Numerical Techniques for the Calculation of Multicomponent Phase Diagrams

HENRI GAYE AND C. H. P. LUPIS

A stepwise method has been developed for the calculation of two-phase boundaries in multicomponent phase diagrams. It is based on a direct minimization of the Gibbs free energy and places no restriction on the number of components. An alternate search technique has also been developed and is used to guard against any possible divergence of the stepwise technique. At infinite dilution of a component m or in the case of an island miscibility gap, the method is not directly applicable. The difficulty is circumvented, however, through a study of the slopes of the phase boundaries at infinite dilution of component m and a calculation of the critical points of the miscibility gap. Finally, a computer program is described and its applications are illustrated by examples of calculation of ternary diagrams.

In a previous paper, a method was presented for the calculation of the compositions of two phases in equilibrium in a binary system. In a ternary system, if three phases are in equilibrium at a given temperature, their compositions are fixed and can be simply obtained as intersections of two tie-lines (determined from the calculation of two-phase equilibria). In a quaternary or higher order system, the domain corresponding to the equilibrium coexistence of more than two phases may still be deduced from the equilibrium between two phases (e.g., as the intersection of two surfaces). Thus a method to calculate the composition of two phases in equilibrium is sufficient to calculate a ternary phase diagram in its entirety, and is necessary for the calculation of higher order phase diagrams.

The method presented for binary systems consists in solving two equations expressing the equality of the chemical potentials of each component in the two phases. A method based on the same principle has been used by Kaufman et al. to compute isothermal sections of ternary phase diagrams. It uses a Newton-Raphson iteration technique to solve the system of the three equations expressing the equality of the chemical potentials (of each of the three components in the two phases) and is similar to that devised by Hurte and Pike, also for ternary mixtures. Ansara et al. start with essentially the same equations but solve them by a different technique based on a winnowing of compositions. These methods become somewhat cumbersome with a large number of components and a direct minimization of the Gibbs free energy of the system appears preferable. Spencer et al. used this principle to adapt a simplex technique developed by Nelder and Mead. The present contribution adopts the same principle but develops a different technique based on a quadratic representation of the Gibbs free energy of the system. (This technique was briefly outlined in a previous publication; it is presented here in detail).

EXPRESSION OF THE CONDITION FOR EQUILIBRIUM BETWEEN TWO PHASES BY MINIMIZATION OF THE GIBBS FREE ENERGY

Consider an isothermal section of the boundaries of a two-phase field in a multicomponent phase diagram, as schematized in Fig. 1. A point P in that field describes a system of composition described by the mole fractions $X_i$ (for $i = 1, 2, \ldots, m$), and consisting of $n_a$ moles of phase $a$ and $n_b$ moles of phase $b$. The compositions of these phases are represented by the points $Q_a$ and $Q_b$ and described by the mole fractions $X_i^a$ and $X_i^b$ (for $i = 1, 2, \ldots, m$) which define the tie-line $Q_aQ_b$.

A mass balance provides $(m + 2)$ relations, or “constraints”, among the $(2m + 2)$ unknowns $n_a$, $n_b$, $X_i^a$ and $X_i^b$ (for $i = 1, 2, 3, \ldots m$) that define the tie-line $Q_aQ_b$.

The $m$ remaining relations necessary to determine the tie-line $Q_aQ_b$ have to be obtained by stating that the system is at equilibrium. Consequently, the values of the mole fractions $X_i^a$, $X_i^b$, and the amounts of phases $n_a$, $n_b$ must be such that they minimize the total Gibbs free energy of the system, $G_s$, while obeying the constraints [1]. Note that:

$$G_s = n_aG^a + n_bG^b$$

where $G^a$ and $G^b$ represent the molar free energies of the phases $a$ and $b$. At a given temperature $T$, $G^\nu$ (for $\nu = a$ or $b$) can be expressed in terms of the variables $X_i$ (for $i = 1, 2, \ldots m$) as the sum of “Raoultian” standard chemical potentials (i.e., corresponding to the pure components in the $\nu$ phase), ideal free energy of mixing and excess free energy:

$$G^\nu = \sum_{i=1}^{m} X_i \mu_i^{\nu} + RT \sum_{i=1}^{m} X_i \ln X_i + G^E$$

for $\nu = a, b$.

The standard chemical potentials $\mu_i^{\nu}$ are independent of composition and the excess free energy can generally be described by a polynomial in terms of the mole fraction $x_i$.

fractions $X^\alpha, \ldots X^m$ (This assumption, however, is not necessary to the technique described below).

The problem is much simplified when one of the phases is a pure component. For example, if $\beta$ consists of pure component 1 (i.e., $X_i^\beta = 1, X_j^\beta = 0$ for $i = 2, \ldots, m$), the molar free energy $G^\beta$ is a constant equal to $\mu^\beta_i$, and only one of the variables has to be deduced from the minimization of the free energy.

The objective function $G_s$ to be minimized contains both logarithmic and polynomial terms and the constraints $[1c]$ are nonlinear; time consuming search techniques or gradient methods could be necessary to solve the problem formulated in this manner. Instead, a simpler stepwise procedure has been developed.

**STEPWISE CALCULATION OF AN ISOTHERMAL SECTION OF THE EQUILIBRIUM PHASE BOUNDARIES**

Let us consider the two neighboring equilibrium states represented in Fig. 2 by the points $P$ and $P'$. The free energy difference $\Delta G_s$ associated to these states, i.e., when going from the known equilibrium state $(X_{-1}, X_{-2})$ of overall composition $X_0$ to the unknown equilibrium state of overall composition $(X_1^0 + dX_1^0)$, can be approximated by a second order Taylor series in terms of the variables $d\alpha, d\beta, \ldots d\gamma$ (for $i = 2, \ldots, m$). Noting that $d\alpha = -d\beta$,

$$\Delta G_s = \left( G^\alpha - \sum_{i=2}^{m} n_{\alpha} G_i^\alpha \right) d\alpha + \sum_{i=2}^{m} \left[ G_i^\alpha dX_i^0 - G_i^\beta dX_i^0 \right] d\alpha$$

$$+ \sum_{i=2}^{m} \left[ \sum_{i=2}^{m} G_i^\alpha dX_i^0 - G_i^\gamma dX_i^0 \right] d\gamma$$

$$+ \sum_{i=2}^{m} \left[ \sum_{i=2}^{m} \sum_{j=2}^{m} G_{ij}^\alpha dX_i^0 dX_j^0 \right] d\gamma$$

The matrices $G_i^\alpha$ and $G_{ij}^\alpha$ represent the first and second derivatives of the molar free energy in the phase $\nu$ with respect to mole fractions, evaluated at the point $Q_\beta$. They are equal to:

$$G_i^\nu = \mu_i^{\nu} + RT \ln (X_i^\nu/X_i^0) + \frac{\partial G^\nu E^\nu}{\partial X_i^\nu}$$

(for $\nu = \alpha, \beta; i = 2, \ldots, m$)

[5]

and

$$G_{ij}^\nu = RT \left( \frac{\delta_{ij}}{X_i^\nu} + \frac{1}{X_i^\nu} \right) + \frac{\partial^2 G^\nu E^\nu}{\partial X_i^\nu \partial X_j^\nu}$$

(for $\nu = \alpha, \beta; i = 2, \ldots, m$)

[6]

where $\delta_{ij}$ represents Kronecker's symbol.

In terms of the variables $d\alpha, dX_i^0, \ldots dX_j^0$, the constraints expressing the mass balances $[1c]$ can be approximated by their differential forms, obtained by differentiation of Eq. $[1c]$:

$$dX_i^0 = \frac{1}{2} \left( \frac{\partial G_s^\alpha}{\partial X_i^0} + \sum_{j=2}^{m} \frac{\partial G_s^\gamma}{\partial X_j^0} \right)$$

(for $i = 2, \ldots, m$)

[7]

Both constraints $[1a]$ and $[1b]$ are implicitly satisfied in Eqs. $[4]$ and $[7]$. The new $(2m - 1)$ variables $d\alpha, dX_i^0$ and $d\beta_i$ (for $i = 2, \ldots, m$), defining the unknown tie-line $Q_\alpha Q_\beta$, must now minimize $\Delta G_s$ in Eq. $[4]$ and obey the constraints $[7]$.

This may be recognized as a quadratic programming problem, usually solved by the simplex algorithm. A more direct technique will be adopted here, taking advantage of the particular form of the constraints which do not include inequalities. Replacing in Eq. $[4]$ the $(m - 1)$ variables $d\gamma_i$ by their expressions in terms of the $m$ variables $d\alpha, dX_i^0$ (for $i = 2, \ldots, m$) given in Eq. $[7]$, the solution is obtained by writing that the derivatives of $\Delta G_s$ with respect to the latter $m$ variables are zero. This results in a system of $m$ linear equations with respect to the $m$ variables $d\alpha, dX_i^0$ (for $i = 2, \ldots, m$).

These equations may be expressed in matrix and vector notation by:

$$(A) \mathbf{Z} = \mathbf{B}_1 + \mathbf{B}_2$$

where the elements of the matrix $(A)$ and vectors $\mathbf{Z}, \mathbf{B}_1$ and $\mathbf{B}_2$ are:

$$A_{ij} = \sum_{i=2}^{m} \sum_{j=2}^{m} (X_i^0 - X_j^0) (X_i^0 - X_j^0) G_{ij}^\alpha$$

[9a]

$$A_{ij} = \sum_{i=2}^{m} \sum_{j=2}^{m} (X_i^0 - X_j^0) (X_i^0 - X_j^0) G_{ij}^\alpha$$

[9b]

$$Z_i = d\alpha$$

[10a]

$$Z_i = dX_i^0$$

[10b]

$$B_{1i} = n_{\alpha} G_i^\alpha - \sum_{i=2}^{m} (X_i^0 - X_i^0) G_i^\alpha$$

[11a]

$$B_{1i} = n_{\beta} G_i^\alpha - \sum_{i=2}^{m} (X_i^0 - X_i^0) G_i^\alpha$$

[11b]

$$B_{2i} = \sum_{i=2}^{m} \sum_{j=2}^{m} G_{ij}^\alpha dX_j^0$$

[12a]

$$B_{2i} = \sum_{i=2}^{m} \sum_{j=2}^{m} G_{ij}^\alpha dX_j^0$$

[12b]

It may be noted that when the $\beta$ phase is the pure component 1, the only variable to be calculated in Eq. $[8]$ is $d\alpha$. It is readily obtained as: