

Chapter 4 Criteria for Equilibria and Calculation Techniques

Two kinds of phase equilibria calculations are presented here namely calculations of the critical points and binodal equilibria. These criteria will form the basis of calculations presented in Chapters 5 and 6. The theoretical method has been described elsewhere (Sadus, 1992, 1994) and also in Chapter 2 we reviewed conformal solution and perturbation theories. In Chapter 3, equations of state and mixing rules were given.

4.1 Criteria for Phase Equilibria

4.1.1 Criteria for Vapour-Liquid Phase Coexistence --- Pure Component

It is well known that the liquid phase of a one component fluid is in equilibrium with its vapour if (i) the temperature (T) and pressure (p) of both phases are equal (mechanical equilibrium), and (ii) the chemical potential (m) of the vapour and liquid are equivalent (material equilibrium), i. e.,

$$T' = T'' \quad (4.1)$$

$$p' = p'' \quad (4.2)$$

$$m' = m'' \quad (4.3)$$

where the primes distinguish between the vapour and liquid phases, respectively. For a one component fluid, it is more convenient to replace Eq.(4.3) with the equivalent condition that the Gibbs function of molecules of either phase is equal,

$$G' = G'' \quad (4.4)$$

where G denotes the Gibbs function. The Gibbs function can be obtained directly from an equation of state via the thermodynamic relationship

$$G = A + pV \quad (4.5)$$

in which the Helmholtz function (A) is obtained by integrating pressure (p) with respect to volume (V),

$$A = -\int p dV \quad (4.6)$$

Consequently, the vapour pressure of a one component fluid at a specified temperature can be simply obtained by employing an equation of state to obtain the volumes of the coexisting liquid and vapour phases which simultaneously satisfy Eq. (4.6). This can be readily achieved by applying Maxwell's criterion of equal areas (Walas, 1985).

4.1.2 Criteria for Phase Coexistence --- Binary and Multicomponent Mixtures

Extending the above criteria to binary and multicomponent mixtures,

$$T' = T'' = T''' = \dots \quad (4.7)$$

$$p' = p'' = p''' = \dots \quad (4.8)$$

$$m_1' = m_1'' = m_1''' = \dots \quad (4.9)$$

.....

$$m_m' = m_m'' = m_m''' = \dots \quad (4.10)$$

The chemical potentials are simply related to the Gibbs function by:

$$G = \sum_{i=1}^m x_i m_i \quad (4.11)$$

$$x_1 = 1 - \sum_{i=2}^m x_i \quad (4.12)$$

For determining the equilibrium conditions of a two-phase binary fluid, by using the above criteria ($G = x_1 \mathbf{m}_1 + x_2 \mathbf{m}_2$, $x_1 = 1 - x_2$, $\mathbf{m}_1' = \mathbf{m}_1''$, $\mathbf{m}_2' = \mathbf{m}_2''$), the equilibrium criterion can be expressed in terms of the Gibbs function as (Sadus, 1992)

$$\left(\frac{\partial G}{\partial x_2} \right)_{T,p}' = \left(\frac{\partial G}{\partial x_2} \right)_{T,p}'' \quad (4.13)$$

$$G' - x_2' \left(\frac{\partial G}{\partial x_2} \right)_{T,p}' = G'' - x_2'' \left(\frac{\partial G}{\partial x_2} \right)_{T,p}'' \quad (4.14)$$

Transforming the above equations in terms of the Helmholtz function (Eq. (4.6)),

$$\left[\frac{\partial A}{\partial x_2} \right]_{T,V}' = \left[\frac{\partial A}{\partial x_2} \right]_{T,V}'' \quad (4.15)$$

$$\left[A + pV - x_2 \left(\frac{\partial A}{\partial x_2} \right)_{T,V} \right]' = \left[A + pV - x_2 \left(\frac{\partial A}{\partial x_2} \right)_{T,V} \right]'' \quad (4.16)$$

where A , V and x denote the Helmholtz function, volume and mole fraction, respectively.

Similarly, for determining the equilibrium conditions of a two-phase ternary fluid, by using $G = x_1 \mathbf{m}_1 + x_2 \mathbf{m}_2 + x_3 \mathbf{m}_3$, $x_1 = 1 - x_2 - x_3$, $\mathbf{m}_1' = \mathbf{m}_1''$, $\mathbf{m}_2' = \mathbf{m}_2''$, $\mathbf{m}_3' = \mathbf{m}_3''$ the equilibrium criterion can be expressed as (Prigogine and Defay, 1954, Sadus, 1992)

$$\left(\frac{\partial G}{\partial x_2} \right)_{T,p}' = \left(\frac{\partial G}{\partial x_2} \right)_{T,p}'' \quad (4.17)$$

$$\left(\frac{\partial G}{\partial x_3} \right)_{T,p}' = \left(\frac{\partial G}{\partial x_3} \right)_{T,p}'' \quad (4.18)$$

$$G' - x_2' \left(\frac{\partial G}{\partial x_2} \right)_{T,p}' - x_3' \left(\frac{\partial G}{\partial x_3} \right)_{T,p}' = G'' - x_2'' \left(\frac{\partial G}{\partial x_2} \right)_{T,p}'' - x_3'' \left(\frac{\partial G}{\partial x_3} \right)_{T,p}'' \quad (4.19)$$

4.2 Critical Criteria for Multicomponent Mixtures

The classical critical conditions of a m -component fluid mixture are due to Gibbs (1928). A critical transition is observed when the boundary between stable and metastable states (spinodal curve) and the coexistence boundary between different stable phases (binodal curve) meet. The critical transition can be geometrically interpreted as a point of inflection of the chemical potential with respect to composition. Hence, the first and second derivatives of chemical potential with respect to composition are equal to zero whereas a higher derivative must be positive in order to observe a stable critical transition. The critical properties of a m -component fluid can be obtained by determining the temperature (T), volume (V) and composition (x) which satisfy the critical conditions,

$$W = \begin{vmatrix} -\left(\frac{\mathcal{J}^2 A}{\mathcal{J} V^2} \right)_T & -\left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_1 \mathcal{J} V} \right)_T & \dots & -\left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_{m-1} \partial V} \right)_T \\ \left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_1 \mathcal{J} V} \right)_T & \left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_1^2} \right)_{T,V} & \dots & \left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_1 \partial x_{m-1}} \right)_{T,V} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_{m-1} \partial V} \right)_T & \left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_{m-1} \partial x_1} \right)_{T,V} & \dots & \left(\frac{\mathcal{J}^2 A}{\partial x_{m-1}^2} \right)_{T,V} \end{vmatrix} = 0 \quad (4.20)$$

$$X = \begin{vmatrix} \left(\frac{\mathcal{J} W}{\mathcal{J} V} \right)_T & \left(\frac{\mathcal{J} W}{\mathcal{J} x_1} \right)_{T,V} & \dots & \left(\frac{\partial W}{\partial x_{m-1}} \right)_{T,V} \\ \left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_1 \mathcal{J} V} \right)_T & \left(\frac{\mathcal{J}^2 A}{\mathcal{J} x_1^2} \right)_{T,V} & \dots & \left(\frac{\partial^2 A}{\partial x_1 \partial x_{m-1}} \right)_{T,V} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \left(\frac{\partial^2 A}{\partial x_2 \partial V} \right)_T & \left(\frac{\partial^2 A}{\partial x_1 \partial x_2} \right)_{T,V} & \dots & \left(\frac{\partial^2 A}{\partial x_{m-1}^2} \right)_{T,V} \end{vmatrix} = 0 \quad (4.21)$$

$$Y = \begin{vmatrix} \left(\frac{\mathcal{J}X}{\mathcal{J}V} \right)_T & \left(\frac{\mathcal{J}X}{\mathcal{J}x_1} \right)_{T,V} & \dots & \left(\frac{\partial X}{\partial x_{m-1}} \right)_{T,V} \\ \left(\frac{\mathcal{J}^2 A}{\mathcal{J}x_1 \mathcal{J}V} \right)_T & \left(\frac{\mathcal{J}^2 A}{\mathcal{J}x_1^2} \right)_{T,V} & \dots & \left(\frac{\partial^2 A}{\partial x_1 \partial x_{m-1}} \right)_{T,V} \\ \cdot & \cdot & \cdot & \cdot \\ \left(\frac{\partial^2 A}{\partial x_1 \partial x_2} \right)_T & \left(\frac{\partial^2 A}{\partial x_1 \partial x_2} \right)_{T,V} & \dots & \left(\frac{\partial^2 A}{\partial x_{m-1}^2} \right)_{T,V} \end{vmatrix} > 0 \quad (4.22)$$

where A denotes the Helmholtz function and is determined by employing a suitable equation of state. The condition $Y > 0$ (Eq.(4.22)) guarantees the thermodynamic stability of the calculated critical point. Consequently, the calculation of critical equilibria involves locating the temperature, volume and composition which satisfy two simultaneous equations (Eq.(4.20) and Eq.(4.21)) and checking the thermodynamic stability of the solution. Eq.(4.20) to Eq.(4.22) represent the simplest form of the classical critical criteria in terms of the Helmholtz function.

4.3. Calculation of the Helmholtz Function

In our work, the Helmholtz function for the mixture is obtained (Hicks and Young, 1975, Sadus, 1992) from conformal solution theory using the one-fluid model

$$A = f_{es} A_0^*(V/h_{es}, T/f_{es}) - RT \ln h_{es} + A_{cb} \quad (4.23)$$

with

$$A_{cb} = RT \sum_i x_i \ln x_i \quad (4.24)$$

where R is the universal gas constant, A_0^* is the configurational Helmholtz function of the reference substance, the A_{cb} (combinatorial property) term is the contribution from the entropy of mixing, and the "es" subscript denotes the property of the equivalent substance. The configuration contribution can be obtained from an equation of state. In

this work we have used the van der Waals, Guggenheim and Heilig-Franck equations of state (see Chapter 3 for details). The f and h terms are the conformal parameters which can be deduced from the critical temperatures and volume, respectively. It is customary to choose one of the components of the mixture as the reference substance (denoted by the subscript 0) and obtain the conformal properties of the pure substance relative to it, i.e., $f_{11} = T_{11}^C / T_{00}^C$, $h_{11} = V_{11}^C / V_{00}^C$ etc. The pure component data is obtained from a compilation by Ambrose (Ambrose, 1980) in our work.

The conformal parameters for the equivalent substance of mixtures are evaluated from the van der Waals prescriptions (see Chapter 3 for details)

$$f_{es} h_{es} = \sum \sum x_i x_j f_{ij} h_{ij} \quad (4.25)$$

$$h_{es} = \sum \sum x_i x_j h_{ij} \quad (4.26)$$

where the contribution of unlike interactions is given by

$$f_{ij} = \mathbf{x} (f_{ii} f_{jj})^{0.5} \quad (4.27)$$

$$h_{ij} = 0.125 \xi (h_{ij}^{1/3} + h_{ij}^{1/3})^3 \quad (4.28)$$

where ξ and ζ are adjustable parameters used to optimize agreement between theory and experiment. For the detail of mixing rules refer to Chapter 3.

4.4 Calculation Technique for Phase Equilibria --- Newton-Raphson Method

In order to calculate phase equilibria, an effective numerical method is required. There are many techniques (Henrici, 1964; Traub, 1964; Acton, 1970; Press et al., 1988) available for solving two or three simultaneous equations of two or three variables. They commonly involve successively refining an initial approximate solution until convergence is obtained. For isolated n -dimensional root geometries combined with starting values that are noticeably nearer one root than any of the others, almost any reasonable method will converge to the root. If explicit first derivatives are

calculable, Newton-Raphson method is the method of first choice. It is straightforward and converges quadratically. It is simple in concept and it is adequate in many instances (Walas, 1985). In our work, the Newton-Raphson method (Henrici, 1964; Acton, 1970; Walas, 1985; Press et al., 1988) is employed.

4.4.1 Newton-Raphson Method for Binary Mixtures

To calculate the binodal curves of binary mixture at fixed temperature and pressure, the Newton-Raphson method is used to locate second composition x_2 of two phases whereas the first composition x_1 of two phases can be obtained by using $x_1 = 1 - x_2$. For using the Newton-Raphson method, we rewrite the criteria for phase equilibrium, Eq.(4.13) and Eq.(4.14) as,

$$f(x_2', x_2'') = \left(\frac{\partial G}{\partial x_2} \right)_{T,p}' - \left(\frac{\partial G}{\partial x_2} \right)_{T,p}'' = 0 \quad (4.29)$$

$$g(x_2', x_2'') = G' - G'' - x_2' \left(\frac{\partial G}{\partial x_2} \right)_{T,p}' + x_2'' \left(\frac{\partial G}{\partial x_2} \right)_{T,p}'' = 0 \quad (4.30)$$

By applying the experimental or estimated data for the initial values of $x_2'^i$ and $x_2''^i$, the improved values $x_2'^{i+1}$ and $x_2''^{i+1}$ can be obtained by

$$x_2'^{i+1} = x_2'^i - \left[f(x_2', x_2'')^i \left(\frac{\partial g(x_2', x_2'')}{\partial x_2''} \right)^i - g(x_2', x_2'')^i \left(\frac{\partial f(x_2', x_2'')}{\partial x_2''} \right)^i \right] / J \quad (4.31)$$

$$x_2''^{i+1} = x_2''^i - \left[g(x_2', x_2'')^i \left(\frac{\partial f(x_2', x_2'')}{\partial x_2'} \right)^i - f(x_2', x_2'')^i \left(\frac{\partial g(x_2', x_2'')}{\partial x_2'} \right)^i \right] / J \quad (4.32)$$

where

$$J = \left(\frac{\partial f(x_2', x_2'')}{\partial x_2'} \right)^i \left(\frac{\partial g(x_2', x_2'')}{\partial x_2''} \right)^i - \left(\frac{\partial f(x_2', x_2'')}{\partial x_2''} \right)^i \left(\frac{\partial g(x_2', x_2'')}{\partial x_2'} \right)^i \quad (4.33)$$

When these equations are used to calculate binodal curves, the major difficulty is determining the initial values for $x_2'^i$ and $x_2''^i$. Combining the experimental with estimated data, we may have to try several times to get the correct solution.

4.4.2 Newton-Raphson Method for Ternary Mixtures

The method for calculating ternary phenomena must be carefully considered. Before giving details about ternary mixtures calculations, we give the Newton-Raphson method (Henrici, 1964; Acton, 1970; Walas, 1985; Press et al, 1988) from the point of view of mathematics. It is assumed that a method of solving systems of linear equations is known, with determinants if there are only a few variables, or by matrix methods in general. The Newton-Raphson method reduces the set of nonlinear equations in the primary variables into a set of linear ones in corrections to trial values of the primary variables. Taking a system with three unknowns,

$$f(x, y, z) = 0 \quad (4.34)$$

$$g(x, y, z) = 0 \quad (4.35)$$

$$h(x, y, z) = 0 \quad (4.36)$$

estimates of the roots are (x^i, y^i, z^i) and corrections are (a, b, c) , so that

$$x^{i+1} = x^i + a \quad (4.37)$$

$$y^{i+1} = y^i + b \quad (4.38)$$

$$z^{i+1} = z^i + c \quad (4.39)$$

are improved values. The linear equations to be solved for a , b and c are

$$f_i + af_x + bf_y + cf_z = 0 \quad (4.40)$$

$$g_i + ag_x + bg_y + cg_z = 0 \quad (4.41)$$

$$h_i + ah_x + bh_y + ch_z = 0 \quad (4.42)$$

where, for example, $f_i = f(x_i, y_i, z_i)$, $f_x = \partial f / \partial x$ evaluated at (x_i, y_i, z_i) and so on.

The solution in terms of determinants is

$$a = \frac{\begin{vmatrix} f_i & f_y & f_z \\ g_i & g_y & g_z \\ h_i & h_y & h_z \end{vmatrix}}{D} \quad (4.43)$$

$$b = \frac{\begin{vmatrix} f_x & f_i & f_z \\ g_x & g_i & g_z \\ h_x & h_i & h_z \end{vmatrix}}{D} \quad (4.44)$$

$$c = \frac{\begin{vmatrix} f_x & f_y & f_i \\ g_x & g_y & g_i \\ h_x & h_y & h_i \end{vmatrix}}{D} \quad (4.45)$$

$$D = \begin{vmatrix} f_x & f_y & f_z \\ g_x & g_y & g_z \\ h_x & h_y & h_z \end{vmatrix} \quad (4.46)$$

In the next trial the starting values are $x^{i+1} = x^i + a$, $y^{i+1} = y^i + b$ and $z^{i+1} = z^i + c$. This is the mathematical basis of the Newton-Raphson method for three unknown variables.

As we know that for a two-phase ternary fluid, there are three compositions in each phase. When the Newton-Raphson method is applied to a ternary mixture at fixed temperature and pressure, if we use the same procedure $x_1 = 1 - x_2 - x_3$ for each phase, we have four unknown variables, x_2 and x_3 for both phases. In our work, the second composition of phase one (x_2') is fixed. So, there are three variables (x_3', x_2'', x_3'') for the calculations. The conditions for ternary phase equilibria, Eq.(4.17) to Eq.(4.19), can be re-expressed as follow:

$$f(x_3', x_2'', x_3'') = \left(\frac{\partial G}{\partial x_2} \right)_{T,p}' - \left(\frac{\partial G}{\partial x_2} \right)_{T,p}'' = 0 \quad (4.47)$$

$$g(x_3', x_2'', x_3'') = \left(\frac{\partial G}{\partial x_3} \right)_{T,p}' - \left(\frac{\partial G}{\partial x_3} \right)_{T,p}'' = 0 \quad (4.48)$$

$$h(x_3', x_2'', x_3'') = G' - G'' + x_2'' \left(\frac{\partial G}{\partial x_2} \right)_{T,p}' + x_3'' \left(\frac{\partial G}{\partial x_3} \right)_{T,p}' - x_2' \left(\frac{\partial G}{\partial x_2} \right)_{T,p}' - x_3' \left(\frac{\partial G}{\partial x_3} \right)_{T,p}' = 0 \quad (4.49)$$

Applying $x = x_3'$, $y = x_2''$ and $z = x_3''$ to Eq. (4.34) to Eq.(4.46) we can obtain two points (x_1', x_2', x_3') and (x_1'', x_2'', x_3'') which satisfy the criteria of fluid phase equilibrium of the ternary mixture. The initial values ($x_3'^i, x_2''^i, x_3''^i$) can be obtained from the critical points of ternary mixture or binodal points of binary mixtures. It is apparent that guessing correct initial values is more difficult than obtaining reliable initial estimates for binary calculations.

4.5 Calculation Technique for Critical Points --- Hicks-Young Algorithm

In order to locate all types of critical transitions, the Hicks and Young (Hicks and Young, 1977, Sadus and Young, 1987) algorithm is used in this work. The idea of this algorithm is to track either $X = 0$ (Eq.(4.21)) or $W = 0$ (Eq.(4.20)) at a specified composition, over a search range of the temperature and volume while monitoring the sign of the other function. It is computationally easier to trace $W = 0$ (Eq.(4.20)) rather

than $X = 0$ (Eq.(4.21)) because of the increased complexity of the latter condition. The search procedure is illustrated diagrammatically in Fig. 4.1. Two points (1 and 6) are designated at a small interval on either side of the entry point which lies on one side of a square defined by the points 2, 3, 4 and 5. The Sign of W is compared between the adjacent pairs of points, i.e., between 1 and 2; 2 and 3; 3 and 4; 4 and 5; 5 and 6. A change of sign indicates that condition $W = 0$ passes between the point an odd number of times. The sign of X is checked at these points and if it has changed, then an intersection of W and X has been passed. The search procedure is scaled down until the critical point is accurately found. If the sign of X is unchanged, the new point is used to establish the direction of the $W = 0$ line and the next search square is arranged.

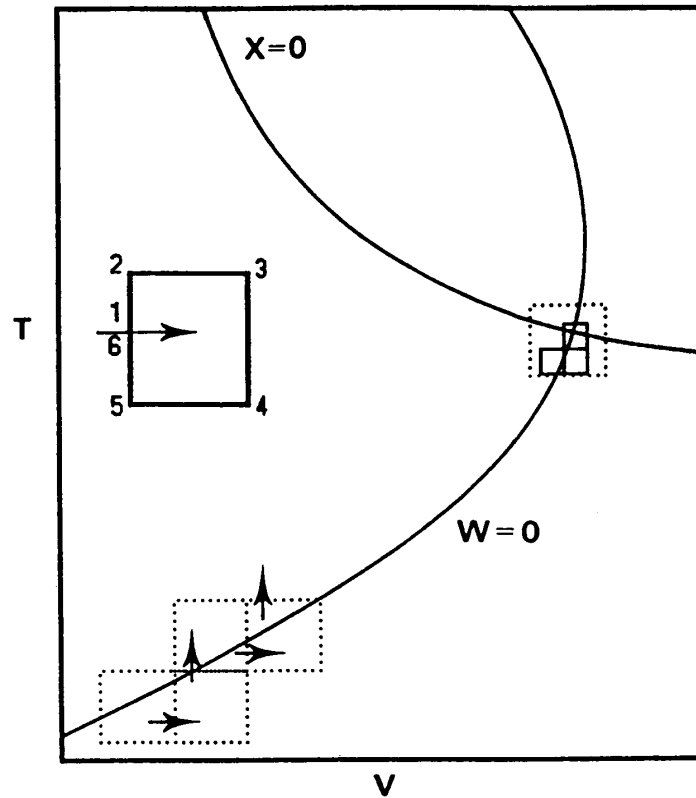


Fig. 4.1 Schematic representation of the Hicks-Young algorithm for locating the critical point.

The major advantages of the Hicks-Young algorithm are that all solutions of the critical conditions are located and that no initial approximations are required. Both

these aspects are very important for the a priori prediction of critical equilibria. Another advantage is that no additional derivatives are required other than those used to obtain Eq. (4.20) to Eq. (4.22). Sadus (1992) has applied the algorithm to the prediction of critical equilibria of ternary mixtures. Recently, Castier and Sandler (1997a & b) also employed the Hicks and Young (1977) algorithm to perform critical point calculations in binary systems.

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