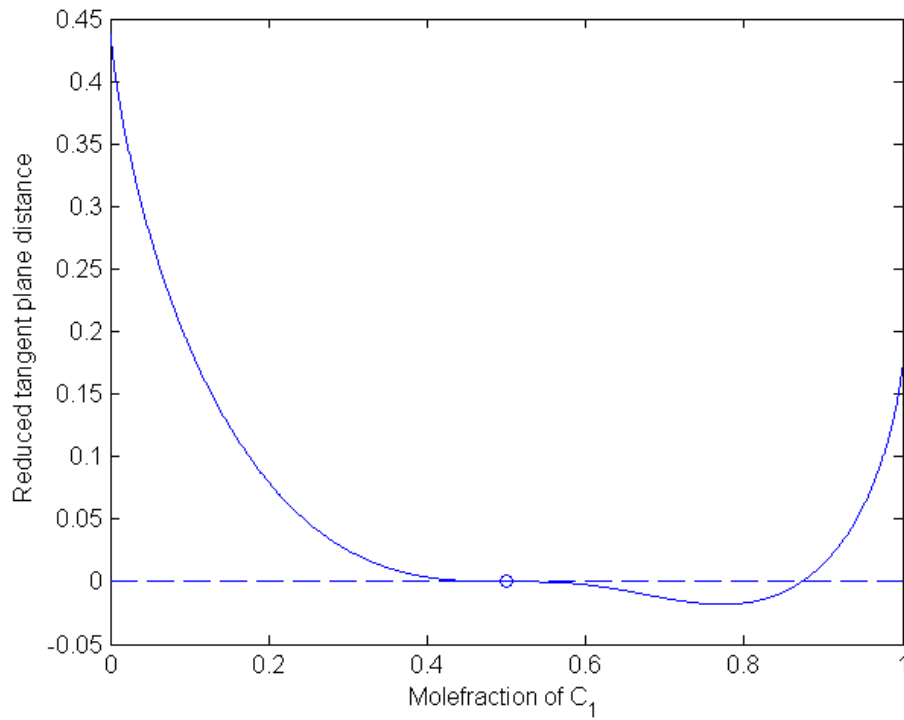


Figure 2. ***tpd*** for a binary system with one non-trivial (vapor like) stationary point.

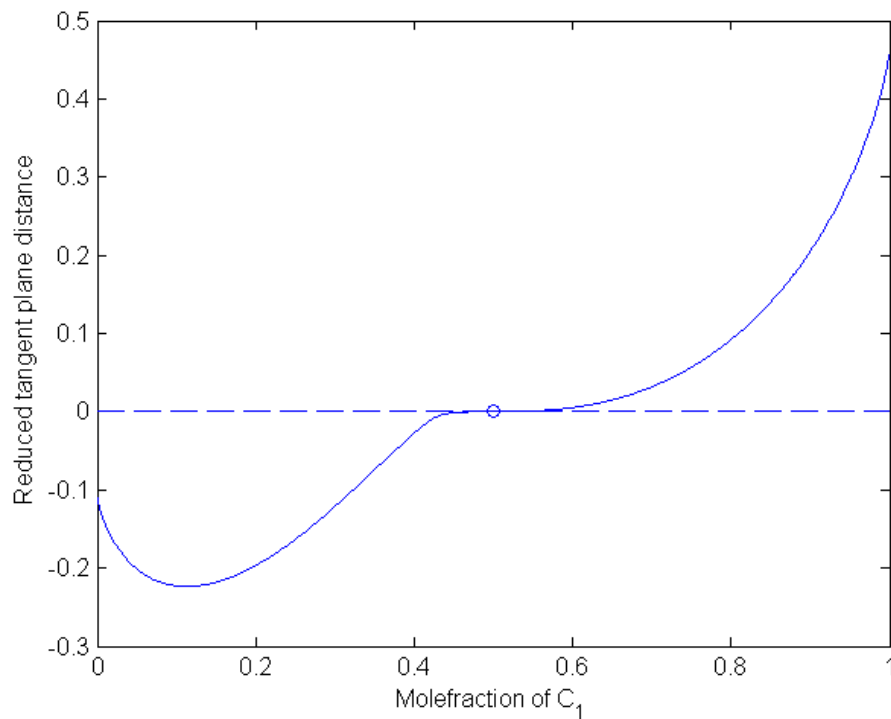


Figure 3. ***tpd*** for a binary system with one non-trivial (liquid like) stationary point.



A fourth example is illustrated in Figure 4 where the ***tpd*** is positive at the stationary point (stable initial composition).

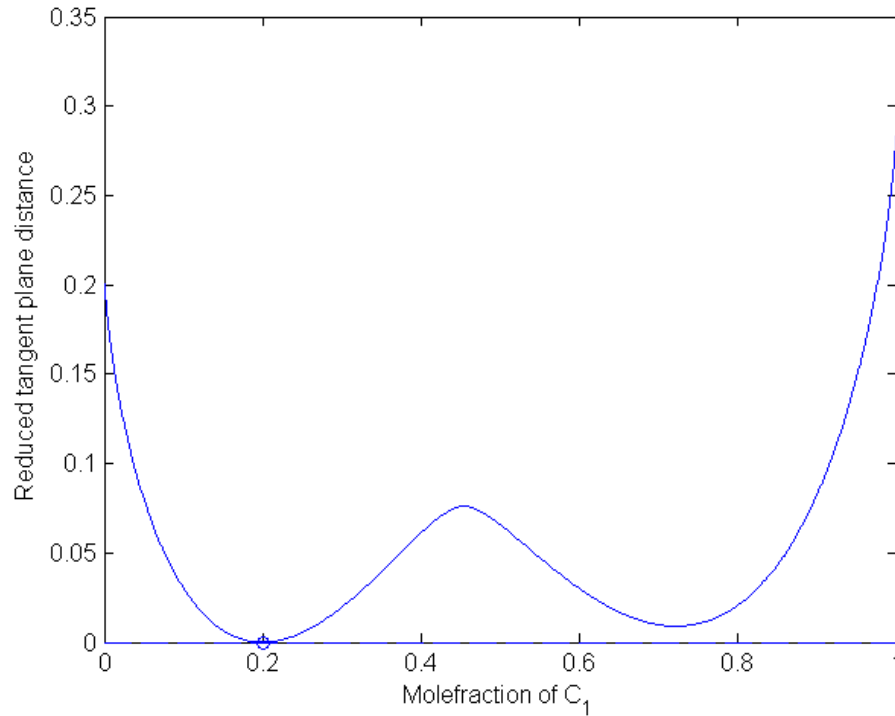


Figure 4. ***tpd*** for a binary system (20/80 mixture) with one non-trivial (vapor like) stationary point. The overall feed is stable.

The last type of solution to the stability test is if both vapor like and liquid like initial estimates converges to the trivial solution. In this case the overall composition will form a single phase only.

### Algorithm

- 1) Calculate the fugacity coefficients for the overall composition  $\underline{z}$  and calculate  $\mathbf{d}_i$  from Eq. (14)
- 2) Generate initial estimates for vapor like and liquid like trial phases from Eq. (39-40)

The following steps are then repeated for both initial estimates

3) Calculate ***tm*** from Eq. (21)

4) Update ***W*** by Eq. (35) and check for **convergence** e.g.

$$r = \sum_{i=1}^{Nc} \left( \ln W_i + \ln \hat{\phi}_i^W - d_i \right)^2 < 10^{-6} \quad (41)$$

5) Check for the **trivial** solution (***W*** ~ ***z***)

6) Repeat from 3) until converged

### Improved estimates for split calculation

If the stability analysis converges to a negative ***tpd*** we can use ***W*** to upgrade our initial estimate for the K-factors for the subsequent split calculation:

1)  $K_i = W_i/z_i$  for vapor-like stationary point

2)  $K_i = z_i/W_i$  for liquid-like stationary point

### References:

1. Michelsen, L. M. "The isothermal flash problem. Part 1: Stability Analysis", Fluid Phase Equilibria, 1981 (8).