

# A STUDY OF EQUATION-SOLVING AND GIBBS FREE ENERGY MINIMIZATION METHODS FOR PHASE EQUILIBRIUM CALCULATIONS

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Phase equilibrium calculations are often involved in the design, simulation, and optimization of chemical processes. Reported methods for these calculations are based on either equation-solving or Gibbs free energy minimization approaches. The main objective of this work is to compare selected methods for these two approaches, in terms of reliability to find the correct solution, computational time, and number of  $K$ -value evaluations. For this, four equation-solving and three free minimization methods have been selected and applied to commonly encountered vapour–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE), and vapour–liquid–liquid equilibrium (VLLE) examples involving multiple components and popular thermodynamic models. Detailed results show that the equation-solving method based on the Rachford–Rice formulation accompanied by mean value theorem and Wegstein’s projection is reliable and efficient for two-phase equilibrium calculations not having local minima. When there are multiple minima and for three-phase equilibrium, the stochastic method, genetic algorithm (GA) followed by modified simplex method of Nelder and Mead (NM) is more reliable and desirable. Generic programs for numerical methods are ineffective for phase equilibrium calculations. These findings are of interest and value to researchers and engineers working on phase equilibrium calculations and/or developing thermodynamic models for phase behaviour.

*Keywords:* equation-solving approach; Gibbs free energy minimization; vapour–liquid equilibrium; liquid–liquid equilibrium; vapour–liquid–liquid equilibrium.

## INTRODUCTION

Reliable and precise phase equilibrium calculations are essential for simulation and optimization of chemical processes. The task in these calculations is to predict precisely the correct number of phases at equilibrium and their compositions. Methods for these calculations, which are equivalent to steady-state simulation of single-stage flash separation at a specified temperature ( $T$ ) and pressure ( $P$ ), have been widely studied for various examples and thermodynamic models. These methods can be classified into two main categories: the equation-solving approach and Gibbs free energy minimization. At equilibrium, the chemical potential (or activity) of each component in a phase must be equal to that in another phase in the system. This iso-activity (or fugacity matching) conditions, which can be expressed in terms of equilibrium constants ( $K$ -values) and component mass balances form the set of equations in the equation-solving approach. Hence, this approach is also known as the mass balance approach<sup>1</sup> and the  $K$ -value method<sup>2</sup>. In this approach, governing equations consisting of mass balances, fugacity-matching and mole fraction summation for an assumed number of phases are solved

numerically. Depending on how these equations are solved, there are two subclasses<sup>3,4</sup>.

In one subclass, referred to here as simultaneous equation-solving (SES), all the governing equations are solved simultaneously for the unknowns. One choice for solving these equations is the popular Newton method since it provides quadratic convergence when the initial estimates are close to the solution. Nelson<sup>5</sup> observed that, for a non-ideal system, convergence of the Newton method may not be rapid as  $K$ -values may change drastically from one iteration to another. There is also a tendency for the Jacobian matrix to become ill-conditioned. These difficulties are compounded by the use of numerical derivatives. One can avoid some of these by using the Marquardt–Levenberg or quasi-Newton method. Sanderson and Chien<sup>6</sup> applied Marquardt’s method for chemical and phase equilibrium problems. Joulia *et al.*<sup>3</sup> proposed a hybrid method, in which quasi-linearization is used first for reliability and then, if necessary, the quasi-Newton method is employed to accelerate convergence.

In the second subclass of the equation-solving approach, the governing equations, along with estimates of  $K$ -values, are often solved in the inner loop. Since  $K$ -values may depend on phase compositions, their estimates are updated

in the outer loop. Various techniques in the second subclass differ mainly in how  $K$ -values are updated in the outer loop. These techniques, referred to as equation-decoupling methods<sup>3</sup>, are often described in textbooks on thermodynamics. A successive (direct) substitution method can be used for updating  $K$ -values in the outer loop. Although this method is reliable, it has only a linear rate of convergence and consequently is slow to converge. Hence, acceleration may be needed for computational efficiency. One of the well-known equation-decoupling methods is the inside-out algorithm of Boston and Britt<sup>7</sup>, which uses a quasi-Newton method for acceleration. Wegstein's projection and general dominant eigenvalue method were used by Prausnitz *et al.*<sup>8</sup> and Michelsen<sup>9</sup>, respectively. Ohanomah and Thompson<sup>1</sup> and Gupta *et al.*<sup>10</sup> have examined various acceleration methods (including Wegstein's projection and the general dominant eigenvalue method) in their studies. Mehra *et al.*<sup>11</sup> have proposed three acceleration techniques, and compared their performance with non-accelerated successive substitution and the Newton method (SES method) for vapour-liquid equilibrium (VLE) examples. In one example, trivial solution (with both phases having the same composition) occurred for the Newton method when near the phase boundary. All the tested methods have shown an increase of iterations near the critical point of the mixture. Mehra *et al.*<sup>11</sup> noted that accelerated successive substitution is more efficient than the Newton method as no matrix manipulations are involved. Note that the equation-solving approach requires a good initial estimate for the iterative calculations. In the absence of good initial estimates or precautions, iterations may converge to a trivial solution, especially in the critical region<sup>12</sup>.

Many of the earlier methods assume that the correct number of phases at equilibrium is known *a priori*, for example, from bubble- and dew-point calculations, and they also focus mainly on VLE. Nelson<sup>5</sup> proposed a simple procedure, assuming a maximum of three phases, to determine the number of phases rapidly and then perform phase equilibrium calculations. For VLE calculations without knowing the correct number of phases, Bullard and Biegler<sup>13</sup> introduced pseudo-pressure in the governing equations. They successfully solved the resulting minimization problem for several VLE examples by successive linear programming (SLP). This strategy was later modified by introducing other pseudo-parameters for application to multi-phase systems<sup>14,15</sup>.

Although the equation-solving approach seems to be favoured by engineers and practitioners for its computational efficiency, it does not guarantee the minimization of Gibbs free energy, which is the thermodynamic requirement for equilibrium. This is simply because the iso-activity criterion is only a necessary condition for free energy minimization. The correct solution to the phase equilibrium problem should not only satisfy the sufficient condition but also the corresponding free energy should be at the global minimum. Hence, free energy minimization is favoured, particularly by researchers in process systems engineering, for its reliability. Earlier studies<sup>16–19</sup> have focussed on local minimization methods. Very recently, Lucia *et al.*<sup>20</sup> applied successive quadratic programming (SQP) for multiphase equilibrium flash calculations. Their algorithm iteratively follows a logical sequence of adding phases until the global minimum of Gibbs free energy is found.

Since Gibbs free energy function is highly non-linear and complex, a reliable and accurate method for global minimization is highly desired for phase equilibrium calculations. Both deterministic and stochastic methods are available for global minimization. McDonald and Floudas<sup>2,21–23</sup> have developed two global methods for phase equilibrium calculations: a decomposition-based approach (transformation and partitioning) for using with the NRTL model; and a branch and bound method for UNIQUAC, UNIFAC, ASOG, and TK-Wilson models. Both these methods are deterministic methods having the desirable property of guaranteed convergence to the global minimum. Another deterministic approach for global minimization is interval analysis, which was applied by Hua *et al.*<sup>24</sup> and Tessier *et al.*<sup>25</sup> to phase stability. This analysis is independent of initialization and thermodynamic model, and can find all the stationary points of the objective function. Hua *et al.*<sup>24</sup> found that it can solve the phase stability problems with complete reliability, but, as the number of components increases, the computational performance is less predictable and it may require unreasonable computation time. Later, Tessier *et al.*<sup>25</sup> introduced an enhanced method to improve the computational efficiency, especially for larger problems.

Among the stochastic methods, Pan and Firoozabadi<sup>26</sup> and Lee *et al.*<sup>27</sup> have respectively demonstrated that simulated annealing (SA) and the multi-pass Luus-Jaakola (LJ) are capable of locating the global minimum of free energy for multi-phase equilibrium calculations. The application of genetic algorithms (GA) and SA to phase equilibrium calculations and phase stability problems<sup>28</sup>, shows that both have good reliability for global minimization of free energy and tangent plane distance function, and that GA is more efficient than SA. Major advantages of stochastic methods are that they are applicable even to ill-structure or unknown-structure problems<sup>29</sup>, not restricted to any specific thermodynamic model, and can easily be used for developing new models<sup>30</sup>.

Until now, only Ohanomah and Thompson<sup>1,31,32</sup> have conducted a comparative study of several methods for phase equilibrium calculations. The above review, as well as recent books<sup>33–35</sup> show that there have been significant developments in global minimization. Also, with the increasing availability of computational power, reliability of calculations is perhaps more important than computational efficiency, even though many phase equilibrium calculations are frequently involved in a process simulation or optimization. Therefore, the main objective of this work is to evaluate the reliability and efficiency of methods for two- and three-phase equilibrium calculations. The selected methods include equation decoupling methods and SES (both belonging to the equation-solving approach), and local and global methods for free energy minimization. These methods are tested exhaustively on VLE, liquid-liquid equilibrium (LLE) and vapour-liquid-liquid equilibrium (VLLE) examples involving multiple components and commonly used thermodynamic models. Some methods are implemented using readily available computer programs for numerical methods to find their effectiveness for phase equilibrium calculations. This is of importance and interest since these programs are convenient and appealing to use, and hence sometimes recommended for phase equilibrium calculations<sup>36</sup>.

## GOVERNING EQUATIONS

## Equation-Solving Approach

The problem formulation for VLE of  $nc$  components is presented below, and the simplification for VLE and LLE is described in Appendix A. The governing mass balances and summation equations for VLE are:

$$F = V + L_1 + L_2 \quad (1)$$

$$z_i F = y_i V + x_i^{L1} L_1 + x_i^{L2} L_2; \quad i = 1, 2, \dots, nc \quad (2)$$

$$\sum_{i=1}^{nc} x_i^{L1} = 1.0 \quad (3)$$

$$\sum_{i=1}^{nc} x_i^{L2} = 1.0 \quad (4)$$

$$\sum_{i=1}^{nc} y_i = 1.0 \quad (5)$$

The superscripts, L1 and L2, on  $x_i$  refer to liquid phases 1 and 2, respectively. The phase number (L1 or L2) is arbitrary to distinguish the two liquid phases that may coexist. The iso-activity criterion gives:

$$y_i = K_{i1} x_i^{L1} \quad i = 1, 2, \dots, nc \quad (6a)$$

and

$$y_i = K_{i2} x_i^{L2} \quad i = 1, 2, \dots, nc \quad (6b)$$

In the above  $3nc + 4$  equations (equations (1) to (6)), the number of unknowns is  $3nc + 3$  only. Hence, equations (3) to (5) are often combined into two equations.

In equation (6), equilibrium constants,  $K_{i1}$  and  $K_{i2}$  can be expressed in terms of thermodynamic quantities:

$$K_{i1} = \frac{\hat{\phi}_i^{L1}}{\hat{\phi}_i^V}; \quad K_{i2} = \frac{\hat{\phi}_i^{L2}}{\hat{\phi}_i^V} \quad (7)$$

or

$$K_{i1} = \frac{\gamma_i^{L1} P_i^{\text{sat}}}{\hat{\phi}_i^V P}; \quad K_{i2} = \frac{\gamma_i^{L2} P_i^{\text{sat}}}{\hat{\phi}_i^V P} \quad (8)$$

Equation (7) is applicable if both liquid and vapour phases are described by an equation of state (EOS) model for liquid fugacity coefficients ( $\hat{\phi}_i^{L1}$  and  $\hat{\phi}_i^{L2}$ ) and vapour fugacity coefficient ( $\hat{\phi}_i^V$ ). Equation (8) is applicable when the liquid and vapour phases are described by an activity coefficient model (for  $\gamma_i^{L1}$  and  $\gamma_i^{L2}$ ) and EOS model (for  $\hat{\phi}_i^V$ ), respectively. Where the ideal vapour phase is assumed,  $\hat{\phi}_i^V$  is set to unity.

Substituting equation (6) into equation (2), and rearranging yields:

$$y_i = \frac{z_i K_{i1} K_{i2}}{K_{i1} K_{i2} + \theta^{L1} K_{i2} (1 - K_{i1}) + \theta^{L2} K_{i1} (1 - K_{i2})}; \quad i = 1, 2, \dots, nc \quad (9)$$

$$x_i^{L1} = \frac{z_i K_{i2}}{K_{i1} K_{i2} + \theta^{L1} K_{i2} (1 - K_{i1}) + \theta^{L2} K_{i1} (1 - K_{i2})}; \quad i = 1, 2, \dots, nc \quad (10)$$

$$x_i^{L2} = \frac{z_i K_{i1}}{K_{i1} K_{i2} + \theta^{L1} K_{i2} (1 - K_{i1}) + \theta^{L2} K_{i1} (1 - K_{i2})}; \quad i = 1, 2, \dots, nc \quad (11)$$

where  $\theta^{L1}$  and  $\theta^{L2}$  are the fractions of molar flow rate of each liquid phase with respect to the overall feed,  $F$ . Applying the well-known Rachford–Rice formulation to combine the three equations (3) to (5) into two, we have:

$$\sum_{i=1}^{nc} (y_i - x_i^{L1}) = \sum_{i=1}^{nc} \frac{z_i K_{i2} (K_{i1} - 1)}{K_{i1} K_{i2} + \theta^{L1} K_{i2} (1 - K_{i1}) + \theta^{L2} K_{i1} (1 - K_{i2})} = 0 \quad (12)$$

$$\sum_{i=1}^{nc} (y_i - x_i^{L2}) = \sum_{i=1}^{nc} \frac{z_i K_{i1} (K_{i2} - 1)}{K_{i1} K_{i2} + \theta^{L1} K_{i2} (1 - K_{i1}) + \theta^{L2} K_{i1} (1 - K_{i2})} = 0 \quad (13)$$

## Gibbs Free Energy Minimization Approach

Total Gibbs free energy of a system of  $np$  phases is calculated by summing the molar Gibbs energy of all phases.

$$G = \sum_{k=1}^{np} n^k g^k = \sum_{k=1}^{np} \left( \sum_{i=1}^{nc} n_i^k \right) g^k \quad (14)$$

Since mole fractions involved in  $g^k$  are given by  $x_i^k = n_i^k / n^k$ , the unknown variables are only  $n_i^k$  (total number:  $nc \times np$ ). At physical phase equilibrium (without any chemical reaction), moles of each component should be conserved and  $n_i^k$  should also be non-negative. Hence, free energy minimization should satisfy the following constraints and bounds.

$$\sum_{k=1}^{np} n_i^k = z_i F; \quad i = 1, 2, \dots, nc \quad (15)$$

$$0 \leq n_i^k \leq z_i F; \quad i = 1, 2, \dots, nc \quad (16)$$

Total free energy,  $G$ , can be simplified for different situations by eliminating constant terms (for a particular system). The final dimensionless equations are presented below. For details, the reader should refer to McDonald<sup>37</sup> and Rangaiah<sup>28</sup>.

The dimensionless  $G/RT$  is shown as below if vapour and liquid phases are described by different thermodynamic models:

$$\frac{G}{RT} = \sum_{k \in np (\text{Liquid phase only})} \sum_{i=1}^{nc} n_i^{L(k)} [\ln(x_i^{L(k)} \gamma_i^{L(k)} P_i^{\text{sat}})] + \sum_{i=1}^{nc} n_i^V [\ln(y_i \hat{\phi}_i^V P)] \quad (17)$$

where the superscript, L(k) and V refer to liquid phase  $k$  and vapour phase, respectively. The first summation in the first term is for all liquid phases only. Also, the first term in equation (17) is valid only for activity coefficient models. For EOS models, it can be modified as:

$$\frac{G}{RT} = \sum_{k \in np (\text{Liquid phase only})} \sum_{i=1}^{nc} n_i^{L(k)} [\ln(x_i^{L(k)} \hat{\phi}_i^{L(k)})] + \sum_{i=1}^{nc} n_i^V [\ln(y_i \hat{\phi}_i^V)] \quad (18)$$

If only liquid phases exist, equation (17) can be simplified by ignoring  $P_i^{\text{sat}}$  (which remains unchanged in a particular example) and by eliminating the second term for vapour phase, to

$$\frac{G}{RT} = \sum_{k=1}^{np} \sum_{i=1}^{nc} n_i^{L(k)} [\ln(x_i^{L(k)} \gamma_i^{L(k)})] \quad (19)$$

## SELECTED METHODS

### Equation-Solving Approach

For the present study, four equation-solving methods are selected. Of these, three belong to the equation decoupling group and one is an SES method. The four methods are now described.

#### Rachford–Rice–Mean value theorem–Wegstein’s projection (RMW) method

Ohanomah and Thompson<sup>1</sup> have tried various acceleration algorithms and formulations for solving VLE problems by the equation-solving approach. Their results show that the Rachford–Rice formula accompanied by the mean value theorem and Wegstein’s projection is the best among the formulations and algorithms tested. This RMW method was also extended to LLE<sup>31</sup>. Since acceleration is not used for updating  $K$ -values, it may not be the fastest method among the equation-solving approach, but its reliability is good. The steps in the RMW method for VLE are as follows<sup>1</sup>:

- (1) Initialize  $\{K_{i1}\}$  and  $\theta^V$ , where  $\theta^V$  is the molar fraction of the vapour phase with respect to overall feed,  $F$ . Note that  $\{\}$  implies ‘for all components,  $i$ ’.
- (2) Compute  $\{y_i\}$  and  $\{x_i^{L1}\}$  from equations (A1) and (A2), respectively. If necessary, normalize the calculated mole fractions.
- (3) Evaluate  $\{K_{i1}\}$  based on specified thermodynamic models, using the current  $\{y_i\}$  and  $\{x_i^{L1}\}$ .
- (4) Apply mean value theorem and Wegstein’s projection to equation (A3) for updating  $\theta^V$ .
- (5) Check for convergence criteria. If satisfied, stop; otherwise, go to step (2).

Note that equation (A3) is not solved for  $\theta^V$  (until convergence) in step (4). To implement RMW for LLE, the same steps listed above can be used with some changes: replace  $\theta^V$  by  $\theta^{L2}$ ,  $\{y_i\}$  by  $\{x_i^{L2}\}$ , and equations (A1) to (A3) by equations (A10) to (A12).

#### Accelerated successive substitution (Acc-SS-xy) method

Gupta *et al.*<sup>10</sup> have examined various successive substitution algorithms for VLE systems modeled by the Peng–Robinson (PR) EOS model. They classified the algorithms into (a) successive substitution on the  $K$ -value; and (b) successive substitution on liquid and vapour mole fractions. A comparison was made based on the number of iterations and number of thermodynamic (i.e.,  $K$ -value) evaluations. The results of Gupta *et al.*<sup>10</sup> on two VLE examples show that accelerated successive substitution on liquid and vapour mole fractions (Acc-SS-xy) requires fewer thermodynamic evaluations and exhibits less oscillatory behaviour than others tried. Hence, the Acc-SS-xy method is selected for the present study. This method involves

successive substitution on liquid and vapour mole fractions, which are updated in two separate loops. The dominant eigenvalue method of Orbach and Crowe<sup>38</sup> was used for acceleration purpose since it does not require any storage or multiplication of vectors and matrices. Besides, the acceleration factor is evaluated based on the norm of the error and hence no extra evaluations are needed. More details on Acc-SS-xy can be found in Gupta *et al.*<sup>10</sup>

#### Nelson’s method

The above two methods can be used only after knowing the number of phases at equilibrium. Nelson<sup>5</sup> proposed a simple method to determine the number of phases rapidly, followed by flash calculations. He described the method for a maximum of three phases (i.e., VLLE). Based on simple criteria involving  $K$ -values, the possibility of single vapour (V), single liquid phase 1 (L1), single liquid phase 2 (L2), V-L1, V-L2, and L1-L2 at equilibrium, is examined. If the criteria for these six possibilities are not satisfied, the algorithm proceeds to VLLE calculations. If two phases are detected, VLE or LLE calculations are performed using the Newton method. Complete details of these steps are available in Nelson<sup>5</sup>. For highly composition-dependent  $K$ -values, Nelson’s method may wrongly converge to a single phase situation. The method can be extended to handle more than three phases.

#### Simultaneous equation-solving (SES) method

This method of solving simultaneously the mass balances, iso-activity and summation equations, is conceptually simple and straightforward since many chemical engineers are familiar with these equations. Further, computer programs for solving non-linear equations are readily available. Hence, the SES method is attractive and recommended for phase equilibrium calculations<sup>36</sup>. For VLE calculations, the governing  $2nc + 1$  can be written as

$$\sum_{i=1}^{nc} (y_i - x_i^{L1}) = 0 \quad (20)$$

$$z_i F - x_i^{L1} F (1 - \theta^V) - y_i F \theta^V = 0; \quad i = 1, 2, \dots, nc \quad (21)$$

$$x_i^{L1} K_{i1} - y_i = 0; \quad i = 1, 2, \dots, nc \quad (22)$$

which have to be solved for the unknowns ( $x_i^{L1}$ ,  $y_i$  and  $\theta^V$ ). Similar equations for LLE can be obtained by replacing  $y_i$  by  $x_i^{L2}$  and  $\theta^V$  by  $\theta^{L1}$ . On the other hand, VLLE calculations by the SES method require the simultaneous solution of the following  $3nc + 2$  equations for  $x_i^{L1}$ ,  $x_i^{L2}$ ,  $y_i$  and  $\theta^{L1}$  and  $\theta^{L2}$ .

$$\sum_{i=1}^{nc} (y_i - x_i^{L1}) = 0 \quad (23)$$

$$\sum_{i=1}^{nc} (y_i - x_i^{L2}) = 0 \quad (24)$$

$$z_i F - x_i^{L1} F \theta^{L1} - x_i^{L2} F \theta^{L2} - y_i F (1 - \theta^{L1} - \theta^{L2}) = 0; \quad i = 1, 2, \dots, nc \quad (25)$$

$$x_i^{L1} K_{i1} - y_i = 0; \quad i = 1, 2, \dots, nc \quad (26)$$

$$x_i^{L2} K_{i2} - y_i = 0; \quad i = 1, 2, \dots, nc \quad (27)$$

In the present study, the above equations are solved using the IMSL subroutine, DNEQBF that incorporates factored

secant (quasi-Newton) update with a finite-difference gradient approximation for initializing the Jacobian. The calculations stop when the scaled norm of the functions is less than the specified tolerance. Although this and other parameter settings in DNEQBF can be changed by the user for improved performance, default settings are employed in the present study unless otherwise stated.

### Gibbs Free Energy Minimization

Three optimization methods are tried for free energy minimization. Two are local optimization methods and the third is a global optimization method.

#### Linearly constrained minimization (LCM)

The free energy minimization problem (with either equation (17), (18) or (19) as the objective function) essentially consists of a non-linear objective function subject to a set of linear constraints and bounds on the decision variables  $n_i^k$  (for  $i = 1, 2, \dots, nc$ ;  $k = 1, 2, \dots, np$ ). This problem can be solved, for example, using the IMSL subprogram, DLCONF that is based on Powell's TOLMIN<sup>39</sup>. It employs the finite difference gradient of the objective function and BFGS formula for updating the second derivative approximation.

#### Minimization subject to bounds (UCM)

The free energy minimization problem can be simplified by introducing new variables  $\beta_i^k$  (for  $i = 1, 2, \dots, nc$ ;  $k = 1, 2, \dots, np - 1$ ) instead of mole numbers  $n_i^k$  (for  $i = 1, 2, \dots, nc$ ;  $k = 1, 2, \dots, np$ ) as the decision variables. The new variables,  $\beta_i^k$ , each of which is bounded by 0 and 1, are related to  $n_i^k$  by:

$$n_i^1 = \beta_i^1 z_i F; \quad i = 1, 2, \dots, nc \quad (28)$$

$$n_i^k = \beta_i^k (z_i F - \sum_{j=1}^{k-1} n_i^j); \quad i = 1, 2, \dots, nc; \\ k = 2, \dots, np - 1 \quad (29)$$

$$n_i^{np} = (z_i F - \sum_{j=1}^{np-1} n_i^j); \quad i = 1, 2, \dots, nc \quad (30)$$

Thus the equality constraints in equation (15), which are satisfied due to equations (28) to (30), need not be considered during minimization and the number of decision variables is reduced to  $nc(np - 1)$ . The bounds on decision variables are set as:

$$1 \times 10^{-15} \leq \beta_i^k \leq 1.0; \quad i = 1, 2, \dots, nc \quad (31)$$

The lower bound of  $1 \times 10^{-15}$  instead of 0 is employed to avoid numerical difficulties in evaluating free energy when moles of a component in a phase are zero.

The simplified problem can now be solved using an unconstrained optimization method. Of the many methods for this, quasi-Newton methods are preferred. The IMSL subroutine DBCONF, which is based on one of the quasi-Newton methods (namely, BFGS formula) and which can also account for bounds on variables, is selected. This program employs the finite-difference gradient, and the calculations stop when the norm of the gradient is less

than the given gradient tolerance or when the scaled distance between the last two steps is less than the step tolerance.

#### Global minimization subject to bounds

For phase equilibrium calculations by global minimization of free energy, GA, which has found many applications in chemical engineering, is selected. GAs are stochastic methods, highly likely to locate the global minimum and require only the objective function values. Unlike other optimization methods, GA works on a *population* of points (or *chromosomes*) and combines (*crossover*) and modifies (*mutation*) some chromosomes according to specified genetic operations to generate a new population with better points. Initial population is randomly generated and iterations are often terminated after a specified number of generations.

Currently, GA exists in many forms due to the wide variety of coding, selection schemes, and genetic operators available. There is no universal GA that would always produce the best performance for all optimization problems. Several variants of GA were tried for phase equilibrium calculations<sup>40</sup>. The best results were produced by the GA with floating-point coding, stochastic universal sampling, modified arithmetic crossover (probability = 0.8), non-uniform mutation (probability = 0.1), population of 200 chromosomes and 100 generations. Since GA does not give an accurate global minimum, which is required in phase equilibrium calculations, a local optimizer, namely, the modified simplex method of Nelder and Mead (NM) was used to further refine the solution obtained by the GA. The NM method is compatible with GA since it also does not require derivatives.

As in the minimization subject to bounds,  $\beta_i^k$  are used in equations (28) to (30) as the decision variables instead of  $n_i^k$ . By using  $\beta_i^k$  as decision variables, the mole balance for each component is ensured and all points generated in the GA will be feasible. This facilitates easier and more efficient implementation of the algorithm. The vapour phase needs to be assigned as either the first phase ( $k = 1$ ) or the last phase ( $k = np$ ) if different thermodynamic models are employed. Interestingly, this phase setting along with the definition of  $\beta_i^k$  by equations (28) to (30), was observed to affect the reliability of GA for one example, which is discussed later.

### SELECTED EXAMPLES

For the present study, 11 VLE examples, 6 LLE examples, and 5 VLLE examples are selected. Components and feed conditions in these selected examples are summarized in Table 1. The reference given for each example in this table often contains the phase equilibrium results, which can be used to verify the results obtained by a method. Sources for critical and/or thermodynamic data for each example are given in Table 2. Note that even a minor difference in these data or thermodynamic equations could alter phase equilibrium results. Selection of the appropriate mixing rule for EOS models is also important: one such situation involving the Soave-Redlich-Kwong (SRK) model is described in Appendix B.

The number of components in the selected examples varies from 2 to 11, and some systems are at high pressure and/or near the critical region. The examples also cover commonly used thermodynamic models, namely SRK,

Table 1. Selected examples for vapour–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE) and vapor–liquid–liquid equilibrium (VLLE).

Example no.	Mixture	Feed	Pressure & temperature	Model	Reference
<i>Vapour–liquid equilibrium (VLE)</i>					
1	Methane (1), propane (2)	$F = 1.0$ mole $z_i = \{0.68, 0.32\}$	100 bar, 277.6 K	SRK	42
2	Carbon dioxide (1), methane (2)	$F = 1.0$ mole $z_i = \{0.20, 0.80\}$	60.8 bar, 220 K	PR	42
3	Hydrogen sulfide (1), methane (2)	$F = 1.0$ mole $z_i = \{0.0187, 0.9813\}$	40.53 bar, 190 K	SRK	42
4	Nitrogen (1), carbon dioxide (2), hydrogen sulfide (3)	$F = 1.0$ mole $z_i = \{0.15, 0.30, 0.55\}$	76 bar, 270 K	PR	42
5	Methane (1), carbon dioxide (2), hydrogen sulfide (3)	$F = 1.0$ mole $z_i = \{0.4989, 0.0988, 0.4023\}$	48.6 bar, 227.55 K	PR	44
6a	Benzene (1), acetonitrile (2), water (3)	$F = 1.0036$ moles $z_i = \{0.34359, 0.30923, 0.34718\}$	0.1 atm, 300 K	Ideal (V) NRTL (L)	18
6b	Benzene (1), acetonitrile (2), water (3) (Numerical results are shown in Table 6)	$F = 1.0036$ moles $z_i = \{0.34359, 0.30923, 0.34718\}$	0.1 atm, 300 K	Ideal (V) UNIFAC (L)	—
7	Nitrogen (1), argon (2), oxygen (3) (Numerical results are shown in Table 7)	$F = 9.38529$ moles $z_i = \{0.78112, 0.00930, 0.20958\}$	607.95 kPa, 100.79 K	PR	45
8	Methane (1), ethane (2), propane (3), i-butane (4), n-butane (5), i-pentane (6), n-pentane (7), n-hexane (8), n-pentadecane (9)	$F = 0.96890$ moles $z_i = \{0.61400, 0.10259, 0.04985, 0.00898, 0.02116, 0.00722, 0.01187, 0.01435, 0.16998\}$	19.84 atm, 314 K	SRK	18
9	Mixture of 10 hydrocarbons (Refer to Table 8 for details)	$F = 35.1080$ moles	3998.95 kPa, 287.48 K	PR	41
10	Mixture of 11 chemicals (Refer to Table 9 for details)	$F = 10.0$ moles	101.325 kPa, 303.15 K	Ideal (V) NRTL (L)	41
<i>Liquid–liquid equilibrium (LLE)</i>					
11a	n-butyl-acetate (1), water (2)	$F = 1.0$ mole $z_i = \{0.50, 0.50\}$	1.0 atm, 298 K	NRTL	46
11b	n-butyl-acetate (1), water (2)	$F = 1.0$ mole $z_i = \{0.50, 0.50\}$	1.0 atm, 298 K	UNIFAC	23
12	Toluene (1), water (2)	$F = 1.0$ mole $z_i = \{0.50, 0.50\}$	1.0 atm, 298 K	NRTL	18
13	Furfural (1), 2,2,4-trimethyl pentane (2), cyclohexane (3)	$F = 1.0$ mole $z_i = \{0.10, 0.10, 0.80\}$	1.0 atm, 298 K	UNIQUEAC	8
14	Benzene (1), acetonitrile (2), water (3)	$F = 1.0036$ moles $z_i = \{0.34359, 0.30923, 0.34718\}$	1.0 atm, 333 K	NRTL	18
15	Toluene (1), water (2), aniline (3)	$F = 0.9987$ moles $z_i = \{0.29989, 0.20006, 0.50005\}$	1.0 atm, 298 K	NRTL	18
<i>Vapour–liquid–liquid equilibrium (VLLE)</i>					
16	Benzene (1), acetonitrile (2), water (3)	$F = 1.0036$ moles $z_i = \{0.34359, 0.30923, 0.34718\}$	0.769 atm, 333 K	Ideal (V) NRTL (L)	18
17	Methanol (1), methyl acetate (2), water (3)	$F = 1.0$ mole $z_i = \{0.15, 0.45, 0.40\}$	0.965 atm, 325 K	Ideal (V) UNIFAC (L)	23
18	Ethanol (1), benzene (2), water (3)	$F = 1.0$ mole $z_i = \{0.20, 0.35, 0.45\}$	1.0 atm, 338 K	Ideal (V) UNIFAC (L)	47
19	Ethylene glycol (1), dodecanol (2), nitromethane (3), water (4)	$F = 1.0$ mole $z_i = \{0.30, 0.10, 0.50, 0.10\}$	0.43 atm, 350 K	Ideal (V) UNIFAC (L)	23
20	2,2,4-trimethyl pentane (1), furfural (2), cyclohexane (3), benzene (4)	$F = 1.0$ mole $z_i = \{0.10, 0.30, 0.40, 0.20\}$	10.0 kPa, 288 K	Virial (V) UNIQUEAC (L)	48

Table 2. Sources for critical properties and thermodynamic data for all examples.

Example no.	$P_c$ , $T_c$ , $V_c$ , $\omega$	Thermodynamic data
1	Ref. 42	Ref. 42
2	Ref. 53	Ref. 42
3	Ref. 53	Ref. 42
4	Ref. 42	Ref. 42
5	Ref. 54	Ref. 49
6a <sup>a</sup>	Not applicable	Ref. 18
6b <sup>a</sup>	Not applicable	Ref. 50
7	Hysys.Plant simulator <sup>41</sup>	Hysys.Plant simulator <sup>41</sup>
8	Ref. 54	Ref. 18
9	Hysys.Plant simulator <sup>41</sup>	Hysys.Plant simulator <sup>41</sup>
10 <sup>b</sup>	Not applicable	Hysys.Plant simulator <sup>41</sup>
11a	Not applicable	Ref. 46
11b	Not applicable	Ref. 51
12	Not applicable	Ref. 2
13	Not applicable	Ref. 8
14 <sup>a</sup>	Not applicable	Ref. 18
15	Not applicable	Ref. 2
16 <sup>a</sup>	Not applicable	Ref. 2
17 <sup>a</sup>	Not applicable	Ref. 52
18 <sup>a</sup>	Not applicable	Ref. 52
19 <sup>a</sup>	Not applicable	Ref. 52
20 <sup>c</sup>	Ref. 55	Ref. 8

<sup>a</sup>The constants of the saturated vapour pressure equation are taken from Ref. 54.

<sup>b</sup>The constants of the saturated vapour pressure equation are taken from Hysys.Plant<sup>41</sup>.

<sup>c</sup>The constants of the saturated vapour pressure equation are taken from Ref. 55 and the critical constants for the second component (furfural) are taken from Ref. 8.

Peng–Robinson (PR), Non-Random Two Liquid (NRTL), Universal Quasi-Chemical (UNIQUAC) and UNIQUAC Functional-group Activity Coefficients (UNIFAC). Two examples (6 and 11) were also tried with different thermodynamic models. Many of the selected examples have been employed by researchers in their studies (refer to cited references in Table 1) while three are examples used in commercial simulators. Example 7 is selected from SIMSCI Pro/II case-book. Examples 9 and 10 are taken from Hysys.Plant (version 2.0) User's Manual on Applications<sup>41</sup>.

All the selected methods except GA for phase equilibrium calculations require initialization for  $K$ -values, phase fractions, and/or mole fractions. Initialization schemes selected

for the present study are briefly described in Appendix C. For each example, the same initialization is consistently used irrespective of the method (except GA). Fortran programs for RMW, Acc-SS-xy, Nelson's method, SES, LCM, and UCM are developed and tested for one example for which phase compositions and  $G/RT$  are available in the literature. Further, these programs are able to converge to the global minimum when the corresponding compositions are given as initial estimates, thus confirming their accuracy. The GA program of Lee<sup>40</sup> is employed in this study. All the programs are in double precision and are compiled using Compaq Visual Fortran (version 6.1) on a Pentium 300 MHz computer. Computational (CPU) time reported in this paper is for the execution of the program in seconds, and does not include compilation time. Printing of intermediate results is minimal.

## RESULTS AND DISCUSSION

The results obtained in this study were compared with those available in the literature in terms of phase quantities, compositions, and Gibbs free energy. Results for Examples 6a, 11a, 11b, 12, 14, and 15 are exactly the same as those given by McDonald and Floudas<sup>2,23</sup>, whereas the results for Example 13 were those of Prausnitz *et al.*<sup>8</sup>. However, results for Examples 1 to 5 show small discrepancies from those reported in the literature. These are likely due to differences in physical property data since the sources for these data are not given in the earlier references. All these confirm the accuracy and validity of the data, equations, and programs employed in this study.

### Two-Phase Equilibrium Calculations

Performance (i.e., number of  $K$ -value evaluations and computation time) of all methods for VLE and LLE examples, is summarized in Tables 3 and 4 respectively. A few methods failed to give the correct solution for some examples; instead, either a local, trivial, or near-global solution is obtained. All are shown in Tables 3 and 4. In trivial solution, the two phases have the same composition as the feed (i.e.,  $x_i = y_i = z_i$ ). In a few cases, the converged solution is near the global minimum (i.e., having 1–5% discrepancy in  $G/RT$  from the global minimum). Such solutions may be

Table 3. No. of  $K$ -value evaluations and computation time for VLE examples.

Example no.	No. of $K$ -value evaluations (computation time in seconds)						
	RMW	Acc-SS-xy	Nelson	SES	LCM	UCM	GA <sup>a</sup>
1	123 (0.28)	Trivial solution	NA	Trivial solution	Trivial solution	Trivial solution	20,677 (1.52)
2	108 (0.22)	25 (0.06)	NA	Failure	Trivial solution	Trivial solution	20,204 (1.62)
3	22 (0.05)	12 (0.05)	NA	123 (0.28)	Trivial solution	Failure	20,176 (1.56)
4	65 (0.22)	499 (0.88)	75 (0.55)	311 (0.71)	Trivial solution	171 (0.44)	22,963 (2.86)
5	21 (0.06)	58 (0.11)	37 (0.22)	333 (0.83)	364 (0.94)	Failure	25,549 (3.41)
6a	13 (0.01)	24 (0.05)	Single phase	Failure	441 (0.99)	118 (0.71) <sup>b</sup>	21,237 (1.62)
6b	13 (0.05)	34 (0.06)	Single phase	Failure	637 (1.70)	115 (0.27) <sup>b</sup>	20,469 (2.04)
7	8 (0.05)	9 (0.05)	6 (0.05)	84 (0.22)	189 (0.55)	65 (0.17)	22,484 (3.92)
8	6 (0.05)	9 (0.05)	5 (0.06)	274 (1.26)	1919 (12.52)	773 (4.61)	22,389 (7.92)
9	6 (0.05)	19 (0.11)	9 (0.11)	252 (1.21)	3192 (20.60)	Trivial solution	Trivial solution
10	6 (0.05)	4 (0.05)	11 (0.16)	Failure	3059 (21.69)	1674 (11.86)	22,310 (6.08)

<sup>a</sup>GA successfully converged to the global minimum in all 25 trials on all examples (except examples 3 and 9). Success rate of finding the global minimum is 80% in example 3, and GA converged to the trivial solution in all 25 trials on example 9. Average number of  $K$ -value evaluations and computation time in all 25 trials are shown.

<sup>b</sup>In these cases, the converged solution is near the global minimum.

Table 4. No. of *K*-value evaluations and computation time for LLE examples.

Example no.	No. of <i>K</i> -value evaluations (computation time in seconds)						
	RMW	Acc-SS-xy	Nelson	SES	LCM	UCM	GA <sup>a</sup>
11a	Local solution	Local solution	NA	Local solution	Local solution	Local solution	20,160 (1.05)
11b	24 (0.06)	16 (0.06)	NA	142 (0.27)	250 (0.49)	82 (0.17)	20,138 (1.44)
12	10 (0.06)	12 (0.06)	NA	236 (0.49)	525 (1.04)	110 (0.22)	20,154 (1.05)
13	45 (0.11)	50 (0.11)	Singe phase	Trivial solution	Trivial solution	Trivial solution	21,648 (2.21)
14	41 (0.06)	362 (0.61)	47 (0.33)	151 (0.38)	308 (1.27)	168 (0.44)	20,631 (1.80)
15	32 (0.11)	70 (0.11)	Single phase	539 (1.10)	735 (2.31)	Trivial solution	20,496 (1.60)

<sup>a</sup>GA successfully converged to the global minimum in all 25 trials. Average number of *K*-value evaluations and computation time are shown.

due to local minima or premature convergence of the method. In any case, these solutions are not acceptable since accurate phase equilibrium results are required for process design. In some cases, a particular method/program gave a false solution that did not satisfy the governing equations (e.g., equations (23) to (27) for VLLE), or the program terminated without a solution. Termination may occur due to built-in error checks in the IMSL subprogram or non-existence of a real root for the compressibility factor (*Z*) for the EOS model. In Tables 3 and 4, both the false solution and program termination are classified as 'Failure', and convergence to a trivial solution, which is mainly due to the nature of the phase equilibrium problem, is noted as 'Trivial solution'.

Among the problems tried, Examples 1 and 11a appear to be the most difficult problems. In the former, the system is near the critical point of the mixture<sup>42</sup> and only RMW and GA succeeded in finding the correct solution. All methods except GA gave the local solution in Example 11a. Performance results in Tables 3 and 4 show that RMW, Acc-SS-xy and GA methods are the most successful and reliable for VLE and LLE. Of these, the two-equation-solving methods, RMW and Acc-SS-xy, are computationally very efficient. They require a fraction of the number of *K*-value evaluations and CPU time taken by GA. Hence, RMW and Acc-SS-xy have been chosen for further evaluation by applying them to Examples 1 to 15 but at different conditions giving two-phase equilibrium. For a system described by the EOS model, about 20 sets of temperature, pressure, and feed compositions are considered. For those systems involving activity coefficient models, many sets of feed composition and pressure at a fixed temperature are selected. This is because the parameters in the thermodynamic model are temperature dependent and the range of the applicable

temperature is unknown. The results of this exhaustive study are summarized in Table 5. From the results in Tables 3 to 5, it is clear that RMW has outperformed Acc-SS-xy as it found the correct solution in all cases except Example 11a, for which both the methods converged to the local minimum. Also, the former seems to be computationally more efficient than the latter.

Nelson's method<sup>5</sup> was tried on VLE and LLE examples having more than two components since the method assumes the possibility of three phases. It identified incorrectly that only one phase exists in Examples 6a, 6b, 13, and 15 (Tables 3 and 4), which seems to be a difficult problem for this method as *K*-values are strongly dependent on compositions. In effect, Nelson's method succeeded in only 7 out of 11 systems tried. Thus, although Nelson's method, unlike other methods, incorporates determination of phases at equilibrium, its reliability seems to be limited.

Equilibrium solutions for Examples 6b, 7, 9, and 10, which were tried for the first time in this study, are given in Tables 6 to 9, respectively. The simple and straightforward strategy of using standard programs, namely, SES, LCM, and UCM, performed poorly for VLE and LLE examples: SES succeeded in only 10 out of 17, UCM in only 7 out of 17, and LCM in only 11 out of 17 systems. Besides, these three methods are less efficient with an increasing number of components. As stated earlier, the DNEQBF program in IMSL for the quasi-Newton method was used for simultaneous solution of equations in the SES method. Another program, DNEQNF in IMSL was also tried but its performance was poorer than DNEQBF. This is likely due to the use of the Newton method with finite-difference approximation for derivatives, in DNEQNF. Trials with non-default settings in these programs showed that their performance may be improved marginally. Since this requires fine tuning for each example, it was not considered practical. These observations are particularly important since phase equilibrium calculations by SES using IMSL or other software are convenient and sometimes recommended<sup>36</sup>. Of the two programs, DLCONF for LCM and DBCONF for UCM,

Table 5. Success rate of RMW and Acc-SS-xy for VLE and LLE applications.

Example	No. of sets of conditions	Success rate (%)	
		RMW	Acc-SS-xy
1, 2, 3, 4	27	100	100
5	27	100	93
6a	20	100	95
6b	20	100	85
7, 8, 9, 10	18	100	100
11a <sup>a</sup>	8	0	0
11b, 12	8	100	100
13, 14, 15	10	100	100

<sup>a</sup>The two methods converged to the local minimum for all conditions tried.

Table 6. Feed and equilibrium compositions for Example 6b (VLE).

Components	Feed (moles)	$x_i$	$y_i$
Benzene	0.34483	0.000158	0.347991
Acetonitrile	0.31034	0.022651	0.312897
Water	0.34843	0.977191	0.339112
Total moles	1.00360	0.012690	0.990910
<i>G/RT</i>	—	−3.412249	



Table 7. Feed and equilibrium compositions for Example 7 (VLE).

Components	Feed (moles)	$x_i$	$y_i$
Nitrogen	7.33100	0.60012	0.78532
Argon	0.08729	0.01336	0.00921
Oxygen	1.96700	0.38652	0.20547
Total moles	9.38529	0.21323	9.17206
$G/RT$	—	—	-6.53936

Table 8. Feed and equilibrium compositions for Example 9 (VLE).

Components	Feed (moles)	$x_i$	$y_i$
Methane	6.864	0.18837	0.79589
Ethane	5.133	0.14632	0.13696
Propane	3.714	0.10665	0.03293
i-butane	3.778	0.10871	0.01529
n-butane	3.451	0.09934	0.01024
i-pentane	3.128	0.09011	0.00427
n-pentane	2.696	0.07767	0.00284
n-hexane	3.170	0.09135	0.00123
n-heptane	1.815	0.05231	0.00027
n-octane	1.359	0.03917	0.00008
Total moles	35.108	34.69509	0.41291
$G/RT$	—	—	-161.5416

the former is more reliable than the latter. This may be due to reformulation (equations (28) to (30)) for the latter, since both the programs are essentially based on BFGS formulae. However, CPU time for LCM is generally more than that for UCM as a greater number of variables and constraints are involved in the solution by LCM.

Since the performance of GA depends on random numbers, 25 trials were carried out for each example; in each trial, the seed to initiate random number generation is changed, thus altering random numbers generated and consequently search for the optimum. Since the number of phases at equilibrium may not be known *a priori*, an extra phase (second liquid phase) was assumed in examples with more

Table 9. Feed and equilibrium compositions for Example 10 (VLE).

Components	Feed (moles)	$x_i$	$y_i$
Ethanol	0.26900	0.027469	0.007117
Water	9.46411	0.972440	0.040769
Carbon dioxide	0.26600	0.000000	0.952098
Methanol	2.69303E-04	0.000027	0.000011
Acetic acid	3.32604E-05	0.000003	0.000000
1-propanol	9.07710E-05	0.000009	0.000001
2-propanol	9.09610E-05	0.000009	0.000002
1-butanol	6.57808E-05	0.000007	0.000000
3-methyl-1-butanol	2.14802E-04	0.000022	0.000000
2-pentanol	5.42606E-05	0.000006	0.000000
Glycerol	6.64008E-05	0.000007	0.000000
Total moles	10.00000	9.72061	0.27939
$G/RT$	—	—	-31.640032

than two components (i.e., Examples 4–10 and 13–15). This also increases the complexity of the problem. Despite this, GA succeeded in all 25 trials on all VLE and LLE examples tried, except on Examples 3 (with 80% success rate) and 9 (with 0% success rate) (see Tables 3 and 4). The number of  $K$ -values and computational time given in Tables 3 and 4 are the average of all 25 trials on each example; they also include the calculations required for the NM method. Interestingly, GA did not have any difficulty in reliably solving Example 11a, which could not be solved by any of the other methods tried. While GA was successful in 80% of the 25 trials on Example 3, it converged to the trivial solution in all 25 trials on Example 9, which did not improve even if the right number of phases was assumed. The objective function,  $G/RT$ , for this trivial solution is -161.5364, very close to the global minimum of -161.5416. One reason for this closeness is the small value of  $\theta^V = 0.01176$ . Figure 1 shows search points generated by GA, in two dimensions as a plot of  $G/RT$  versus average absolute deviation defined as:

$$\text{Dev} = \frac{1}{(nc)(np)} \sum_{k=1}^{np} \sum_{i=1}^{nc} |n_i^k - n_i^{k(*)}| \quad (32)$$

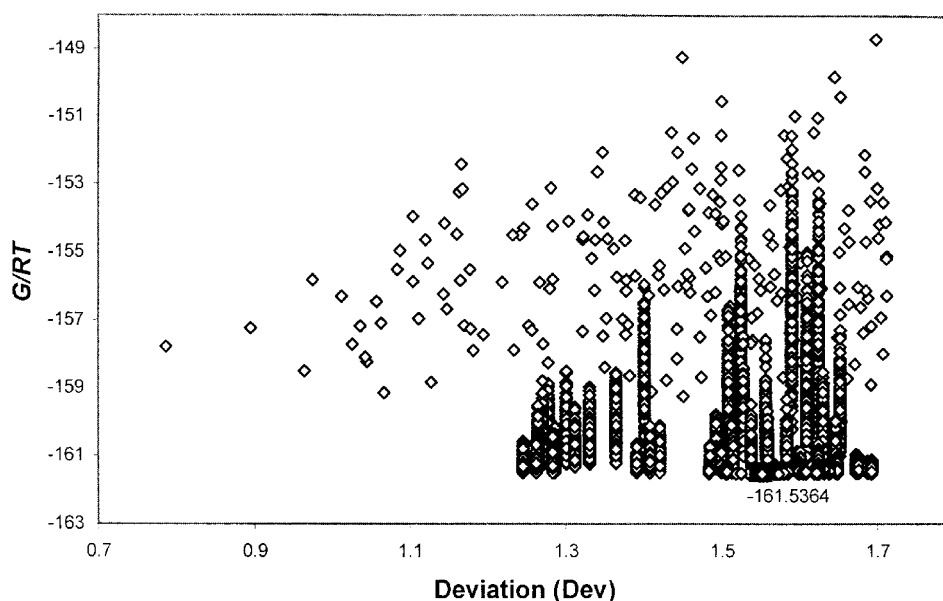


Figure 1. Search points generated by GA in one trial for Example 9. The global minimum is -161.5416 at Dev = 0, compared to the local minimum of -161.5364.

Table 10. Application of GA to Example 9 at other temperatures and pressures.

No.	T and P conditions	Success rate (%, 25 trials)	Vapour split fraction	G/RT	
				Correct solution	Trivial solution
9.1	287.48 K, 100 kPa	100	0.7565	−85.306861	—
9.2	287.48 K, 2050 kPa	0	0.1785	−142.692021	−140.754111
9.3	287.48 K, 4000 kPa	0	0.0117	−161.549270	−161.544177
9.4	362.48 K, 400 kPa	0	0.9909	−79.622227	−79.616305
9.5	362.48 K, 3450 kPa	100	0.3261	−106.421271	—
9.6	362.48 K, 6500 kPa	0	0.0172	−121.820240	−121.816750
9.7	437.48 K, 3300 kPa	0	0.9884	−86.767680	−86.766097
9.8	437.48 K, 5325 kPa	100	0.7594	−92.895576	—
9.9	437.48 K, 7000 kPa	100	0.4909	−97.688334	—

Note: For the feed composition at the specified T and P in each of cases 9.2 to 9.9, only one real root exists for compressibility factor (Z) by PR EOS; two real roots exist for Example 9.1.

where  $n_i^{k(*)}$  denotes the molar flow rate of component  $i$  in phase  $k$  at the global minimum. The multi-dimensional search space is thus condensed into one dimension in terms of the deviation of the point from the global minimum. Most of the search is concentrated around the trivial solutions with Dev in the range 1.2 to 1.7, perhaps due to their very comparable  $G/RT$  to global minimum. Note that there could be a range of trivial solutions having different phase quantities.

To further test GA, phase equilibrium of the mixture in Example 9 at nine other sets of  $T$  and  $P$  was tried. The results of these trials are presented in Table 10, which includes the correct solutions obtained using RMW and then confirmed with Acc-SS-xy method. GA found the correct solution for only four conditions (nos. 9.1, 9.5, 9.8 and 9.9), and it gave trivial solutions for the remaining five conditions (nos. 9.2 to 9.4, 9.6 and 9.7). Vapour split fraction given in column 4 indicates that equilibrium solutions for these five conditions are close to the phase boundary. Moreover, there is only one positive real root for the compressibility factor ( $Z$ ) by the PR EOS model for the feed composition,  $T$  and  $P$  in Examples 9, 9.2 to 9.9, and there are two positive real roots for the conditions of Example 9.1. A single root permits a trivial solution as a potential solution for phase equilibrium even though there exists two phases at equilibrium. A single root of the EOS model combined with closeness of the feed to the phase boundary is thus contributing to the failure of GA to find the global minimum. They could also cause problems for other methods for solving phase equilibrium problems. Success of

RMW for these difficult situations is perhaps due to good initialization.

Comparing GA for global minimization of free energy with other methods tried for two-phase equilibrium calculations, the former is computationally expensive. For other methods (except Nelson’s method), we have assumed the number of phases at equilibrium, which can be found from bubble- and dew-point calculations. Although this requires additional computations, GA will still be inefficient. Among other methods tested, RMW seems to be the most reliable method. These findings, including the failure of GA for Example 9, indicate the need to improve both the efficiency and reliability of global minimization of free energy by GA or other methods. Results of this study suggest that RMW is perhaps the most efficient and reliable method, and hence recommended for two-phase equilibrium calculations, in conjunction with a separate step for phase determination.

Three-Phase Equilibrium Calculations

The results for the five VLE examples by Nelson’s method, SES, UCM, LCM, and GA are given in Table 11. Results obtained for examples 16 to 19 are identical to those reported by McDonald and Floudas<sup>2,21,22</sup>. Results for Examples 19 and 20 are shown in Tables 12 and 13, as local VLE solutions for these have not been reported earlier. Local solutions were also obtained for Examples 17 and 18, and they are the same as those reported by McDonald and Floudas<sup>21,22</sup>. All these local solutions were found to satisfy the governing equations (e.g., equations (23) to (27)). The

Table 11. No. of K-value evaluations and computation time for VLE Examples.

No.	No. of K-value evaluations (computation time in seconds)				
	Nelson	SES	LCM	UCM	GA <sup>a</sup>
16	72 (0.77)	Failure	770 (3.41)	528 (1.92)	20,976 (1.64)
17	Local VLE solution	Failure	1130 (4.67)	Local VLE solution	20,714 (2.29)
18	13 (0.11)	Failure	Local VLE solution	Local VLE solution	20,719 (2.28)
19	58 (0.66)	Local VLE solution	1092 (5.61)	500 (2.36) <sup>b</sup>	22,007 (5.18)
20	90 (0.93)	Local VLE solution	702 (4.62)	654 (4.56)	20,398 (9.14) <sup>c</sup>

<sup>a</sup>GA successfully converged to the global minimum in all 25 trials on examples 16, 18, and 19. Success rate of finding the global minimum is 84% in example 17. The average number of K-value evaluations and computation time in all 25 trials are shown.

<sup>b</sup>In this case, the converged solution is near the global minimum.

<sup>c</sup>These results were obtained by using UCM (instead of NM) after GA.

Table 12. Feed and equilibrium compositions for Example 19 (VLLE).

Components	Feed	Local VLE solution		Global solution		
		$x_i$	$y_i$	$x_i^{L1}$	$x_i^{L2}$	$y_i$
Ethylene glycol	0.30	0.389956	0.012963	0.183998	0.795464	0.011656
Dodecanol	0.10	0.131250	0.000286	0.220593	0.006932	0.000309
Nitromethane	0.50	0.404837	0.803652	0.557331	0.069171	0.818524
Water	0.10	0.073957	0.183098	0.038077	0.128432	0.169511
Total moles	1.00	0.761386	0.238614	0.444433	0.270155	0.285412
$G/RT$	—	-3.242667		-3.265524		

Table 13. Feed and equilibrium compositions for Example 20 (VLLE).

Components	Feed	Local VLE solution		Global solution		
		$x_i$	$y_i$	$x_i^{L1}$	$x_i^{L2}$	$y_i$
2,2,4-trimethyl pentane	0.10	0.101791	0.084901	0.145248	0.030281	0.075072
Furfural	0.30	0.334703	0.007471	0.143016	0.620203	0.007048
Cyclohexane	0.40	0.356482	0.766837	0.500805	0.159480	0.757234
Benzene	0.20	0.207024	0.140791	0.210931	0.190037	0.160647
Total moles	1.00	0.893951	0.106049	0.578318	0.349536	0.072146
$G/RT$	—	-4.539724		-4.548170		

global solution for Example 20 is comparable to that reported by Han and Rangaiah<sup>15</sup> with minor differences, which were found to be due to incorrect input of properly data in the earlier study.

Nelson's method<sup>5</sup> was successful in solving four of the five examples; for Example 17, it converged to a local VLE solution. SES failed for three examples and gave a local solution for the other two examples. Of the two local minimization methods, LCM performed well, giving the local solution in only one example. On the other hand, UCM is not so successful, giving the local solution in two examples and failing in another example. As before, reformulation (equations (28) to (30)) is perhaps causing this poor performance of UCM. Comparing the computational effort for Nelson's method and LCM, the former is efficient and also includes phase determination. On the other hand, the latter requires the additional step of phase determination.

Results on VLLE examples by GA assuming three phases show that it converged to the global minimum with 100% success rate in all 25 trials on Examples 16, 18, and 19. For Example 17, GA converged to the global VLLE solution in only 21 out of 25 runs; in the remaining four runs, the local VLE solution was obtained. These results were obtained when the vapour was assigned as the last phase ( $np$ ) in the calculations. Interestingly, if the vapour was assigned as the first phase ( $k = 1$ ), GA gave the global solution in only 6 out of 25 runs and converged to the local VLE solution in the remaining runs. Similar behaviour (100% and 4% success rate with vapour as the last and first phase, respectively) was observed in Example 18 too. These indicate that the search is perhaps very different depending on the assignment of the vapour phase, and it can be used to our advantage to find the global minimum by making two trials with vapour as the first or last phase.

For Example 20, the final results by GA followed by NM, although close to the global minimum, differ from one trial to another. The reason for this was suspected to be due to flat objective function at the global minimum leading to

premature convergence of NM. This was then confirmed when 100% success was obtained in all trials by GA followed by UCM. Note that UCM, unlike NM, is a gradient search method with better capability to find the minimum accurately. The results for Example 20 shown in Table 11 are for GA followed by UCM. Although GA requires a greater number of  $K$ -value evaluations than other methods, CPU time for it is comparable to that for LCM. Further, GA, with its success even with extra phases, can be employed without a separate step to determine phases at equilibrium.

### Other Comments

Although free energy minimization by deterministic methods is not included in the present study, results for Examples 11a, 11b, 17 and 19 in McDonald and Floudas<sup>23</sup> can be used to compare the computational efficiency of GA with that of GLOPEQ, which guarantees global solution. Computational results in McDonald and Floudas<sup>23</sup> were obtained on an HP9000/730 computer, which, according to the Linpack benchmark<sup>43</sup>, is marginally faster than the Pentium 300 employed in the present study. Comparative results in Table 14 show that for Examples 11a and 11b involving two components and two phases, GA is less efficient than GLOPEQ. However, for VLLE Examples 17

Table 14. Comparison of GA with GLOPEQ of McDonald and Floudas<sup>23</sup>.

Example no. and details	Computation time (s) for	
	GA on Pentium II/300	GLOPEQ on HP 9000/730
11a (LLE, NRTL)	1.05	0.23
11b (LLE, UNIFAC)	1.44	0.37
17 (VLLE, UNIFAC)	2.29	8.8
19 (VLLE, UNIFAC)	4.71	1493.3

and 19 with three and four components, respectively, the former is faster than the latter.

Comparison of equation-solving and free energy minimization methods should consider the context in which they are likely to be used since reliable and accurate solutions are required for process simulation and other applications. As stated earlier, equation-solving methods require a prior step to determine the number of phases at equilibrium. Also, they may have to be tried with different initializations. Since stochastic methods do not yet have 100% success rate for all examples, they may have to be run a few times for free energy minimization, or their results should be verified by a phase stability test, which, for example, can be done efficiently and reliably by GA itself<sup>28</sup>. Even though these aspects are not considered here, results of this study are useful to formulate a reliable and efficient procedure for phase equilibrium calculations.

## CONCLUSIONS

In this study, several equation-solving and free energy minimization methods for phase equilibrium calculations are selected and thoroughly tested on 11 VLE, 6 LLE, and 5 VLLE examples. The results show that, for two-phase equilibrium calculations, the equation-solving method, RMW, is both efficient and reliable among the methods tested. Hence, this method, in conjunction with good initialization and a prior phase determining step, seems to be satisfactory for many VLE and LLE problems. Although GA is highly reliable, it requires a relatively large computational effort for two-phase equilibrium calculations. Hence, it is perhaps attractive for applications where not many phase equilibrium calculations are involved. The results show that Nelson's method is both efficient and successful for four of the five VLLE examples tested. However, in view of its poor performance for VLE and LLE, care should be exercised in its selection and use. Only the global minimization of free energy, for example by GA, seems to be a reliable method for three-phase equilibrium calculations. It also does not require a separate step to determine phases at equilibrium. As can be seen from the poor performance of SES, LCM and UCM, the simple and straightforward approach of using generic programs for solving non-linear equations and local minimization is inadequate and not recommended for phase equilibrium calculations. The findings of this study highlight the challenges in phase equilibrium calculations, which arise from multiple minima, trivial solutions, global minimum very comparable to local minimum, and flat objective function at the global minimum. These characteristics put extra demands on GA and, hence, this method requires further improvement for global minimization of free energy accurately and reliably.

## NOMENCLATURE

$a, b, A, B$	parameters in SRK EOS
$F$	total molar flow rate of feed
$G/RT$	dimensionless Gibbs free energy, defined by equations (17), (18), and (19)
$K_i$	equilibrium constant of component $i$ , defined by equations (A6) and (A7)
$K_{i1}$	equilibrium constant of component $i$ , defined by equations (6) to (8)
$K_{i2}$	equilibrium constant of component $i$ , defined by equations (6) to (8)

$k_{ij}$	binary interaction parameter
$L_1$	total molar flow rate of liquid phase 1
$L_2$	total molar flow rate of liquid phase 2
$nc$	total number of components
$np$	total number of phases
$n^k$	total number of moles in phase $k$
$n_i^k$	number of moles of component $i$ in phase $k$
$P$	system pressure
$P_c$	critical pressure
$P_i^{\text{sat}}$	saturated vapour pressure of component $i$
$P_{r_i}$	reduced pressure of component $i$
$T$	system temperature
$T_c$	critical temperature
$T_{r_i}$	reduced temperature of component $i$
$V$	total molar flow rate of vapour
$V_c$	critical volume
$x_i$	mole fraction of component $i$ in liquid phase
$y_i$	mole fraction of component $i$ in vapour phase
$Z$	compressibility factor
$z_i$	mole fraction of component $i$ in the feed

### Greek symbols

$\alpha_i$	correction factor in SRK EOS
$\beta_i$	modified variable, defined by equations (28) to (30)
$\phi_i$	fugacity coefficient of component $i$
$\gamma_i$	activity coefficient of component $i$
$\omega$	acentric factor
$\theta$	phase split fraction

### Subscripts

$i$	component index
$E$	extract solvent
$R$	raffinate solvent

### Superscripts

$k, j$	phase index
$L1$	liquid phase 1
$L2$	liquid phase 2
$V$	vapour phase
$0$	initial value; pure component
$\wedge$	partial property

## APPENDIX A

### Equations for VLE and LLE

Equations for VLLE can be modified for VLE by setting  $L_2 = 0$  in equations (1) and (2),  $\theta^{L2} = 0$  and  $K_{i2} = 1$  in equations (9) and (10). Noting  $\theta^{L1} = 1 - \theta^V$  and ignoring equations (11) and (13), number of unknowns reduces to  $2nc + 1$  and the final equations are:

$$y_i = \frac{z_i K_{i1}}{1 + \theta^V (K_{i1} - 1)}; \quad i = 1, 2, \dots, nc \quad (\text{A1})$$

$$x_i^{L1} = \frac{z_i}{1 + \theta^V (K_{i1} - 1)}; \quad i = 1, 2, \dots, nc \quad (\text{A2})$$

$$\sum_{i=1}^{nc} (y_i - x_i^{L1}) = \sum_{i=1}^{nc} \frac{z_i (K_{i1} - 1)}{1 + \theta^V (K_{i1} - 1)} = 0 \quad (\text{A3})$$

As for VLE, LLE also consists of  $2nc + 1$  unknowns. The material balances for LLE are

$$F = L_1 + L_2 \quad (\text{A4})$$

$$z_i F = x_i^{L1} L_1 + x_i^{L2} L_2; \quad i = 1, 2, \dots, nc \quad (\text{A5})$$

and the equilibrium relation is

$$x_i^{L2} = K_i x_i^{L1}; \quad i = 1, 2, \dots, nc \quad (\text{A6})$$

where the equilibrium constant,  $K$ -value, is defined in terms of the thermodynamic parameter ( $\gamma_i$ ), which can be calculated from an activity coefficient model.

$$K_i = \frac{\gamma_i^{L1}}{\gamma_i^{L2}} \quad (\text{A7})$$

By substituting equation (A6) into equation (A5) and rearranging, expressions for mole fractions are:

$$x_i^{L1} = \frac{z_i F}{L_1 + L_2 K_i}; \quad i = 1, 2, \dots, nc \quad (\text{A8})$$

$$x_i^{L2} = \frac{z_i F K_i}{L_1 + L_2 K_i}; \quad i = 1, 2, \dots, nc \quad (\text{A9})$$

These two equations can be further simplified by introducing phase fraction,  $\theta^{L2} = L_2/F$  and using equation (A4):

$$x_i^{L1} = \frac{z_i}{1 + \theta^{L2}(K_i - 1)}; \quad i = 1, 2, \dots, nc \quad (\text{A10})$$

$$x_i^{L2} = \frac{z_i K_i}{1 + \theta^{L2}(K_i - 1)}; \quad i = 1, 2, \dots, nc \quad (\text{A11})$$

Application of the Rachford–Rice formulation gives:

$$\sum_{i=1}^{nc} (x_i^{L2} - x_i^{L1}) = \sum_{i=1}^{nc} \frac{z_i (K_i - 1)}{1 + \theta^{L2}(K_i - 1)} = 0 \quad (\text{A12})$$

## APPENDIX B

### Mixing Rule for SRK EOS

The following two equations are available in the literature for calculating the fugacity coefficient of the  $i$ th component by SRK EOS.

$$\ln \hat{\phi}_i = \frac{B_i}{B} (Z - 1) - \ln(Z - B) - \frac{A}{B} \left( \frac{2 \sum_{j=1}^{nc} x_j a_{ij}}{a} - \frac{B_i}{B} \right) \ln \left( 1 + \frac{B}{Z} \right) \quad (\text{B1})$$

$$\ln \hat{\phi}_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{B} \left( \frac{2 \sqrt{a_i}}{\sqrt{a}} - \frac{b_i}{b} \right) \ln \left( 1 + \frac{B}{Z} \right) \quad (\text{B2})$$

For example, equations (B1) and (B2) are given by Walas<sup>56</sup> and by Winnick<sup>36</sup>, respectively. The parameters involved in both equations are:

$$\alpha_i = \left[ 1 + \left( 1 - \sqrt{Tr_i} \right) (0.480 + 1.574\omega_i - 0.176\omega_i^2) \right]^2$$

$$a_i = 0.42747 \frac{\alpha_i (RTc_i)^2}{Pc_i}; \quad b_i = 0.08664 \frac{RTc_i}{Pc_i}$$

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j a_{ij}; \quad a_{ij} = (1 - k_{ij}) \sqrt{(a_i a_j)};$$

$$b = \sum_{i=1}^{nc} x_i b_i$$

$$A = \frac{aP}{(RT)^2}; \quad A_i = \frac{a_i P}{(RT)^2}; \quad B = \frac{bP}{RT}; \quad B_i = \frac{b_i P}{RT}$$

and  $Z$  is the root of  $Z^3 - Z^2 + Z(A - B - B^2) - AB = 0$ .

In general, the two equations (B1) and (B2) are not the same, and hence the calculated fugacity coefficients will be different. For example, consider a liquid mixture of 0.6583 moles of methane and 0.3417 moles of propane at 277.6 K and 100 bar; binary interaction parameter,  $k_{ij}$  for these two components is 0.029. Application of equation (B1) gives  $\hat{\phi}_1^L = 1.05485$  and  $\hat{\phi}_2^L = 0.11082$ . The corresponding values by equation (B2) are 1.03495 and 0.10769, respectively. The discrepancy in the calculated fugacity coefficient by the two equations is 2 to 3%. If equations (B1) and (B2) are used for phase equilibrium calculations, phase equilibrium results will definitely be different.

The difference between the two equations is the term,  $(2 \sum_{j=1}^{nc} x_j a_{ij})/a$  in equation (B1) versus the term,  $(2 \sqrt{a_i})/\sqrt{a}$  in equation (B2). The two equations (B1) and (B2) and consequently, fugacity coefficients will be the same if and only if  $k_{ij} = 0$  and the mixing rule is  $a = (\sum_{j=1}^{nc} x_j \sqrt{a_j})^2$ , which is applicable only when  $k_{ij} = 0$ <sup>57</sup>. It is improper to use the mixing rule,  $a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j a_{ij}$  with  $a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j}$  in equation (B2). With this mixing rule, equation (B1) is the appropriate one. Hence, the mixing rule should be properly selected for the SRK EOS model.

## APPENDIX C

### Initialization Schemes

In this work, the following initialization schemes are employed in all the selected methods, except GA.

#### Initialization scheme for VLE

Initial estimates are needed for  $\{K_{i1}\}$  and  $\theta^V$ . The former is initialized using the Wilson equation for  $K$ -values:

$$\ln K_{i1} = 5.373(1 + \omega_i) \left( 1 - \frac{1}{Tr_i} \right) - \ln Pr_i; \quad i = 1, 2, \dots, nc \quad (\text{C1})$$

which is independent of mole fractions. The following procedure proposed by Ohanomah and Thompson<sup>1</sup> is used for initializing  $\theta^V$ . Based on initial  $\{K_{i1}\}$ , calculate  $S_1 = \sum_{i=1}^{nc} z_i K_{i1} - 1$ ,  $S_2 = 2 \sum_{i=1}^{nc} (z_i (K_i - 1)) / (1 + K_i)$  and  $S = S_2 / (S_2 - S_1)$ . If  $S > 0$ , then set  $\theta^{V(0)} = 0.5(1 - S)$ ; else, calculate  $S_3 = 2 \sum_{i=1}^{nc} z_i / (K_{i1} + 1) - 1$  and  $S_4 = \sum_{i=1}^{nc} z_i / K_{i1} - 1$ , and then set  $\theta^{V(0)} = (S_3 - 0.5S_4) / (S_3 - S_4)$ .

#### Initialization scheme for LLE

Initial estimates needed for LLE, namely,  $\{K_{i1}\}$  and  $\theta^{L2}$  are found using the following procedure of Ohanomah and Thompson<sup>31</sup>:

- (1) Set  $\{x_i^{L1} = z_i\}$ , calculate  $\{\gamma_i^{L1}\}$  and then  $\{x_i^{L2} = z_i \gamma_i^{L1}\}$ .
- (2) Normalize  $\{x_i^{L2}\}$ , calculate  $\{\gamma_i^{L2}\}$  and  $\{K_i = \gamma_i^{L1} / \gamma_i^{L2}\}$ .
- (3) Identify the component having the lowest  $K_i$  as the raffinate solvent, and its feed composition is denoted as  $z_R$ .
- (4) Similarly, identify the component having the largest  $K_i$  as the extract solvent, and its feed composition is denoted as  $z_E$ .
- (5) Set  $x_R^{L1} = x_E^{L2} = 0.98$  and  $x_E^{L1} = x_R^{L2} = 0.02$ . Re-evaluate  $K_E = x_E^{L2} / x_E^{L1}$  and  $K_R = x_R^{L2} / x_R^{L1}$ .
- (6) Finally, initial estimate of second liquid phase split,  $\theta^{L2(0)} = [z_E(1 - 1/K_E) + z_R K_R] / (z_E + z_R)$ .

### Initialization scheme for VLLE

For VLLE, initialization for  $\{K_{i1}\}$ ,  $\{K_{i2}\}$ ,  $\theta^{L1}$ , and  $\theta^{L2}$  are required. The initialization for  $\{K_{i1}\}$  and  $\{K_{i2}\}$  given by Trebble<sup>57</sup> is applied to examples involving SRK EOS. In this work, the same procedure is used for initialization even if an activity coefficient model is involved. The procedure is as follows:

- (1) Evaluate  $\{P_i^{\text{sat}}\}$ , set  $\{x_i^{L1} = z_i\}$  and then calculate  $\{\gamma_i^{L1}\}$  using the chosen thermodynamic model.
- (2) Evaluate  $y_i = \exp(\ln x_i^{L1} + \ln \gamma_i^{L1} P_i^{\text{sat}} - \ln \phi_i^{V(0)})$ , where  $\phi_i^{V(0)}$  is the pure vapour fugacity coefficient of component  $i$ , assumed to be 1.0.
- (3) Evaluate  $x_i^{L2} = \exp(\ln x_i^{L1} + \ln \gamma_i^{L1} P_i^{\text{sat}} - \ln \phi_i^{L(0)})$ , where  $\phi_i^{L(0)}$  is the pure liquid fugacity coefficient of component  $i$ , assumed to be  $P_i^{\text{sat}}/P$ .
- (4) Find the estimates of  $\{K_{i1}\}$  and  $\{K_{i2}\}$  from equation (6). Using these estimates of  $\{K_{i1}\}$  and  $\{K_{i2}\}$ , solve equations (12) and (13) by the Newton method to find the initial values of  $\theta^{L1}$  and  $\theta^{L2}$ .

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