# ออพติไมเซชันของสมดุลวัฏภาคโดยใช้ดิฟเฟอเรนเชียลอีโวลูชันกับวิธีแก้ไขแบบอาศัยความชัน

นายพิชิต ตั้งธาราวิวัฒน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551

# PHASE EQUILIBRIUM OPTIMIZATION USING DIFFERENTIAL EVOLUTION WITH THE GRADIENT-BASED REPAIR METHOD

Mr. Phichit Tungtharawiwat

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
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……………………………………………. Dean of the Faculty of Engineering

(Associate Professor Boonsom Lerdhirunwong, Dr. Ing.)

THESIS COMMITTEE

Montree Wongsri ……………………. Chairman

(Assistant Professor Montree Wongsri, D. Sc.)

Soorathep Kheawhom ……………………. Advisor

(Soorathep Kheawhom, Ph. D.)

Amornchai Arpornwichanop ……………………. Examiner

(Assistant Professor Amornchai Arpornwichanop, D. Eng.)

……………………………………………. Examiner

(Associate Professor Sarawut Rimdusit, Ph. D.)

Weerawat ……………………………. External Examiner

(Assistant Professor Weerawat Patthaveekongka, D. Eng)

พิชิต ตั้งธาราวิวัฒน์ : ออพติไมเซชันของสมดุลวัฏภาคโดยใช้ดิฟเฟอเรนเชียลอีโวลูชันกับวิธีแก้ไขแบบอาศัยความชัน. (PHASE EQUILIBRIUM OPTIMIZATION USING DIFFERENTIAL EVOLUTION WITH THE GRADIENT-BASED REPAIR METHOD) อ. ที่ปรึกษาวิทยานิพนธ์ หลัก : อ. ดร. สุรเทพ เขียวหอม, 72 หน้า.

การคำนวณสมดุลวัฏภาคโดยใช้วิธีการหาค่าพลังงานอิสระของกิบส์ที่ต่ำที่สุด (Gibbs free energy minimization) เพื่อให้สอดคล้องกับสมดุลมวลสาร และ แบบจำลองทางอุณหพลศาสตร์ของระบบ เป็นปัญหาแบบโกลบอลออพติไมเซชันซึ่งมักแก้ปัญหาโดยใช้ระเบียบวิธีเชิงวิวัฒนาการ (Evolutionary algorithm) แต่อย่างไรก็ตาม การจัดการกับเงื่อนไขแบบสมการ (Equality constraint) ของระเบียบวิธีเหล่านี้ยังไม่มีประสิทธิภาพมากนัก ดังนั้นวัตถุประสงค์ของงานวิจัยนี้ คือการพัฒนาระเบียบวิธีเชิงวิวัฒนาการเพื่อใช้คำนวณสมดุลวัฏภาคให้มีประสิทธิภาพมากขึ้น โดยนำหลักการของระเบียบวิธีแบบอาศัยความชัน (Gradient-based algorithm) มาจัดการเงื่อนไขแบบสมการในระเบียบวิธีดิฟเฟอเรนเชียลอีโวลูชัน (Differential Evolution, DE) นอกจากนี้ งานวิจัยนี้ได้นำเสนอฟังก์ชันวัตถุประสงค์ที่ถูกจำลองด้วยสมการสถานะ SAFT (Statistical Associating Fluid Theory) โดยที่ฟังก์ชันวัตถุประสงค์ที่ได้เสนอขึ้นนี้ ได้อาศัยความรู้จากสมการพื้นฐานทางอุณหพลศาสตร์ (Fundamental equation) แทนที่การใช้สมการฟูกาซิตี (Fugacity equation) ที่มีอยู่เดิม

ผลที่ได้แสดงให้เห็นว่าคำตอบที่ได้จากออพติไมเซชันของสมดุลวัฏภาคด้วย DE ที่พัฒนาขึ้น พบว่าคำตอบที่ได้มีค่าความเบี่ยงเบนจากสมการเงื่อนไขน้อยกว่า การใช้ DE เดิม นอกจากนี้ ค่าพลังงานอิสระของกิบส์ และ จำนวนครั้งของการคำนวณค่าฟังก์ชันวัตถุประสงค์ ยังได้ถูกนำมาใช้ในการศึกษาอีกด้วย สำหรับฟังก์ชันวัตถุประสงค์ที่ถูกจำลองด้วยสมการสถานะ SAFT ที่ได้เสนอในงานวิจัยนี้ เมื่อออพติไมเซชันด้วยระเบียบวิธีที่พัฒนาขึ้น พบว่าผลที่ได้มีความสอดคล้องกับงานวิจัยและผลการทดลองที่ผ่านมา สำหรับระบบที่ไม่มีอันตรกิริยาระหว่างโมเลกุล (Non-associating molecule)

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต พิชิต ตั้งธาราวิวัฒน์
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ. ที่ปรึกษาวิทยานิพนธ์ หลัก สุรเทพ เขียวหอม
ปีการศึกษา 2551

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Phase equilibrium computations using the Gibbs free energy minimization correspond to mass balance and thermodynamic model of the system are the global optimization problem and usually solved by the Evolutionary Algorithms (EAs). However, the equality constraint-handling techniques of the EAs have been still insufficient. Thus, the aim of this work is to develop the EAs for the efficient phase equilibrium computation by using the gradient-based algorithm to handle the equality constraints in Differential Evolution (DE). Moreover, a new objective function for the phase equilibrium problems modeled with the SAFT (Statistical Associating Fluid Theory) equation of state is proposed in this work. The new objective function uses the thermodynamic fundamental equation information in stead of the fugacity equation.

The results show that the solutions obtained from our developed DE have smaller constraint violation than that of traditional DE. In addition, the Gibbs free energy value obtained and the number of function evaluation are also investigated in this work. The solutions obtained by our developed method with the SAFT model agree well with previous research and experimental works for the system of non-associating molecule.

Department : Chemical Engineering Student's Signature : Phichit Tungtharawiwat
Field of Study : Chemical Engineering Advisor's Signature : Soorathep Kheawhom
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Finally, my appreciation goes to all those individuals who are (and also those who are not) mentioned and who contributed to my knowledge and understanding, and as such find their contribution reflected in my thesis.

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# CHAPTER I

# INTRODUCTION

## 1.1 Importance and Motivation

Phase equilibrium computation for prediction of phase behavior is extremely important in chemical engineering design and chemical process simulation. Insufficient accuracy of the computation methodology and mathematical-related model can undermine the reliability of the obtained solutions from these works. Over a decade ago, various studies have shown an increasingly popular computation technique when solving the phase equilibrium problem is to formulate it as the Gibbs free energy minimization with the stochastic-based optimization (Reynolds, Mulholland and Gomatam, 1997; Lee, Rangaiah, and Luus, 1999; Rangaiah, 2001; Teh and Rangaiah, 2003; Srinivas and Rangaiah, 2007). Previous works not only proposed how to obtain the global solution using several stochastic-based algorithms but also recommend Differential Evolutionary Algorithm (Storn and Price, 1997), the resent evolutionary computation, for the efficient phase equilibrium computation. Although, Differential Evolution (DE) have been performed very effectively for several phase equilibrium problems, none of them suggested any constraint-handling techniques and indicated an appropriate constraint violation of the obtained solution. In fact, these are the key task when applied to the evolutionary computation for constrained optimization problems.

In general, minimization of the Gibbs free energy function usually deals with the equality constraints (e.g. mass balance, thermodynamic model, etc.). This is a significant problem because the traditional search operators of DE and another Evolutionary Algorithms (EAs) are normally blind to these constraints type. Even though, the penalty function and the repair method (or hybrid algorithm) are commonly used as the constraint-handling technique for various EAs (Coello Coello, 2002); in this case, the repair method seem to be advantage technique over using the penalty function. This is because the repair method is used to make feasible solution from a certain number of infeasible one by establishment the relationship between optimization variables and their constraints when the indicated could be easily characterized; while, The penalty method by converting the constrained optimization problem to an unconstrained one with a penalty term are complicated by setting the appropriate penalty parameters to guide the search obtain the reliable solutions. Moreover, the penalty methods usually fail to handle the problem with highly equality constraints. As a result, using the repair methods could be suitable for deal with the equality constraints in phase equilibrium computation.

Recently, the gradient-based repair method has been proposed as one of the constraint-handling techniques (Chootinan and Chen, 2006). This method was derived from the gradient information, namely the Newton method, to the constraint set of the optimization problem. Genetic Algorithm (GA), one of traditional EAs, is used to prove its capability. Their results showed that, this method works well when applied to handle highly equality constraints and can guarantee a feasibility of the solution for any search optimization. As above mentioned, DE algorithm has been recommended for computation of various phase equilibrium problems. Thus, in this dissertation, DE with the gradient-based repair technique are developed in order to use as a new efficient algorithm for more reliability of the obtained solution from the phase equilibrium computation and furthermore in any constrained optimization problems.

Additionally, phase equilibrium computation with the statistical associating fluid theory (SAFT) equation of state (Huang and Radosz, 1990, 1991, 1993) is included in the test problems. This statistical thermodynamic-based model has been widely occurred in many applications to modeling fluid and solid phase equilibria for recent years (Zhong and Yang, 2005; Ji, Feng, and Tan, 2007). Their works have shown that, the SAFT equation of state is a useful thermodynamically model for several phase equilibrium problems. However, the complexity of the given model has been caused the computational difficulties when applied this model for the phase equilibrium calculations. Then, the expression with the fugacity equation cannot be an appropriate model for the Gibbs free energy minimization. Hence, a new methodology to formulate phase equilibrium optimization problem based on the SAFT model is proposed in this research. A new expression uses the fundamental equation to model the Gibbs free energy function instead of using the fugacity equation. The binary systems of non-associating are investigated through using the developed DE.

## 1.2 The Aim of the Thesis

DE and the gradient-based repair technique are developed with the aim of more reliability of the obtained solution in phase equilibrium optimization. Not only obtained the efficient algorithm for phase equilibrium computation but also the dissertation proposes a new methodology for solving phase equilibrium problem modeled with the SAFT equation of state using the developed DE or other stochastic-based methods.

## 1.3 Scope of the Thesis

The thermodynamic models based on the Wilson, NRTL, UNIFAC, SRK (Soave-Redlich-Kwong), and also the SAFT equation of state are investigated and applied in the developed algorithm and compare the constraint violation and the total Gibbs free energy of the system of the obtained results with original DE, and prior works. The 7 test problems are included with 5 problems benchmark and 2 problems with the SAFT model, as follow in table 1.1

**Table 1.1** List of test problems in this work

| Problem | System | Condition | Predicted phase | Model | Reference |
|---|---|---|---|---|---|
| 1 | *n*-Butyl Acetate and Water | 298 K, 1 atm | Liquid-Liquid Equilibrium | UNIFAC | McDonald and Floudas, 1995 |
| 2 | Benzene, Acetonitrile and Water | 333 K, 0.769 atm | Vapor-Liquid-Liquid Equilibrium | NRTL | Castillo and Grossmann, 1981 |
| 3 | Esterification of Acetic Acid with Ethanol | 355 K, 1 atm | Vapor-Liquid Equilibrium | Wilson | McDonald and Floudas, 1995 |
| 4 | Mixture of nine hydrocarbons | 314 K, 19.84 atm | Vapor-Liquid Equilibrium | SRK | Castillo and Grossmann, 1981 |
| 5 | Reduction of Ferric Oxide | 1363 K, 1 atm | Gas-Solid Equilibrium | Ideal | Castillo and Grossmann, 1981 |
| 6 | Non-associating system of Ethene and *n*-Eicosane | 423 K, 20 and 250 bar | Vapor-Liquid Equilibrium | SAFT | Xu et al., 2002 |
| 7 | Non-associating system of Methane and *n*-Hexadecane | Isothermal 543, 623, and 703 K | Vapor-Liquid Equilibrium | SAFT | Lin et al., 1980 |

# CHAPTER II

# LITERATURE REVIEWS

## 2.1 Evolutionary Computation for Phase Equilibrium Problems

Stochastic-based approaches for phase equilibrium computation have been shown increasingly popular techniques to obtain the global solution. One of these is the evolutionary computations (or evolutionary algorithms, EAs); see the books of Bäck, Fogel, and Michalewicz for algorithms and operators. These methods are usually quite simple to implement and use, and they do not require transformation of the original problem. Furthermore, these techniques can locate the vicinity of the global solutions with efficiency. This chapter provides background for computation via stochastic-based approaches for phase equilibrium problems. Not only EAs but also other stochastic-based algorithms are investigated from the prior works.

Reynolds, Mulholland and Gomatam, 1997 computed phase equilibrium problems via minimization of the Gibbs free energy for all the species in the system is conducted using the technique of simulated annealing (SA). Their work has discussed how to solve difficult computational minimization problems in a way which can incorporate the physical properties of the species involved in these systems, including phase change, multi-phase conditions and phase and chemical equilibria problems.

Lee, Rangaiah, and Luus, 1999 used direct search optimization for phase and chemical equilibrium calculations. The selected method is the random search optimization procedure of Luus and Jaakola (LJ), which has been show that successful for solving difficult global optimization problem. Their results obtained with typical examples for vapor-liquid equilibrium and vapor-liquid equilibrium with reaction, where the liquid and vapor phases may be non-ideal, show that the LJ optimization procedure can be used to find very accurately the global minimum in only a few seconds of computation time on a personal computer.

Rangaiah, 2001 studied two stochastic optimization techniques, namely, Genetic Algorithm (GA), one of the traditional EAs, and Simulate Annealing (SA). These algorithms are evaluated and compared for phase equilibrium and phase stability problems. Typical examples and different thermodynamic models are considered. The results show that GA is generally more efficient and reliable than SA for phase equilibrium calculation. But both of GA and SA exhibited poor reliability for locating the global minimum of the Gibbs free energy function. For this problem, a hybrid GA incorporating SA for individual learning, is proposed and shown that can improve success rate to find the global minimum.

Teh and Rangaiah, 2003 studied Tabu search algorithm for the global optimization of phase equilibrium computations. They used enhanced continuous TS (ECTS) for their research. Performance of ECTS is compared with a genetic algorithm (GA). The results show that both the modified TS and GA have high reliability in locating the global minimum, and that the modified TS converges faster than GA due to reducing the computational time and number of function evaluations.

Srinivas and Rangaiah, 2007 studied Differential Evolution (DE), the recent EAs, and Tabu search (TS) for phase equilibrium and phase stability computations. They used DE and TS with the Quasi-Newton method (QN) to optimization of the local solutions. Their results show that DE-QN is more reliable than TS-QN because the escaping mechanism (via mutation and crossover) in DE-QN is more effective than that of TS-QN, and that TS-QN is computationally more efficient than DE-QN, perhaps due to avoiding revisits to the same place during the search process.

Srinivas and Rangaiah, 2007 developed Differential Evolution (DE) and Tabu list (TL) for phase equilibrium and phase stability computations. In their work, DE is modified to incorporate the concept of Tabu Search (TS) (i.e., avoiding revisits to the same place during the search); it improves the diversity among members of the population and eventually contributes to the computational efficiency. Revisits during the search in DE are avoided by using a TL (which keeps track of previous search points that are already evaluated), and hence, the proposed method is named differential evolution with tabu list (DETL).

## 2.2 Computation with the Statistical Thermodynamic-Based Model

The use of equations of state (EoS) has been the generally accepted method for the calculation of many fluid physical properties. Over the last twenty years, statistical mechanical approaches have meanwhile grown allowing the development of powerful engineering equations of state. In particular, this chapter investigates how equations that are based on the association term of Wertheim’s theory (Wertheim, 1984a, 1984b, 1986a, and 1986b) can improve significantly the predictive power in chemical engineering applications and also prior work with computational tools for solving phase equilibrium problems modeled with these equations.

The effect of molecular associations on the phase coexistence properties of fluids are investigated since Chapman et al.’s proposal (Chapman et al., 1988a, 1988b, 1988c, 1990) in 90th decade. After that, Huang and Radosz have developed an equation of state from the concept of the statistical associating fluid theory (SAFT) previously proposed by Chapman et al. (Huang and Radosz, 1990, 1991, 1993). This equation of state is generally known as the SAFT equation of state. Unlike the cubic equations of state, the SAFT equation of state does not only provide physical meaning from the concept of hard sphere effect, indicated in cubic model, but also includes chain effect and association of molecules.

Various works have reported that the SAFT model is preferable for the prediction of various fluid properties. In the work by Ji et al., 2007, the SAFT model was used to predict the density of aqueous solutions of amino acid. The modeling is accomplished by extending the previously developed new method to determine the SAFT parameters for amino acids (Feng, van der Kooi, and de Swaan Arons, 2005). The density of binary solutions of amino acids has been correlated or predicted with a high precision. And then the density of multi-component aqueous solutions of amino acids has been modeled based on the modeling results of binary systems, and a high accuracy of density calculations has been obtained.

In addition, Zhong and Yang, 2005 studied the systems containing fluid-solid equilibrium mixture. The SAFT equation of state combined with a one-parameter mixing rule was used to evaluate the capability of the SAFT approach for modeling the solubility of solid aromatic compounds in supercritical fluids (SCFs) with co-solvents. Binary interaction parameters were obtained by fitting the phase equilibrium data of the constituent binary systems. The SAFT model was used to predict the solubility of solids in carbon dioxide with co-solvents. Their work demonstrates that the SAFT approach is useful for modeling the solubility of solids in SCFs with co-solvents with reasonable accuracy.

Because of the complexity of the SAFT model lies on the computational difficulties, development of the reliable computation technique for prediction of phase behavior from a given model can be a very challenging computational problem.

However, only a few works have been shown in development computational algorithm such Xu et al., 2002. Their work formulated the phase equilibrium problem based on the SAFT model as a two-stage algorithm. Firstly, the phase stability of the stationary points obtained from the equi-fugacity conditions are examined. If the stationary points previously obtained are stable, secondly, the equilibrium solutions are then obtained by solving the global optimization problem of minimum Gibbs free energy. To accomplish the computational strategy, they used the gradient-based optimization algorithm based on the interval analysis approach for solving the problems. Their algorithm performed well in a case of binary system. Unfortunately, it requires the derivatives with respect to each component during each computation.

Therefore, to overcome this drawback, the dissertation proposes a new methodology using the minimization of the total Gibbs free energy of the system to solve the phase equilibrium problem modeled with the SAFT approach as a single stage problem. Moreover, the Gibbs free energy is expressed in terms of the fundamental equations instead of the fugacity equation. The optimization problem formulated is solved using stochastic-based method.

# CHAPTER III

# ALGORITHMIC DESCRIPTION FOR COMPUTATION OF PHASE EQUILIBRIUM PROBLEM

## 3.1 Problem Formulation

For description any open systems, that can exchange matter with surroundings, Gibbs showed equation (3.1) can be extended to open system by adding chemical work terms of the form $\mu_i dn_i$, where $\mu_i$ is the chemical potential of species *i* and $n_i$ is the amount of species *i* in system. The first law of thermodynamics for homogeneous one phase system is given as

$$dU = dQ - dw \tag{3.1}$$

and for open system

$$dU = dQ - dw + \sum_{i=1}^{N} \mu_i dn_i \tag{3.2}$$

where, *N* is the number of species in the system; *U* is the internal energy for the system; *Q* is heat adding to the system by the surroundings; and *w* is work done on the surroundings by the system. Assume that expression of work is only pressure-volume work is involved

$$dw = PdV \tag{3.3}$$

where, *P* is pressure and *V* is volume of the system; and the second law of thermodynamics

$$dS = \frac{dQ}{T} \tag{3.4}$$

where, $S$ is entropy and $T$ is temperature of the system. So that, the combine first and second law and for the open system is

$$dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dn_i \tag{3.5}$$

several important results are obtained by manipulation of equation (3.5) with the substitutions of molar properties as $U = n\overline{U}$; $S = n\overline{S}$; $V = nv$; $n_i = nx_i$; where, $\overline{U}$ is the molar internal energy; $\overline{S}$ is the molar entropy; $v$ is the molar volume; $x_i$ is the mole fraction of species $i$; and $n$ is the total amount of mole of the system. From equation (3.5), the expanded and rearranged result is

$$\begin{aligned} nd\overline{U} + \overline{U}dn &= n\left(Td\overline{S} - Pdv + \sum_{i=1}^{N} \mu_i dx_i\right) \\ &+ \left(T\overline{S} - Pv + \sum_{i=1}^{N} \mu_i x_i\right)dn \end{aligned} \tag{3.6}$$

since $n$ and $dn$ are arbitrary, so that

$$d\overline{U} = Td\overline{S} - Pdv + \sum_{i=1}^{N} \mu_i dx_i \tag{3.7}$$

$$\overline{U} = T\overline{S} - Pv + \sum_{i=1}^{N} \mu_i x_i \tag{3.8}$$

from equation (3.8), multiply both side by the total amount of mole of the system, the result is

$$U = TS - PV + \sum_{i=1}^{N} \mu_i n_i \tag{3.9}$$

thus, equation (3.5) and equation (3.9) are the differential form and expression form for the internal energy. Note that equation (3.7) and equation (3.8) are the molar form of equation (3.5) and equation (3.9) respectively.

Although the internal energy provide a criterion for whether a process can occur spontaneously, this is not very useful. Because of the entropy and volume are not easily controlled. However, more useful thermodynamics properties can be define by based on the internal energy. For consideration to closed system or at constant composition, equation (3.5) can neglect the term of the summation of the chemical potential, that is

$$dU = TdS - PdV \tag{3.10}$$

for spontaneous process (irreversible process), the second law of thermodynamics is

$$dS \geq \frac{dQ_{irrev}}{T} \tag{3.11}$$

then equation (3.10) can be rearranged to

$$dU + PdV - TdS \leq 0 \tag{3.12}$$

at constant temperature and pressure, this equation become

$$d(U + PV - TS)_{T,P} \leq 0 \tag{3.13}$$

define the quantity in parentheses as the quantity of particularly thermodynamic property that call the Gibbs free energy, thus

$$d(G)_{T,P} \leq 0 \tag{3.14}$$

where, $G$ is the Gibbs free energy of the system. From equation (3.9), the Gibbs free energy can be expressed in form

$$G = \sum_{i=1}^{N} \mu_i n_i \tag{3.15}$$

thus, if any spontaneous process (irreversible process) occur at constant temperature and pressure, then from equation (3.14) make know that the change in the Gibbs free energy of the system decrease. Recall equation (3.9), after differentiation

$$dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dn_i + SdT - VdP + \sum_{i=1}^{N} n_i d\mu_i \tag{3.16}$$

from equation (3.5) and equation (3.16), which can be rearranged in form

$$0 = -SdT + VdP - \sum_{i=1}^{N} n_i d\mu_i \tag{3.17}$$

add both side of equation (3.17) by the differential form of equation (3.15), the result show that

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i \tag{3.18}$$

furthermore, the molar form of the differential form and the expression form of the Gibbs free energy equation can show that

$$d\overline{G} = -\overline{S}dT + vdP + \sum_{i=1}^{N} \mu_i dx_i \tag{3.19}$$

$$\overline{G} = \sum_{i=1}^{N} \mu_i x_i \tag{3.20}$$

from equation (3.18), $\mu_i dn_i$ is the change in the Gibbs free energy that occurs when $dn_i$ moles of species *i* are added or removed at constant temperature and pressure.

thus, when the transfer is in equilibrium (no spontaneous change), the change in the Gibbs free energy always decrease to the minimum

$$d(G)_{T,P} = 0 \tag{3.21}$$

note that, an above equation is the very important equation because it provide the useful criteria for the any equilibrium system. Consider equation (3.18), (3.19), and (3.21), the Gibbs free energy of the system will reach to minimum when thermal, mechanical, chemical equilibrium occur simultaneously. Then, condition for equilibrium state of the system can determined as fallow

$$\left.\begin{aligned} T^{(1)} &= T^{(2)} = \ldots \\ P^{(1)} &= P^{(2)} = \ldots \\ \mu_i^{(1)} &= \mu_i^{(2)} = \ldots \end{aligned}\right\} \tag{3.22}$$

where the superscripts indicate to each phase of the system at equilibrium state. The equation (3.22) is used for thermodynamic equilibrium calculation when no transfer of heat and mass occur in the equilibrium at fixed *T* and *P*.

### 3.1.1 Computation using the Fugacity Equation

The concept of fugacity arises from a consideration of change in the Gibbs free energy those results from change in pressure and temperature. Because of $\mu_i = \overline{G}_i$, from equation (3.19) with neglect the change of an amount of each component, the chemical potential of the system can be expressed as fallow

$$d\overline{G} = -\overline{S}dT + vdP \tag{3.23}$$

for an ideal gas at constant temperature

$$d\overline{G} = vdP = RT(d\ln P) \tag{3.24}$$

and for component $i$ of an ideal mixture in which the partial pressure $P_i = x_i P$; from equation (3.19)

$$d\overline{G}_i \quad = \quad -\overline{S}_i dT \quad + \quad v_i dP \tag{3.25}$$

$$d\overline{G}_i \quad = \quad v_i dP \quad = \quad RT(d\ln P_i) \tag{3.26}$$

the simple forms of these relations may be preserved for other substances and mixtures by defining terms called "fugacity" and "partial fugacity" at a fixed temperature as

$$d\overline{G} \quad = \quad vdP \quad = \quad RT(d\ln f) \tag{3.27}$$

$$d\overline{G}_i \quad = \quad v_i dP \quad = \quad RT(d\ln \hat{f}_i) \tag{3.28}$$

in view of the following auxiliary conditions, the fugacity and partial fugacity can reduce to the pressure and partial pressure at low values

$$\lim_{P\to 0}\frac{f}{P} \quad = \quad \lim_{P\to 0}\phi \quad = \quad 1 \tag{3.29}$$

$$\lim_{P\to 0}\frac{\hat{f}_i}{x_i P} \quad = \quad \lim_{P\to 0}\hat{\phi}_i \quad = \quad 1 \tag{3.30}$$

where, the ratios $\phi$ and $\hat{\phi}_i$ are called fugacity coefficient and partial fugacity coefficient respectively, then

$$f \quad = \quad \phi P \tag{3.31}$$

and for each component in the mixture

$$\hat{f}_i \quad = \quad x_i \hat{\phi}_i P \tag{3.32}$$

For pure substances, when the volume is known as a function of the temperature, either from direct measurement or from an empirical equation of state, changes in fugacity may be found by integration, thus

$$\ln\frac{f_2}{f_1} \quad = \quad \frac{1}{RT}\int_{P_1}^{P_2} v dP \tag{3.33}$$

since $f \rightarrow P$ when $P \rightarrow 0$, absolute values of the fugacity coefficient are determinable by set $P_1 = P^* \rightarrow 0$ and $P_2 = P$, thus

$$\ln\frac{f}{P^*} \quad = \quad \frac{1}{RT}\int_{P^*}^{P} v dP \tag{3.34}$$

$$\ln\frac{f}{P^*} + \ln\frac{P^*}{P} \quad = \quad \frac{1}{RT}\int_{P^*}^{P} v dP + \int_{P^*}^{P}\frac{1}{P}dP \tag{3.35}$$

$$\ln\phi \quad = \quad \ln\frac{f}{P} \quad = \quad \frac{1}{RT}\int_{0}^{P}(v - \frac{RT}{P})dP \quad = \quad \int_{0}^{P}\frac{z-1}{P}dP \tag{3.36}$$

clearly, the integrands represent deviation from ideal-gas behavior and vanish at $P \;=\; 0$. Since pressure-explicit equations of state are the more common types, a useful relation for finding fugacity coefficients is

$$\ln\phi \quad = \quad z - 1 - \ln z + \frac{1}{RT}\int_{v}^{\infty}(P - \frac{RT}{v})dv \tag{3.37}$$

In a homogeneous mixture at a fixed temperature, the fugacity of a particular component of a mixture is defined by equation (3.28) and equation (3.32). A change in partial fugacity with pressure is evaluated by integration of the partial molar volume at constant composition

$$\ln \frac{\hat{f}_{i2}}{\hat{f}_{i1}} = \frac{1}{RT}\int_{P_1}^{P_2} v_i dP \tag{3.38}$$

absolute values of the partial fugacity coefficient are obtainable by taking advantage of equation (3.32), which makes $\hat{f}_i \rightarrow x_i P$ when $P \rightarrow$ 0. The pressure integrals have several useful equivalents

$$\ln \frac{\hat{f}_i}{x_i P^*} + \ln \frac{P^*}{P} = \frac{1}{RT}\int_{P^*}^{P} v_i dP + \int_{P}^{P} \frac{1}{P} dP \tag{3.39}$$

$$\ln \hat{\phi}_i = \ln \frac{\hat{f}_i}{x_i P} = \frac{1}{RT}\int_{0}^{P} (v_i - \frac{RT}{P}) dP = \int_{0}^{P} \frac{\bar{z}_i - 1}{P} dP \tag{3.40}$$

all integrands vanish at $P$ = 0, the equation (3.35) can express in form

$$RT \ln \hat{\phi}_i = \int_{v}^{\infty} \left[ \frac{\partial P}{\partial n_i} - \frac{RT}{v} \right] dv - RT \ln z \tag{3.41}$$

When use the fugacities for phase equilibrium calculation, the equation (3.27) and (3.28) are integrated at constant temperature to generate integration constants that are functions of temperature

$$\overline{G} = \Delta G^f + RT \ln \frac{f}{f^0} \tag{3.42}$$

for multicomponent system

$$\overline{G_i} = \Delta G_i^f + RT \ln \frac{\hat{f}_i}{f_i^0} \tag{3.43}$$

where, $\Delta G_i^f$ is the standard Gibbs free energy of formation at temperature of the system for component *i* in unit of joule per mole, which can obtain from the Gibbs-Helmholtz equation

$$\left.\frac{\partial(\Delta G_i^f / T)}{\partial T}\right|_P = -\frac{\Delta H_i^f}{T^2} \tag{3.44}$$

where, $\Delta H_i^f$ is the standard enthalpy of formation at temperature of the system for substance in unit of joule per mole. The enthalpy can be expressed in form Kirchhoff equation

$$\left.\frac{\partial \Delta H_i^f}{\partial T}\right|_P = \Delta C_{Pi} \tag{3.45}$$

where, $\Delta C_{Pi}$ is the isobaric heat capacity of substance in unit of joule per mole.

From thermodynamic equilibrium condition, any case of equilibrium between phases requires equality of *T, P*, chemical potential and also partial fugacities of each component through out the system, thus

$$\left.\begin{aligned} \hat{f}_i^{(1)} &= \hat{f}_i^{(2)} = \ldots \\ \Delta G_i^{f(1)} + RT\ln\frac{\hat{f}_i^{(1)}}{f_i^{0(1)}} &= \Delta G_i^{f(2)} + RT\ln\frac{\hat{f}_i^{(2)}}{f_i^{0(2)}} = \ldots \end{aligned}\right\} \tag{3.46}$$

for the standard state fugacities, $f_i^0$, specification of a standard state includes the pressure and the physical state of the substance, usually the one that is stable at the system temperature, but not the temperature itself, so the standard state does depend on the temperature.

For gases the natural reference state is unit fugacity at the temperature of the system, which in most cases is very nearly 1 atm.

For condensed phase, the standard state naturally is chosen as one at which the fugacity is readily calculable. When the vapor pressure is known, the fugacity of the condensed phase may be taken as that of the vapor phase in equilibrium with it at the temperature of the system. Adjustment of that fugacity to the system pressure is given by

$$\ln\frac{f_L}{f^{Sat}} \quad = \quad \int_{P^{Sat}}^{P} \frac{v_L}{RT}\,dP \tag{3.47}$$

For solid, vapor pressure data are not always available; but usually the melting point and sometimes the triple point are known and are nearly the same. The pressure at conditions is the vapor pressure, which can be obtained by extrapolation of a vapor-pressure equation below the freezing point. Subsequent adjustment of the fugacity of the solid to the system pressure and temperature is made with the equation

$$\ln\frac{f_S}{f^{tp}} \quad = \quad \int_{P^{tp}}^{P} \frac{v_S}{RT}\,dP - \int_{T^{tp}}^{T} \frac{\overline{H}-\overline{H}^{id}}{RT^2}\,dT \tag{3.48}$$

at moderate pressure particularly, $\overline{H}-\overline{H}^{id}$ may be taken as the heat of sublimation. When this has not been measured, it may be approximated as the sum of heats of fusion and vaporization, or it may be figured from vapor-pressure data of the solid with the Clausius-Clapeyron equation with Antoine’s constant.

#### 3.1.1.1 *P – v – T* Equation of State Model

Consider the Vapor-Liquid Equilibrium (VLE) system at fixed temperature and pressure, the molar Gibbs of the individual in each phase is

$$\Delta G_{iV}^{f} + RT\ln\frac{\hat{f}_{iV}}{f_{iV}^{0}} \quad = \quad \Delta G_{iL}^{f} + RT\ln\frac{\hat{f}_{iL}}{f_{iL}^{0}} \tag{3.49}$$

from equation (3.46), using equi-fugacity condition, this can be arranged to

$$\hat{f}_{iV} \quad = \quad \hat{f}_{iL} \tag{3.50}$$

when using fugacity equations for both phase, a vapor phase can be expressed as a function of partial fugacity coefficient of each component in the form

$$\hat{f}_{iV} \quad = \quad y_i \hat{\phi}_{iV} P \tag{3.51}$$

where, $\hat{\phi}_{iV}$ and $y_i$ are, respectively, the partial fugacity coefficient and mole fraction of component $i$ in the vapor phase at $T$ and $P$. Likewise, we can define $\hat{f}_{iL}$ for a liquid phase by

$$\hat{f}_{iL} \quad = \quad x_i \hat{\phi}_{iL} P \tag{3.52}$$

where $x_i$ is the mole fraction of component $i$ in the liquid phase and $\hat{\phi}_{iL}$ is the corresponding liquid phase partial fugacity coefficient at $T$ and $P$. Incorporating equation (3.41) and (3.46), the following final expressions for VLE calculation can be obtained

$$y_i \hat{\phi}_{iV} \quad = \quad x_i \hat{\phi}_{iL} \tag{3.53}$$

Because of calculation for the partial fugacity coefficient usually deal with $P - v - T$ Equation of State, the model is a relationship between molar volume (or density), temperature, and pressure. Equations of state play an important role in chemical engineering design, and they have assumed an expanding role in the study of the phase equilibria of fluids and fluid mixtures. There are many advantages in using equations of state for phase equilibria calculations. Equations of state can be used typically over wide ranges of temperature and pressure, and they can be applied to mixtures of diverse components, ranging from the light gases to heavy liquids. They can be used to calculate vapor-liquid, liquid-liquid, and supercritical fluid-phase equilibria without any conceptual difficulties. The van der Waals equation of state was the first equation to predict vapor-liquid coexistence. Later, the Redlich-Kwong equation of state (Redlich and Kwong, 1949) improved the accuracy of the van der Waals equation by introducing tem-perature-dependence for the attractive term. Soave

(1972) and Peng and Robinson (1976) proposed additional modifications to more accurately predict the vapor pressure, liquid density, and equilibria ratios.

Considerable progress has been achieved in the development of equations of state. Many highly successful empirical equations of state have been proposed that can be used to calculate the phase behavior of simple fluids. However, a more sophisticated approach is required for complicated molecules. To meet the challenge posed by large and complicated molecules, equations of state are being developed increasingly with an improved theoretical basis. These new equations are playing an expanding role in the accurate calculation of fluid-phase equilibria. Equation of state development has been aided greatly by new insights into the nature of intermolecular interaction and molecular simulation data. In particular, molecular simulation is likely to have an ongoing and crucial role in the improvement of the accuracy of equations of state. A continuing challenge is to improve the prediction of the phase behavior of mixtures. The main impediment to the prediction of mixture phenomena is our understanding of interactions between dissimilar molecules. This is also an area that is likely to benefit from the input of molecular simulation data.

#### 3.1.1.2 Activity and Activity Coefficient Model

For multi-component and Liquid-Liquid Equilibrium (LLE) system, from equation (3.46), using equi-fugacity condition

$$\hat{f}_{iL}^{(1)} = \hat{f}_{iL}^{(2)} \qquad (3.54)$$

from equation (3.49), hence

$$x_i^{(1)}\gamma_i^{(1)} = x_i^{(2)}\gamma_i^{(2)} \qquad (3.55)$$

the parameters for the activity coefficient model are used the same for both phase. when using activity models for liquid phase

$$\frac{\hat{f}_{iL}}{f_{iL}^{0}} = a_i = x_i\gamma_i \qquad (3.56)$$

**Table 3.1** Partial fugacity coefficient from some equation of state

| EoS | Model | Partial fugacity coefficient |
|---|---|---|
| Virial | $P = 1 + \frac{BP}{RT}$ | $\ln\hat{\phi}_i = \frac{P}{RT}\left\{B_{ii} + 0.5\left[\sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk})\right]\Big]\right\}$<br>$B = \sum\sum y_i y_j B_{ij}$<br>$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii}$<br>$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii}$ |
| vdW | $P = \frac{RT}{v-b} - \frac{a}{v^2}$ | $\ln\hat{\phi}_i = \frac{b_i}{v-b} - \ln\left[z(1-\frac{b}{v})\right] - \frac{2\sqrt{aa_i}}{RTv}$<br>$a = (\sum y_i \sqrt{a_i})^2$<br>$b = \sum y_i b_i$ |
| SRK | $P = \frac{RT}{v-b} + \frac{a\alpha}{v(v+b)}$ | $\ln\hat{\phi}_i = \frac{b_i}{b}(z-1) - \ln\left[z(1-\frac{b}{v})\right]$<br>$+\frac{a\alpha}{bRT}\left[\frac{b_i}{b} - \frac{2}{a\alpha}\sum_j y_j (a\alpha)_{ij}\right]\ln(1+\frac{b}{v})$ |

where $a_i$ is the activity of component $i$; $\gamma_i$ is the activity coefficient of component $i$; so, the final expressions for vapor-liquid equilibrium calculation when using activity model can be obtained

$$y_i\hat{\phi}_{iV} = x_i\gamma_i f_{iL}^{0} \tag{3.57}$$

and for VLLE, express in term

$$\begin{aligned} y_i\hat{\phi}_{iV} &= x_i\gamma_i^{(1)} f_{iL}^{0(1)} \\ y_i\hat{\phi}_{iV} &= x_i\gamma_i^{(2)} f_{iL}^{0(2)} \end{aligned} \tag{3.58}$$

**Table 3.2** Some activity coefficient model

| Model | Activity coefficient |
|---|---|
| Wilson | $\ln\gamma_i = -\ln(\sum_{j=1}^{m} x_j\Lambda_{ij}) + 1 - \sum_{k=1}^{m}\frac{x_k\Lambda_{ki}}{\sum_{j=1}^{m} x_j\Lambda_{jk}}$ |
|  | $\Lambda_{ij} = \frac{v_j^L}{v_i^L}\exp(-\frac{\lambda_{ij}}{RT})$ |
|  | $\Lambda_{ii} = \Lambda_{jj} = 1$ |
| NRTL | $\ln\gamma_i = \frac{\sum_{j=1}^{m}\tau_{ji}G_{ji}x_j}{\sum_{l=1}^{m}G_{li}x_l} + \sum_{j=1}^{m}\frac{x_jG_{ji}}{\sum_{l=1}^{m}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{n=1}^{m}x_n\tau_{nj}G_{nj}}{\sum_{l=1}^{m}G_{lj}x_l}\right)$ |
|  | $\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$ |
|  | $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$ |
|  | $\tau_{ii} = \tau_{jj} = 0$ |
|  | $G_{ii} = G_{jj} = 1$ |
| UNIFAC | $\ln\gamma_i^C = 1 - J_i + \ln J_i - 5q_i(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i})$ |
|  | $\ln\gamma_i^R = q_i\left[1 - \sum_k\left(\theta_k\frac{\beta_{ik}}{s_k} - e_{ki}\ln\frac{\beta_{ik}}{s_k}\right)\right]$ |
|  | $\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R$ |
|  | $J_i = \frac{r_i}{\sum_j r_jx_j} \quad L_i = \frac{q_i}{\sum_j q_jx_j} \quad s_i = \sum_i\theta_l\tau_{li}$ |
|  | $r_i = \sum_k v_k^iR_k \quad q_i = \sum_k v_k^iQ_k \quad e_{ki} = \frac{v_k^iQ_k}{q_i}$ |
|  | $\beta_{ik} = \sum_m e_{mi}\tau_{mk} \quad \theta_k = \frac{\sum_i x_iq_ie_{ki}}{\sum_j x_jq_j} \quad \tau_{mk} = \exp(\frac{-a_{mk}}{T})$ |

#### 3.1.1.3 *K* – values for Phase Equilibrium Computation

An equilibrium ratio is the ratio of mole fraction of a species present in two phases at equilibrium. For the vapor-liquid case, the constant is referred to as the *K* – value or vapor-liquid equilibrium ratio

$$K_i = \frac{y_i}{x_i} \tag{3.59}$$

For the liquid-liquid case, the ratio is referred to as the distribution coefficient or liquid-liquid equilibrium ratio

$$K_{Di} = \frac{x_i^{(1)}}{x_i^{(2)}} \tag{3.60}$$

For equilibrium stage calculations involving the separation of two or more components, separation factors are define by forming ratios of equilibrium ratios. For the vapor-liquid case, relative volatility is define by

$$\alpha_{ij} = \frac{K_i}{K_j} \tag{3.61}$$

For the liquid-liquid case, the relative selectivity is

$$\beta_{ij} = \frac{K_{Di}}{K_{Dj}} \tag{3.62}$$

Equilibrium ratios can be expressed by the quantities partial fugacity and activity coefficient as show in previously.

**Table 3.3** Useful expression for estimating $K$ – value for VLE

| Forms | Equation | Application |
|---|---|---|
| Equation fo State | $K_i = \dfrac{\hat{\phi}_{iL}}{\hat{\phi}_{iV}}$ | Hydrocarbon and light gas mixtures from cryogenic temperatures to the critical region |
| Activity coefficient | $K_i = \dfrac{\gamma_{iL}\phi_{iL}}{\hat{\phi}_{iV}}$ | All mixtures from ambient to near-critical temperature |
| Raoult's law | $K_i = \dfrac{P_i^S}{P}$ | Ideal solutions at near-ambient pressure |
| Modified Raoult's law | $K_i = \dfrac{\gamma_{iL}P_i^S}{P}$ | Nonideal liquid solutions at near-ambient pressure |
| Poynting correction | $K_i = \gamma_{iL}\phi_{iV}^S\dfrac{P_i^S}{P}\exp(\dfrac{1}{RT}\int_{P_i^S}^{P} v_{iL}\,dP)$ | Nonideal liquid solutions at moderate pressure and below the critical-temperature |
| Henry's law | $K_i = \dfrac{H_i}{P}$ | Low to moderate pressures for species at supercritical temperature |

For vapor-solid equilibria, a useful formulation can be derived if the solid phase consists of just one of the components of the vapor phase. In that case, the combination of equation (3.41)gives

$$f_{iS} = \hat{\phi}_{iV} y_i P \tag{3.63}$$

at low pressure, $\hat{\phi}_{iV}$ = 1.0 and the solid fugacity can be approximated by the vapor pressure of the solid to give for the vapor phase mole fraction of the component forming the solid phase

$$y_i \quad = \quad \frac{(P_i^S)_{Solid}}{P} \qquad (3.64)$$

For liquid-solid equilibria, a similar useful formation can be derived if again the solid phase is a pure component. Then the combination gives

$$f_{iS} \quad = \quad \gamma_{iL} x_i f_{iL}^0 \qquad (3.65)$$

at low pressure, the solid fugacity can be approximated by vapor pressure to give, for the component in the solid phase

$$x_i \quad = \quad \frac{(P_i^S)_{Solid}}{\gamma_{iL}(P_i^S)_{Liquid}} \qquad (3.66)$$

### 3.1.2 Minimization of the total Gibbs Free Energy of the System

For multi-component and multiphase system at temperature *T* and pressure *P*, the Gibbs free energy function *G* is expressed as a linear combination of the chemical potential of each component in each phase, the equation (3.15) can rewritten as

$$G \quad = \quad \sum_{i=1}^{N}\sum_{j=1}^{\pi} n_{ij}\mu_{ij} \qquad (3.67)$$

chemical potential can be expressed in terms of Gibbs free energy of formation and fugacity, so equation (3.55) can be rewritten as,

$$G \quad = \quad \sum_{i=1}^{N}\sum_{j=1}^{\pi} n_{ij}\left\{\Delta G_{ij}^{f} + RT\ln\frac{\hat{f}_{ij}}{f_{ij}^{0}}\right\} \qquad (3.68)$$

where, $n_{ij}$ is the number of moles of component $i$ present in phase $j$; $\mu_{ij}$ is the associated chemical potential; $\pi$ is the number of phases at equilibrium; $\Delta G_{ij}^{f}$ is the Gibbs free energy of formation of component $i$ in phase $j$ at standard state; $R$ is the gas constant; $\hat{f}_{ij}$ is the partial fugacity of component $i$ in phase $j$ and $f_{ij}^{0}$ is the fugacity of pure component $i$ at standard state.

#### 3.1.2.1 The Gibbs Free Energy Function

For vapor-liquid (VL) and vapor-liquid-liquid (VLL) equilibrium, for equation of state models for both vapor phase and liquid phase, thus

$$\frac{G}{RT} \quad = \quad \sum_{i=1}^{N}\sum_{L=1}^{\pi^L} n_{iL}\ln(\hat{\phi}_{iL}x_{iL}) + \sum_{i=1}^{N} n_{iV}\ln(\hat{\phi}_{iV}y_i) + \frac{1}{RT}\sum_{i=1}^{N}\sum_{j=1}^{\pi} n_{ij}(\Delta G_{iV}^{f} + RT\ln P) \qquad (3.69)$$

where $\pi^L$ is the number of liquid phase and, thus, the equation can be used as the objective function for VLE and VLLE problems.

Note that, for vapor-liquid (VL) and vapor-liquid-liquid (VLL) equilibrium, the Gibbs free energy of formation of a component in liquid state is related to that in vapor state by

$$\Delta G_{iL}^{f} \quad = \quad \Delta G_{iV}^{f} + RT\ln P_i^{Sat} \qquad (3.70)$$

where $P_i^{Sat}$ is the saturated vapor pressure for pure component $i$ at $T$. This approximation is valid only when component $i$ does not associate in the vapor phase and its vapor pressure is under 2-3 atm.

Therefore, the Gibbs free energy function when use activity model for liquid phase can be modified as follows

$$\frac{G}{RT} \quad = \quad \sum_{i=1}^{N}\sum_{L=1}^{\pi^L} n_{iL}\ln(\gamma_{iL}x_{iL}P_i^{Sat}) + \sum_{i=1}^{N} n_{iV}\ln(\hat{\phi}_{iV}y_iP) + \frac{1}{RT}\sum_{i=1}^{N}\sum_{j=1}^{\pi} n_{ij}\Delta G_{iV}^{f} \qquad (3.71)$$

so, the equation is the simplified objective function for vapor-liquid-liquid equilibrium (VLL) problems. The equation (3.71) is also useable for vapor-liquid equilibrium same as equation (3.58). The difference is the partial fugacity coefficient in liquid phase in equation (3.59) is described by the same thermodynamic model.

For liquid-liquid equilibrium, from equation (3.56), the Gibbs free energy function can be simplified to

$$\frac{G}{RT} = \sum_{i=1}^{N}\sum_{L=1}^{\pi} n_{ij}\ln(\gamma_{ij}x_{ij}) + \frac{1}{RT}\sum_{i=1}^{N}\sum_{j=1}^{\pi} n_{ij}\Delta G_{ij}^{f} \tag{3.72}$$

therefore, the equation is the objective function for liquid-liquid equilibrium (LLE) problems.

### 3.1.2.2 Constraints for Optimization

When only phase equilibrium is involved, the conservation of moles of each component must hold

$$\sum_{j=1}^{\pi} n_{ij} = n_{iT} \tag{3.73}$$

where $n_{iT}$ is the total mole of component i in the system (feed). The boundaries on variables are

$$0 \leq n_{ij} \leq n_{iT} \qquad i = 1,2,\ldots,N \tag{3.74}$$

For simultaneous phase and chemical equilibrium, the conservation of chemical elements must hold

$$\sum_{i=1}^{N}\sum_{j=1}^{\pi} a_{ie}n_{ij} = b_e \tag{3.75}$$

where $e$ = 1, 2, 3, … , $M$; $a_{ie}$ represents the number of gram-atom of element $e$ in component $i$, $b_e$ is the total number of gram-atom of elements $e$ in the system and $M$ is the number of elements. The boundaries on variables are

$$0 \quad \leq \quad a_{ie} n_{ij} \quad \leq \quad b_e \tag{3.76}$$

thus, to obtain phase compositions at equilibrium it is necessary to find the minimum of the Gibbs free energy subject to the constraints and the boundaries imposed by equation (3.61) and (3.62) ,or equation (3.63) and (3.64) for simultaneous chemical equilibrium.

## 3.2 Application to the Statistical Associating Fluid Theory Model

Statistical thermodynamics-based equations of state, particularly the statistical associating fluid theory (SAFT) approaches, have been proven their application in prediction of phase behavior over a decade ago. Huang and Radosz (Huang and Radosz, 1990, 1991, 1993) have developed an equation of state from the concept of the statistical associating fluid theory (SAFT) approach previously proposed by Chapman et al. (Chapman et al., 1988a, 1988b, 1988c, 1989, 1990). This equation of state is generally known as the SAFT equation of state. Unlike the cubic equations of state, the SAFT equation of state does not only provide physical meaning from the concept of hard sphere effect but also includes chain effect and association of molecules.

### 3.2.1 The Statistical Associating Fluid Theory Equation of State

In the SAFT model, the molecules of each species are approximated as chains composed of the equal-sized spherical segments with different number of segments, $m_i$; the temperature-independent segment molar volume, $v_i^{00}$; and the temperature-independent segment interaction energy, $u_i^0$. For the associating molecules, considered through the hydrogen bonding, the association energy parameter, $\kappa^{AB}$; and the association volume parameter, $\varepsilon^{AB}$; are used to characterize the association bounds between sites *A* and *B*. The value of these parameters can be obtained from the works of Huang and Radosz. The SAFT model is generally expressed in term of the molar Helmholtz free energy, *a*; as following expression

$$a \quad = \quad a^{id} + a^{hs} + a^{disp} + a^{chain} + a^{assoc} \tag{3.77}$$

where, the superscripts *id*, *hs*, *disp*, *chain*, and *assoc* represent the contributions of ideal, hard spheres, dispersion, chain, and association, respectively.

### The ideal molar Helmholtz free energy term

The ideal contribution is based on the molecular thermodynamics as expressed by Silbey and Alberty, 2001 and is given by

$$\frac{a^{id}}{RT} = \sum_{i=1}^{N} x_i \ln(N_A \rho_i \Lambda_i^3) - 1 \tag{3.78}$$

for pure components

$$\frac{a^{id}}{RT} = \ln(N_A \rho \Lambda^3) - 1 \tag{3.79}$$

where, $\Lambda_i$ is the de Broglie wavelength of each species *i* in the mixture at temperature, *T*; of the system, and determined from

$$\Lambda_i = \left[\frac{1}{2\pi}\left(\frac{h^2}{M_i k_B T}\right)\right]^{1/2} \tag{3.80}$$

here, $\rho_i$ is the component density of mixture and equal to $x_i\rho$; where, $x_i$ is the mole fraction of component *i* in the mixture, $\rho$ is the molar density. *N* is the number of components in the mixture. $N_A$ is the Avogadro's number. $M_i$ is the molecular mass of each conponent *i* in the mixture. *h*, *R*, and $k_B$ are the Plank's constant, Gas constant and Boltzmann's constant, respectively.

### The hard-sphere molar Helmholtz free energy term

The hard-sphere contribution for a mixture of hard spheres used by Huang and Radosz is expressed as fallow

$$\frac{a^{hs}}{RT} = \frac{6}{\pi N_A \rho}\left[\frac{(\zeta_2)^3 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2(\zeta_3)^2}{\zeta_3(1-\zeta_3)^2} - \left(\zeta_0 - \frac{(\zeta_2)^3}{(\zeta_3)^2}\right)\ln(1-\zeta_3)\right] \qquad (3.81)$$

where $\zeta$ is a function of the molar density, which is given by

$$\zeta_j = \frac{\pi N_A \rho}{6}\sum_{i=1}^{N} x_i m_i d_{ii}^{j} \qquad j = 0,\ldots,3 \qquad (3.82)$$

where, $d_{ii}$ is the temperature-dependent segment diameter of component $i$, this term is determined from

$$d_{ii} = \sigma_{ii}\left[1 - C\exp\left(\frac{-3u_i^0}{k_B T}\right)\right] \qquad (3.83)$$

and $\sigma_{ii}$ is the temperature-independent segment diameter of component $i$, which is determined from

$$\sigma_{ii} = \left(v_i^{00}\frac{6\tau}{\pi N_A}\right)^{1/3} \qquad (3.84)$$

where, $C$ and $\tau$ are equal to 0.12, $\pi\sqrt{2}/6$ respectively. For pure component, the hard-sphere term in equation (3.69) reduced to

$$\frac{a^{hs}}{RT} = m\frac{a_0^{hs}}{RT} \qquad (3.73)$$

where, $a_0^{hs}$ is the hard-sphere Helmholtz free energy per mole of segments, and

$$\frac{a_0^{hs}}{RT} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \qquad (3.85)$$

with a segment packing fraction (pure components)

$$\eta = \frac{\pi N_A \rho}{6} m d^3 \tag{3.86}$$

**The dispersion molar Helmholtz free energy term**

The dispersion contribution used by Huang and Radosz is based on a square-well fluid and expressed as fallow

$$\frac{a^{disp}}{RT} = m\frac{a_0^{disp}}{RT} = m\sum_{i=1}^{4}\sum_{j=1}^{9} D_{ij}\left(\frac{u}{k_B T}\right)^i \left(\frac{\eta}{\tau}\right)^j \tag{3.87}$$

where, $a_0^{disp}$ is the dispersion Helmholtz free energy per mole of segments. $D_{ij}$ are the universal constant. $\eta$ is the average reduced density (segment packing fraction), given by

$$\eta = \zeta_3 = \frac{\pi N_A \rho}{6}\sum_{i=1}^{N} x_i m_i d_{ii}^3 \tag{3.88}$$

There are two approaches to determine the average segment number, *m*; average segment energy, *u*; in mixtures, namely, the van der Waals one-parameter (vdW1) mixing rule

$$m = \sum_{i=1}^{N} x_i m_i \tag{3.89}$$

and

$$\frac{u}{k_B T} = \frac{\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j m_i m_j v_{ij}^0 \left(\frac{u_{ij}}{kT}\right)}{\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j m_i m_j v_{ij}^0} \tag{3.90}$$

$$v_{ij}^{0} = \left\{\frac{1}{2}\left[(v_{ii}^{0})^{1/3} + (v_{jj}^{0})^{1/3}\right]\right\}^{3} \tag{3.91}$$

$$u_{ij} = (1 - k_{ij})(u_{ii}u_{jj})^{1/2} \tag{3.92}$$

where

$$v_{ii}^{0} = v_{i}^{00}\left[1 - c\exp\left(\frac{-3u_{i}^{0}}{k_{B}T}\right)\right]^{3} \tag{3.93}$$

$$u_{ii} = u_{i}^{0}\left(1 + \frac{e}{k_{B}T}\right) \tag{3.94}$$

and the volume fraction (vf) mixing rule

$$m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j m_{ij} \tag{3.95}$$

$$m_{ij} = \frac{1}{2}(m_i + m_j)(1 - l_{ij}) \tag{3.96}$$

and

$$\frac{u}{k_B T} = \sum_{i=1}^{N}\sum_{j=1}^{N} f_i f_j \left[\frac{u_{ij}}{k_B T}\right] \tag{3.97}$$

$$f_i = \frac{x_i (m_i v_{ii}^{0})^{\gamma}}{\sum_{j=1}^{N} x_j (m_j v_{jj}^{0})^{\gamma}} \tag{3.98}$$

where, $u_{ij}$, $v_{ii}^{0}$, and $u_{ii}$ for this mixing rule are obtained from equation (3.81), (3.82), and (3.83) respectively.

**Table 3.4** The universal constant used in equation (3.87)

| | $i = 1$ | $i = 2$ | $i = 3$ | $i = 4$ |
|---|---|---|---|---|
| $j = 1$ | -8.8043 | 2.9396 | -2.8225 | 0.34 |
| $j = 2$ | 4.1646270 | -6.0865383 | 4.7600148 | -3.1875014 |
| $j = 3$ | -48.203555 | 40.137956 | 11.257177 | 12.231796 |
| $j = 4$ | 140.43620 | -76.230797 | -66.382743 | -12.110681 |
| $j = 5$ | -195.23339 | -133.70055 | 69.248785 | 0.0 |
| $j = 6$ | 113.51500 | 860.25349 | 0.0 | 0.0 |
| $j = 7$ | 0.0 | -1535.3224 | 0.0 | 0.0 |
| $j = 8$ | 0.0 | 1221.4261 | 0.0 | 0.0 |
| $j = 9$ | 0.0 | -409.10539 | 0.0 | 0.0 |

In this article, $l_{ij}$ and $\gamma$ for the vf mixing rule are neglected. The constant $e/k_B$ and the binary parameter $k_{ij}$ can be investigated from Huang and Radosz. It should be note that the average segment number in the vdW1 mixing rule sometime can be replaced by the expression of equation (3.84) and (3.85) with neglect the adjustable parameter $l_{ij}$.

### The chain molar Helmholtz free energy term

The chain term, the Helmholtz free energy increment due to the presence of covalent chain-forming bonds among the segments, can be determine from

$$\frac{a^{chain}}{RT} = \sum_{i=1}^{N} x_i(1-m_i)\ln(g_{ii}(d_{ii})^{hs}) \tag{3.99}$$

where, the pair correlation function for a mixture of hard spheres, $g_{ii}(d_{ii})^{hs}$; is given by

$$g_{ii}(d_{ii})^{hs} = \frac{1}{1-\zeta_3} + 3\frac{d_{ii}}{2}\frac{\zeta_2}{(1-\zeta_3)^2} + 2\left(\frac{d_{ii}}{2}\right)^2\frac{(\zeta_2)^2}{(1-\zeta_3)^3} \tag{3.100}$$

the more general pair correlation function, this term is expressed as fallow

$$g_{ij}(d_{ij})^{hs} = \frac{1}{1-\zeta_3} + \frac{3d_{ii}d_{jj}}{d_{ii}+d_{jj}}\frac{\zeta_2}{(1-\zeta_3)^2} + 2\left(\frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}}\right)^2\frac{(\zeta_2)^2}{(1-\zeta_3)^3} \qquad (3.101)$$

In addition, the pair correlation function for a mixture of hard spheres given by equation (3.89) and (3.90) can be used to approximate the pair correlation function for a mixture of hard segments, so, $g_{ij}(d_{ij})^{seg} \approx g_{ij}(d_{ij})^{hs}$; which is used to evaluate the association strength, $\Delta^{A_iB_j}$ ; for expression of the association contribution term.

**The association molar Helmholtz free energy term**

The association term is considered when the mixtures contain associating molecules, considered through the hydrogen bonding. This term is given by

$$\frac{a^{assoc}}{RT} = \sum_{i=1}^{N} x_i\left[\sum_{A_i=1}^{S_i}\left[\ln X^{A_i} - \frac{X^{A_i}}{2}\right] + \frac{S_i}{2}\right] \qquad (3.102)$$

here, $S_i$ is the number of association site of each species $i$; $X^{A_i}$ is the mole fraction of component $i$ not bonded at site $A$; $\sum_{A_i}$ is summation over all site on molecules $i$; and

$$X^{A_i} = \frac{1}{1 + N_A\sum_{j=1}^{N}\sum_{B_j=1}^{S_j}\rho_j X^{B_j}\Delta^{A_iB_j}} \qquad (3.103)$$

and the association strength, $\Delta^{A_iB_j}$

$$\Delta^{A_iB_j} = g_{ij}^{seg}(d_{ij})\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{k_BT}\right) - 1\right]\sigma_{ij}^3\kappa^{A_iB_j} \qquad (3.104)$$

where

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{3.106}$$

### 3.2.2 The Proposed Model for the Gibbs Free Energy Minimization

At constant temperature, *T*; and pressure, *P*; the condition of the thermodynamic equilibrium in any systems is the total Gibbs energy of the system, *G*; must be reach the global minimum. So that, the objective function of this problem is to find the amount of the components and the densities of each phase that minimize

$$\frac{G}{RT} = \sum_{k=1}^{\pi} \sum_{i=1}^{N} n_{ik} \left( \frac{a_k}{RT} + z_k \right) \tag{3.107}$$

The thermodynamic model constraint is expressed as

$$\frac{P}{\rho_k RT} = z_k \tag{3.108}$$

when the systems do not including any chemical reaction, the material balance constraint is

$$n_{iT} = \sum_{k=1}^{\pi} n_{ik} \tag{3.109}$$

and the boundaries constraint

$$0 \leq \rho_k \tag{3.110}$$

$$0 \leq n_{ik} \leq n_{iT} \tag{3.111}$$

where, $k$ is the desired number of phase of the system at equilibrium, $n_{iT}$ is the amount of component $i$ at feed, $n_{ik}$ is the amount of component $i$ in phase $k$ at equilibrium, and $z_k$ is the compressibility factor of each phase, which is determined from

$$z \quad = \quad \rho \left. \frac{\partial \left( a/_{RT} \right)}{\partial \rho} \right|_{x_{ik},T} \qquad (3.112)$$

here, $a_k$ and $z_k$ are determine from using the amounts of components and the density of phase $k$. When the association effect is taken into account, the internal problems for evaluation of $X^{A_i}$ must be solved for equation (3.91). Hence, the equation (3.92) can rewritten as

$$f_{A_i} \quad = \quad X^{A_i} + N_A \sum_{j=1}^{N} \sum_{B_j=1}^{S_j} (\rho_j X^{A_i} X^{B_j} \Delta^{A_i B_j}) - 1 \qquad (3.113)$$

which has the Jacobian elements

$$\frac{\partial f_{A_i}}{\partial X^{A_i}} \quad = \quad 1 + N_A \sum_{j=1}^{N} \sum_{B_j=1}^{S_j} (\rho_j X^{B_j} \Delta^{A_i B_j}) + N_A \rho_i X^{A_i} \Delta^{A_i A_i} \qquad (3.114)$$

$$\frac{\partial f_{A_i}}{\partial X^{B_j}} \quad = \quad N_A \rho_j X^{A_i} \Delta^{A_i B_j} \qquad (3.115)$$

to evaluate the compressibility factor, it needs not only solving for the $X^{A_i}$ but also the derivatives of the $X^{A_i}$ with respect to the density of each phase. From the differentiation of equation (3.92)

$$\frac{\partial X^{A_i}}{\partial \rho} = \begin{matrix} -N_A (X^{A_i})^2 \left\{ \sum_{j=1}^{N} \sum_{B_j=1}^{S_j} x_j X^{B_j} \Delta^{A_i B_j} + \right. \\ \left. \sum_{j=1}^{N} \sum_{B_j=1}^{S_j} (\rho_j \Delta^{A_i B_j} \frac{\partial X^{B_j}}{\partial \rho}) + \sum_{j=1}^{N} \sum_{B_j=1}^{S_j} (\rho_j X^{B_j} \frac{\partial \Delta^{A_i B_j}}{\partial \rho}) \right\} \end{matrix} \qquad (3.116)$$

where

$$\frac{\partial \Delta^{A_i B_j}}{\partial \rho} = \frac{\partial (g_{ij}^{hs}(d_{ij}))}{\partial \rho} \left[ \exp\left( \varepsilon^{A_i B_j} \middle/ k_B T \right) - 1 \right] \sigma_{ij}^3 \kappa^{A_i B_j} \qquad (3.117)$$

and

$$\begin{aligned} \frac{\partial (g_{ij}^{hs}(d_{ij}))}{\partial \rho} = \; & \frac{1}{\rho} \left\{ \frac{\zeta_3}{(1-\zeta_3)^2} + \right. \\ & \frac{3 d_{ii} d_{jj}}{d_{ii} + d_{jj}} \left[ \frac{\zeta_2}{(1-\zeta_3)^2} + \frac{2\zeta_2 \zeta_3}{(1-\zeta_3)^3} \right] + \\ & \left. 2 \left[ \frac{d_{ii} d_{jj}}{d_{ii} + d_{jj}} \right]^2 \left[ \frac{2(\zeta_2)^2}{(1-\zeta_3)^3} + \frac{3\zeta_3 (\zeta_2)^2}{(1-\zeta_3)^4} \right] \right\} \end{aligned} \qquad (3.118)$$

the equation (3.102) can be solved with the linear system of equations, that is

$$\mathbf{Q}\mathbf{y} = \mathbf{c} \qquad (3.119)$$

here, **y** is the $N_s \times 1$ vector comprising the derivatives of the $X^{A_i}$ ,where

$$N_s = \sum_{i=1}^{N} S_i \qquad (3.120)$$

**Q** is an $N_s \times N_s$ matrix with coefficients

$$q_{ii} = 1 + N_A (X^{A_i})^2 \rho_i \Delta^{A_i A_i} \qquad (3.121)$$

$$q_{ij} = N_A (X^{A_i})^2 \rho_j \Delta^{A_i B_j} \qquad (3.122)$$

and **c** is an $N_s \times 1$ vector with elements are given by

$$c^{A_i} = \begin{array}{l} -N_A(X^{A_i})^2\left\{\sum_{j=1}^{N}\sum_{B_j=1}^{S_j} x_j X^{B_j}\Delta^{A_iB_j} + \right. \\ \left. \sum_{j=1}^{N}\sum_{B_j=1}^{S_j}(\rho_j X^{B_j}\ \frac{\partial\Delta^{A_iB_j}}{\partial\rho})\right\} \end{array} \qquad (3.123)$$

noting that, the $X^{A_i}$ for equation (3.100) is bracketed by $X^{A_i}$ = 0 and $X^{A_i}$ = 1 for all association sites. thus, to obtain phase compositions at equilibrium it is necessary to find the minimum of the Gibbs free energy as given by equation (3.95) subject to the constraints imposed by equation (3.96a), (3.96b) and equation (3.97a), (3.97b) with internal problems by equation (3.100) and (3.102).

# CHAPTER IV

# HYBRID DIFFERENTIAL EVOLUTION WITH THE GRADIENT-BASED ALGORITHM

## 4.1 Differential Evolutionary Algorithm

Many chemical engineering designs, control, process simulation or other engineering problems usually result in solution of optimization problems. Different classes of search techniques like gradient-based techniques, random search techniques or stochastic-based techniques are developed to deal with the optimization. Recently, many researchers have reported that evolutionary programming namely Differential Evolution (DE) is successfully used for solution of the optimization problems (Munawar and Babu, 2000; Angira and Babu, 2001). The algorithm is stochastic techniques whose search methods model a natural evolution. That is why the terminology used in DE is taken from biology, which is listed in Table 4.1

**Table 4.1** Differential evolution terminology

| Evolutionary terminology | Mathematical programming equivalent |
|---|---|
| Chromosome or genotype or individual | Vector of decision variables |
| Population | Set of vectors of decision variables |
| Generation | Iteration |
| Fitness or phenotype | Evaluated objective function at iteration |
| Mutation | Perform perturbation vector (referred to DE strategies) for each individual |
| Crossover | Recombination between individual and its perturbation vector to produce its trial vector |
| Selection | Choose a new individual from better fitness of the former individual and its candidate (trial vector) |

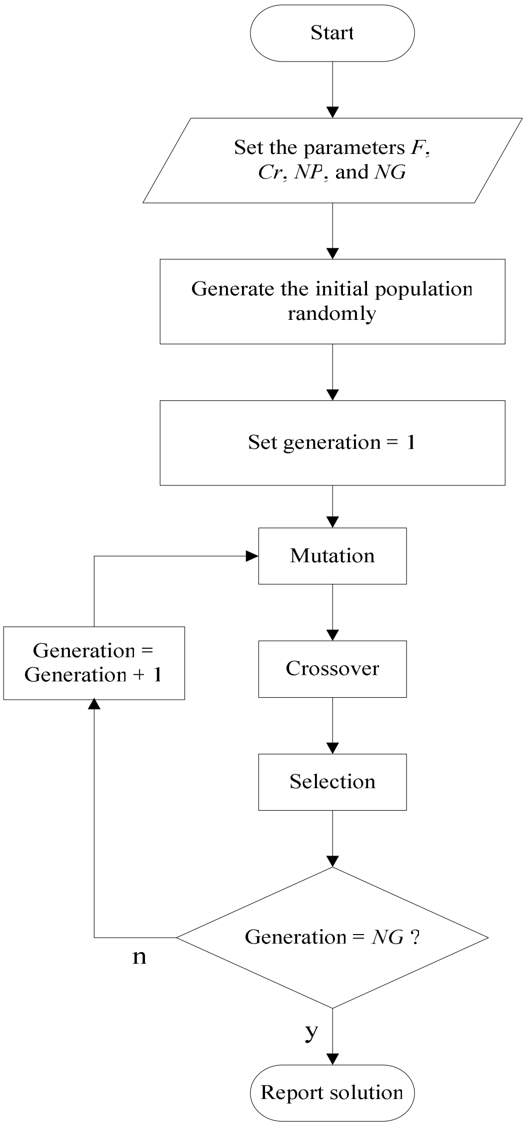

**Figure 4.1** Flow chart of Differential Evolution

DE start with randomly create a population from the search space. The population evolves towards the better chromosomes (obtained solution) by applying special operators modeling the evolution processes occurring in the nature, as follow mutation, recombination or crossover, and selection. Following Fig. 4.2, the algorithm starts with specifying the parameters, namely, amplification factor (*F*), crossover constant (*Cr*), type of strategy, population size (*NP*), and maximum number of generations (*NG*). The three main steps: mutation, crossover, and selection on the population, are carried out. Mutation and crossover operations are performed to diversity the search thus escaping from the local minima. The DE scheme entirely corresponds to a typical Evolutionary Algorithms (EAs). It is close to Genetic Algorithm (GA). The principle difference consists in the mutation operation. In GA, mutation is provided by arithmetical combinations of individuals. The core of this operation is the formation of a difference vector which makes mutate an individual. For DE, the mutation operation is denoted by differentiation.

### Initialization

All variants of Differential Evolution start with initialization of the first generation. The initial populations are created randomly by the algorithm (Fig. 4.2).

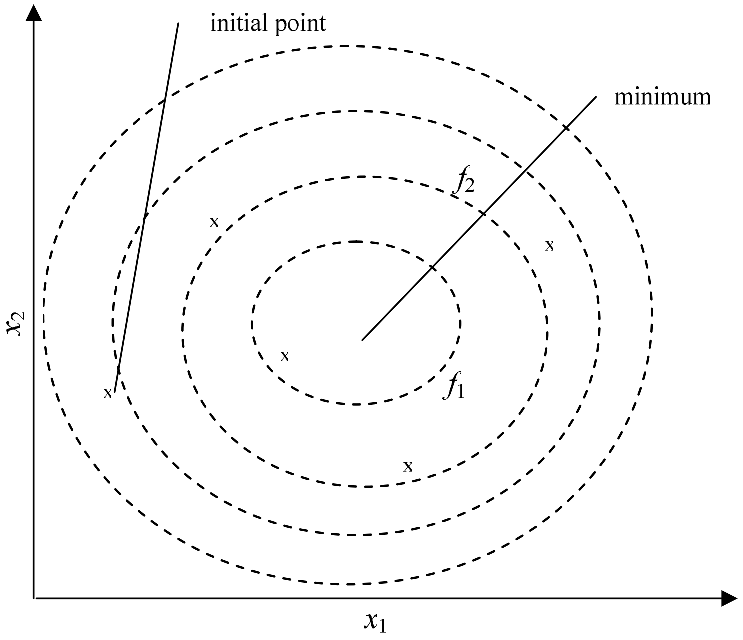

**Figure 4.2** An example of a two-dimensional objective function showing its contour line and the process for generating initial point

Then, for each generation, the individuals for each population are update by reproduction scheme. That consists with the mutation, crossover, and selection operation. To produce a new one, the operation of mutation and crossover are applied one after another. Next the selection operation is used for choose the best from candidate solution.

**Mutation**

For each obtained vector, $\bar{x}_j \quad ; j = 1,2,...,NP$ where *N* is a number of dimension and *NP* is a number of population, a mutant vector is generate according to DE with strategy 7

$$\bar{v}_j \quad = \quad \bar{x}_{r_1} + F \cdot (\bar{x}_{r_2} - \bar{x}_{r_3}) \tag{4.1}$$

where random index $r_1, r_2, r_3 \quad \in \quad \{1,2,...,NP\}$ are not equal to index *j*. *F* is a real and constant factor $\in \quad [0,1]$ which controls the amplification of the differential variation $(\bar{x}_{r_2} - \bar{x}_{r_3})$.

**Crossover**

In order to increase the diversity of the perturbed parameters vectors, crossover is introduced. From the end of mutation, the obtained mutation vector is

$$v_{ij} \quad = \quad (v_{1j}, v_{2j}, ..., v_{Nj}) \tag{4.2}$$

at the end of this operation, the trial vector is formed

$$u_{ij} \quad = \quad \begin{cases} v_{ij} & if\,(rand(i) \leq Cr) \\ x_{ij} & if\,(rand(i) > Cr) \end{cases} \qquad ; i = 1,2,...,N \tag{4.3}$$

in (4.3), *rand(i)* is the *i* th evaluation of random number generator with outcome $\in \quad [0,1]$. *Cr* is the crossover constant $\in \quad [0,1]$ which has to determine by the user. Fig. 4.4 gives example of the crossover mechanism for 10-dimensinal vectors.

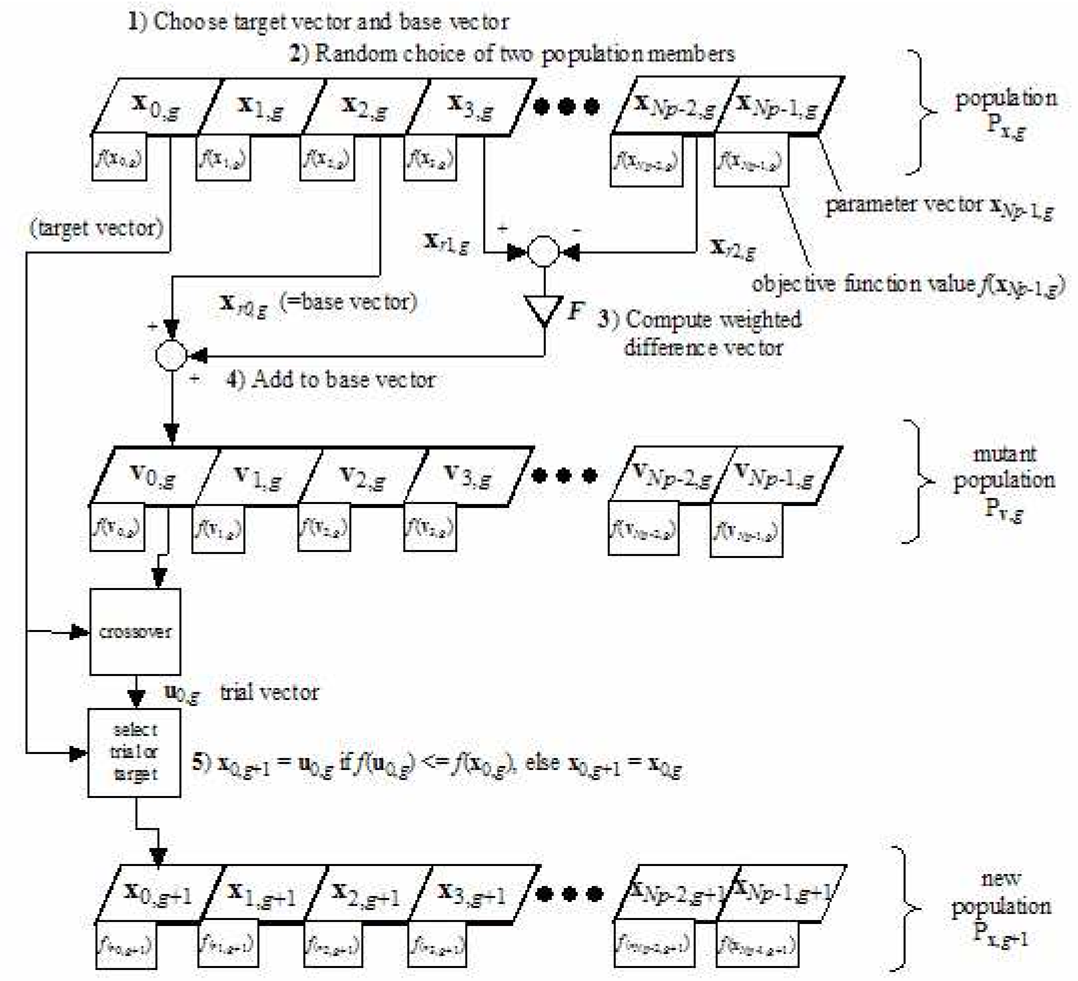

**Figure 4.3** DE flow (http://www.icsi.berkeley.edu/~storn/code.html#csou)

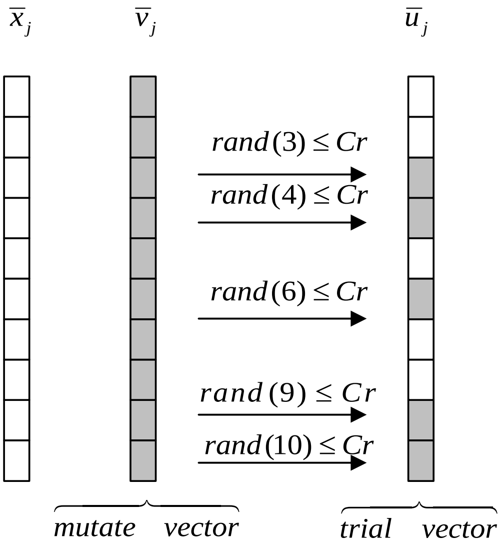

**Figure 4.4** Illustration of the crossover process for 10-dimentional vector

### Selection

To decide whether or not it should become a member of generation $j + 1$, the trial vector $\bar{u}_j$ is compared to the target vector $\bar{x}_j$. If vector $\bar{u}_j$ yield better optimum value than $\bar{x}_j$, then $\bar{x}_j$ set to $\bar{u}_j$, otherwise, $\bar{x}_j$ is retained.

### The strategies in Differential Evolution

In 1997, Price & Storn gave the working principle of DE with single strategy. Later on, they suggested ten different strategies of DE. The general conversion used is *DE/x/y/z*. *DE* stands for Differential Evolution, *x* represents a individual denoting the vector to be perturbed, *y* is the number of difference vectors considered for perturbation of *x*, and *z* stands for the type of crossover being used.

The following are the ten different working strategies proposed by Price & Storn (*exp* stands for exponential crossover, while *bin* stands for binomial crossover).

1. DE/best/1/exp
2. DE/rand/1/exp
3. DE/rand-to-best/1/exp
4. DE/best/2/exp
5. DE/rand/2/exp
6. DE/best/1/bin
7. DE/rand/1/bin
8. DE/rand-to-best/1/bin
9. DE/best/2/bin
10. DE/rand/2/bin

There are described as follows, the best/1 scheme

$$\bar{v}_j \quad = \quad \bar{x}_{best} + F \cdot (\bar{x}_{r_1} - \bar{x}_{r_2}) \tag{4.4}$$

the rand/1 scheme, from equation (4.1)

$$\bar{v}_j \quad = \quad \bar{x}_{r_1} + F \cdot (\bar{x}_{r_2} - \bar{x}_{r_3})$$

the rand-to-best scheme

$$\bar{v}_j \quad = \quad \bar{x}_{indiv} + F \cdot (\bar{x}_{best} - \bar{x}_{indiv}) + F \cdot (\bar{x}_{r_1} - \bar{x}_{r_2}) \tag{4.5}$$

the best/2 scheme

$$\bar{v}_j \quad = \quad \bar{x}_{best} + F \cdot (\bar{x}_{r_1} - \bar{x}_{r_2} + \bar{x}_{r_3} - \bar{x}_{r_4}) \tag{4.6}$$

and the rand/2 scheme

$$\bar{v}_j \quad = \quad \bar{x}_{r_1} + F \cdot (\bar{x}_{r_2} - \bar{x}_{r_3} + \bar{x}_{r_4} - \bar{x}_{r_5}) \tag{4.7}$$

where, *indiv* represents a vector individual *j*; *best* represents individual that has the best objective value in current generation, and $r_1, r_2, r_3, r_4, r_5 \quad \in \quad \{1,2,..., NP\}$ are not equal to *indiv* and *best*.

**The pseudo code for DE/x/y/exp**

The pseudo code for exponential crossover scheme of Differential Evolution is given below

```
(1)  random number of dimension, $i \quad = \quad 1,2,...,N$ ; and set $l$ = 1

(2)  do $u_i \quad = \quad v_i$ (any x/y scheme)
(3)  set $l$ = $l$ + 1, and set $i$ = ($i$ + 1) % $N$

(4)  if random number $\in \quad [0,1] \quad \leq \quad Cr$ and $l \leq N$ do goto (2) else end
```

**The pseudo code for DE/x/y/bin**

The pseudo code for binomial crossover scheme of Differential Evolution is given below

```
(1)  random number of dimension, $i \quad = \quad 1,2,...,N$ , and set $l$ = 1

(2)  if random number $\in \quad [0,1] \quad \leq \quad Cr$ or $l = N$ do $u_i \quad = \quad v_i$
     (any x/y scheme), and then goto (3)
```

(3) if $l < N$ do set $i = (i + 1)\ \%\ N$; set $l = l + 1$; and then goto (2) else end

## 4.2 Typical Constraint Handling Techniques in Evolutionary Algorithms

One of the major problems of any evolutionary computations is the evaluation function. The evaluation of function is used to assign a quality for each individual in a population. Generally, a search space usually consists with feasible and unfeasible subspace. Therefore, it is necessary to assume that the unfeasible solutions have no more quality than the feasible solutions in each generation, although some infeasible solutions have better objective value after evaluation operation.

From Fig. 4.4, shade areas are the feasible region, while bright area represents the infeasible region. Based on Fig. 4.4, the population contain some feasible (*a*, *b*, *c*, *x*) and infeasible individual (*d*, *y*), *x* is the optimum solution of the objective function with constraints, while *y* is the optimum solution when the objective function is without any constraints. The problem of this optimization is how to obtain the feasible optimum solution. For example, assume that

$$evaluate_f(s) \succ evaluate_u(p) \tag{4.8}$$

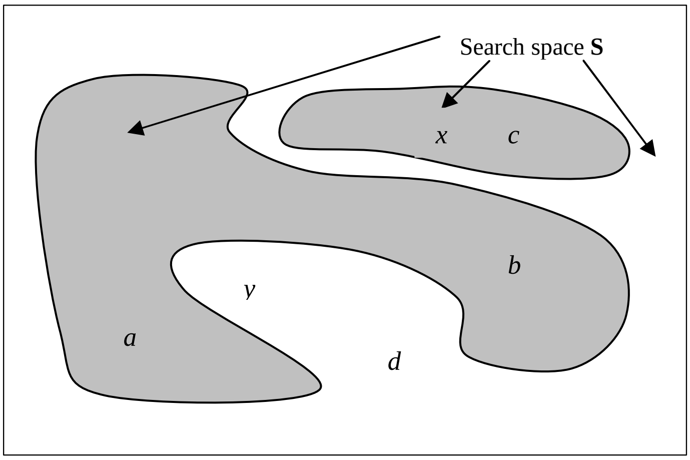

**Figure 4.5** A general search space

for $\forall s \in feasible\,set$, and $\forall p \in infeasible\,set$. Later on, these approaches were developed to the penalty function approach for penalize infeasible individuals. In general, constraint handling scheme in DE or other evolutionary computations usually implemented before the selection process (Fig. 4.5).

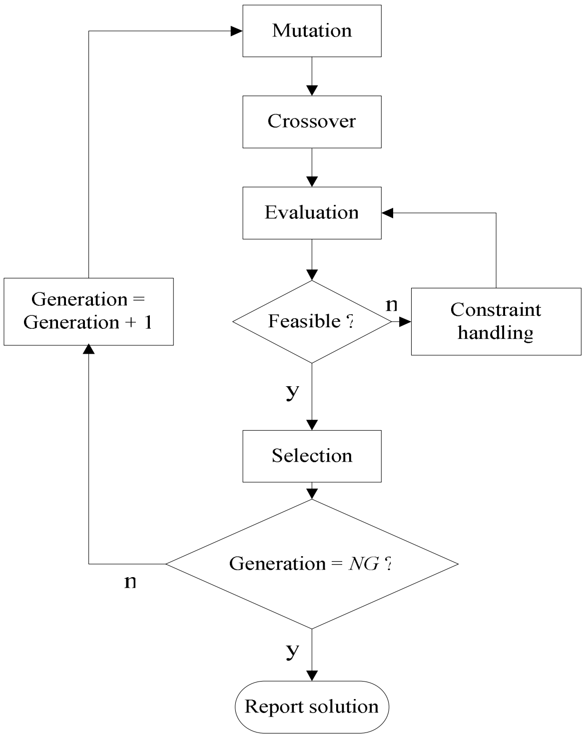

**Figure 4.6** A constraint handling scheme in Differential Evolution

In most applications of DE and other EAs to constrained optimization problems, the penalty function method has been used. In the penalty function method for handling inequality constraints in minimization problems, the fitness function $F(\bar{x})$ is defined as the sum of the objective function $f(\bar{x})$ and a penalty term which depends on the constraint violation, consider a general constrained optimization, as follows

$$\text{Optimize} \quad f(\bar{x})$$

$$\text{Subject to} \quad l_m \leq g_m(\bar{x}) \leq u_m \qquad m = 1,2,...,M \tag{4.9}$$

$$h_n(\bar{x}) = c_n \qquad n = 1,2,...,N$$

where $\bar{x}$ represents the solution vector, $f(\bar{x})$ is the objective function of the problem, while $g_m(\bar{x})$ and $h_n(\bar{x})$ are the inequality and equality constraints, respectively, that define the feasible region. In the application of DE and other EAs to any constrained optimization problems, handling the constraints is one of the difficult tasks. The penalty method is perhaps the most commonly used technique. It basically transforms the constrained problem to an unconstrained one by augmenting the constraints to the objective function as a penalty term. When the solution is infeasible, its objective value is penalized according to the degree of constraint violations. Generally, the penalized objective value is computed using the expression

$$F(\bar{x}) \quad = \quad f(\bar{x}) + p(\bar{x}) \tag{4.10}$$

where $p(\bar{x})$ is the penalty function representing the degree of constraint violation computed as

$$\begin{aligned} p(\bar{x}) \quad = \quad & \sum_{m=1}^{M} w_m^u \cdot Max\{0.0, g_m(\bar{x}) - u_m\} + \sum_{m=1}^{M} w_m^u \cdot Min\{0.0, g_m(\bar{x}) - u_m\} \\ & + \sum_{n=1}^{N} w_n \cdot \left| h_n(\bar{x}) - c_n \right| \end{aligned} \tag{4.11}$$

where $w_m^u$ and $w_m^l$ are the penalty values of the upper and lower bounds of the inequality constraints, and $w_n$ are the penalty values for the equality constraints. For minimization problems, if the solution is infeasible, the objective value is increased by the penalty term. For maximization problems, the penalty term is used to decrease the objective value. In other words, a highly infeasible solution would be penalized and would rarely be selected by the reproduction scheme.

The major concern of this method is how to choose a proper penalty value (*w*) for each constraint so as to efficiently guide the search toward a promising area of the search space. A large penalty value will lead to premature convergence (i.e., trade off too much optimality for feasibility), while a small penalty will not only increase computational time, but also admit too many infeasible solutions (i.e., not enough pressure given to the penalty term to maintain feasibility).

### 4.3 The Proposed Hybrid Algorithm

This constraint handling technique is proposed by Chootinan and Chen in 2006 for repair infeasible individuals in Genetic Algorithm (GA). The main idea of the technique is to utilize the gradient information derived from the constraint set to systematically repair the infeasible solutions. Basically, the gradient information is used to direct the infeasible solutions toward the feasible region. Let $\overline{V}$ consist of vectors of inequality constraints $\overline{g}$ and equality constraints $\overline{h}$

$$\overline{V} = \begin{bmatrix} \overline{g}_{M\times 1} \\ \overline{h}_{N\times 1} \end{bmatrix}_{(M+N)\times 1} \tag{4.12}$$

the derivatives of these constraints with respect to the solution vector,

$$\nabla_x \overline{V} = \begin{bmatrix} \nabla_x \overline{g}_{M\times 1} \\ \nabla_x \overline{h}_{N\times 1} \end{bmatrix}_{(M+N)\times 1} \tag{4.13}$$

therefore, the relationship between changes of constrains with respect to the solution vector, can be evaluated by,

$$\nabla_x \overline{V} \times \Delta\overline{x} = \Delta\overline{V} \quad \Rightarrow \quad \Delta\overline{x} = \nabla_x \overline{V}^{+} \times \Delta\overline{V} \tag{4.14}$$

where $\Delta\overline{V}$ is the degree of constraints violation, and can be evaluate by

$$\Delta\overline{V} = \begin{bmatrix} Min\{0.0, u_m - g_m\} + Max\{0.0, l_m - g_m\} \\ h_n - c_n \end{bmatrix} \tag{4.15}$$

The repair procedure (Chootinan, and Chen, 2006), set the repair rate ($P_r$). It is similar to the probability of mutation ($P_m$). If it is impossible to make the infeasible solution feasible, a very high penalty is applied.

To evaluate the pseudo inverse, in mathematics and in particular linear algebra, the pseudo inverse $A^+$ of a $m \times n$ matrix $A$ is a generalization of the inverse matrix. More precisely, this article talks about the Moore-Penrose pseudo inverse, which was independently described by E. H. Moore in 1920 and Roger Penrose in 1955. Earlier, Fredholm had introduced the concept of a pseudo inverse of integral operators in 1903. The term generalized inverse is sometimes used as a synonym for pseudo inverse. If the columns of $A$ are linearly independent, then $A^TA$ is invertible. In this case, an explicit formula is

$$A^+ \quad = \quad (A^T A)^{-1} A^T \tag{4.16}$$

if the rows of $A$ are linearly independent, then $AA^T$ is invertible. In this case, an explicit formula is,

$$A^+ \quad = \quad A^T (AA^T)^{-1} \tag{4.17}$$

if both columns and rows are linearly independent (that is, for square nonsingular matrices), the pseudo inverse is just the inverse:

$$A^+ \quad = \quad A^{-1} \tag{4.18}$$

The pseudo code for gradient-based repair algorithm can be summarized, as follow

**Step 1**

For any solution, determine the degree of constraint violation, equation (4.15), If the solution is infeasible, generate a random number $\gamma$ from the interval $[0,1]$. If $\gamma \quad \leq \quad P_r$ , set $t$ = 1 and go to step 2, otherwise return.

**Step 2**

Compute $\nabla \overline{V}^+$ and $\Delta \overline{x}$. Note that only non-zero element of $\Delta \overline{V}$ are included for further computations of $\nabla \overline{V}^+$ and $\Delta \overline{x}$.

**Step 3**

Update the solution vector by $\overline{x}^{t+1} \quad = \quad \overline{x}^{t} + \nabla\overline{V}^{+} \times \Delta\overline{V}$ .

**Step 4**

Evaluate the updated solution vector. If $Max_{\forall i}\left|x_i^{t+1} - x_i^{t}\right| \quad \geq \quad \eta$ and solution is still infeasible, set $t$ = $t$ +1 and go to step 2, otherwise return. $\eta$ is the minimum adjustment for the solution vector (e.g. $10^{-4}$).

### 4.4 Test Problems Benchmark

Phase equilibrium examples considered in this study include vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE), vapor-liquid-liquid equilibrium (VLLE) and gas-solid equilibrium examples involving multiple components and popular thermodynamic models. Five typical examples were taken from the dissertation for evaluating the developed DE, original DE using the values of parameters found from the preliminary tests. All programs used in this study, were implemented in C programming language and compiled with Cygwin.

### 4.3.1 *n*-Butyl Acetate and Water Mixture

**Table 4.2** Results for *n*-Butyl Acetate and Water Mixture at 298 K, 1.0 atm

| Quantities | DE with Gradient-Based | | DE | | McDonald and Floudas, 1995 | |
|---|---|---|---|---|---|---|
| | Liquid I | Liquid II | Liquid I | Liquid II | Liquid I | Liquid II |
| $C_6H_{12}O_2$ | 0.00016 | 0.49984 | 0.25584 | 0.24416 | 0.00016 | 0.49984 |
| $H_2O$ | 0.45486 | 0.04514 | 0.34522 | 0.15478 | 0.45486 | 0.04514 |
| $\varphi$ | 0.45502 | 0.54498 | 0.60106 | 0.39894 | 0.45502 | 0.54498 |
| $F$ (mol$^{-1}$) | -0.03407 | | 0.15327 | | -0.3407 | |
| *NFE* | 25796 | | 40278 | | Not report | |
| *CV* | $10^{-15}$ | | $9.32 \times 10^{-9}$ | | Not report | |

### 4.3.2 Benzene-Acetonitrile-Water Mixture

**Table 4.3** Results for Benzene-Acetonitrile-Water Mixture at 333 K, 0.769 atm

| Quantities | DE with Gradient-Based | | | DE | | | McDonald and Floudas, 1995 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Vapor | Liquid I | Liquid II | Vapor | Liquid I | Liquid II | Vapor | Liquid I | Liquid II |
| $C_6H_6$ | 0.07993 | 0.00075 | 0.26415 | 0.06709 | 0.21815 | 0.05959 | 0.10464 | 0.00073 | 0.23946 |
| $CH_3N$ | 0.04630 | 0.02217 | 0.24187 | 0.05434 | 0.19023 | 0.06636 | 0.06163 | 0.02169 | 0.22701 |
| $H_2O$ | 0.03995 | 0.27383 | 0.03465 | 0.12266 | 0.05008 | 0.17546 | 0.05242 | 0.26235 | 0.03365 |
| $\varphi$ | 0.16618 | 0.29675 | 0.54067 | 0.24409 | 0.45846 | 0.30141 | 0.21869 | 0.28477 | 0.50012 |
| $F$ (mol$^{-1}$) | | -1.40964 | | | -1.32703 | | | -1.40852 | |
| *NFE* | | 235235 | | | 338871 | | | Not report | |
| *CV* | | $10^{-15}$ | | | 8.2 x $10^{-4}$ | | | Not report | |

### 4.3.3 Esterification of Acetic Acid with Ethanol

**Table 4.4** Results for Esterification of Acetic Acid with Ethanol at 355 K, 1 atm

| Quantities | DE with Gradient-Based | | DE | | McDonald and Floudas, 1995 | |
|---|---|---|---|---|---|---|
| | Vapor | Liquid | Vapor | Liquid | Vapor | Liquid |
| $C_2H_5OH$ | 0.07322 | 0.00472 | 0.22187 | 0.03498 | 0.07463 | 0.00488 |
| $CH_3COOH$ | 0.05840 | 0.01954 | 0.11237 | 0.14279 | 0.05915 | 0.02036 |
| $CH_3COOC_2H_5$ | 0.41326 | 0.00880 | 0.10092 | 0.14279 | 0.40880 | 0.01168 |
| $H_2O$ | 0.34280 | 0.07926 | 0.13645 | 0.10986 | 0.35772 | 0.06278 |
| $\varphi$ | 0.88768 | 0.11232 | 0.57161 | 0.43042 | 0.90030 | 0.09970 |
| $F$ (mol$^{-1}$) | -90.78336 | | -90.48820 | | -90.7816 | |
| *NFE* | 140544 | | 225044 | | Not report | |
| *CV* | $10^{-15}$ | | 6.1 x $10^{-3}$ | | Not report | |

### 4.3.4 Nine Hydrocarbons Mixture

**Table 4.5** Results for Nine Hydrocarbons Mixture at 314 K, 19.84 atm

| Quantities | DE with Gradient-Based | | DE | | Castillo and Grossmann, 1981 | |
|---|---|---|---|---|---|---|
| | Vapor | Liquid | Vapor | Liquid | Vapor | Liquid |
| Methane | 0.57305 | 0.02186 | 0.29769 | 0.29734 | 0.57323 | 0.02167 |
| Ethane | 0.08506 | 0.01434 | 0.06071 | 0.03863 | 0.08510 | 0.01430 |
| Propane | 0.03216 | 0.01614 | 0.02274 | 0.02558 | 0.03220 | 0.01610 |
| *i*-Butane | 0.00417 | 0.00453 | 0.00423 | 0.00453 | 0.00418 | 0.00452 |
| *n*-Butane | 0.00829 | 0.01221 | 0.00849 | 0.01190 | 0.00830 | 0.01220 |
| *i*-Pentane | 0.00161 | 0.00538 | 0.00320 | 0.00384 | 0.00163 | 0.00537 |
| *n*-Pentane | 0.00220 | 0.00930 | 0.00591 | 0.00559 | 0.00216 | 0.00934 |
| *n*-Hexane | 0.00110 | 0.01281 | 0.00783 | 0.00606 | 0.00110 | 0.01280 |
| *i*-Pentadecane | 0.00000 | 0.16469 | 0.07610 | 0.08861 | 0.00000 | 0.16470 |
| $\varphi$ | 0.70764 | 0.26126 | 0.48690 | 0.48208 | 0.70790 | 0.26100 |
| $F$ (mol$^{-1}$) | -3.13406 | | -2.27968 | | Not report | |
| *NFE* | 1495374 | | 2310698 | | Not report | |
| *CV* | $10^{-15}$ | | $4.6 \times 10^{-4}$ | | Not report | |

### 4.3.5 Reduction of ferric oxide

**Table 4.6** Results for Reduction of ferric oxide at 1363 K, 1.0 atm

| Quantities | DE with Gradient-Based | | | | DE | | | | Castillo and Grossmann, 1981 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Vapor | Solid I | Solid II | Solid III | Vapor | Solid I | Solid II | Solid III | Vapor | Solid I | Solid II | Solid III |
| CO | 2.73494 | - | - | - | 0.59074 | - | - | - | 2.73489 | - | - | - |
| $CO_2$ | 0.00604 | - | - | - | 0.23716 | - | - | - | 0.00606 | - | - | - |
| $H_2$ | 0.74702 | - | - | - | 0.41955 | - | - | - | 0.74701 | - | - | - |
| $O_2$ | 0.00000 | - | - | - | 0.67645 | - | - | - | $10^{-10}$ | - | - | - |
| $H_2O$ | 0.00298 | - | - | - | 0.33165 | - | - | - | 0.00299 | - | - | - |
| Fe | - | 1.00000 | - | - | - | 1.0 | - | - | - | 1.0 | - | - |
| FeO | - | - | 0.00000 | - | - | - | 0.00000 | - | - | - | $10^{-10}$ | - |
| C | - | - | - | 0.00902 | - | - | - | 1.91600 | - | - | - | 0.00905 |
| $\varphi$ | 3.49098 | 1.00000 | 0.00000 | 0.00902 | 2.25555 | 1.0 | 0.00000 | 1.91600 | 3.49095 | 1.0 | $10^{-10}$ | 0.00905 |
| $F$ (mol$^{-1}$) | -57.97944 | | | | -28.85774 | | | | Not report | | | |
| *NFE* | 141144 | | | | 225044 | | | | Not report | | | |
| *CV* | $10^{-15}$ | | | | $8.9 \times 10^{-3}$ | | | | Not report | | | |

## 4.4 Test Problems with the Statistical Associating Fluid Theory Model

Three different binary mixtures were used in the dissertation. The first mixture is non-associating system; the next two are 1 site self-associating, and the final one is 2 site self-associating. For all problems, the SAFT parameters used for each component were taken from Huang and Radosz.

Test problem 1 and 2, non-associating System, These system are mixture of ethene (1) and *n*-eicosane (2); and methane (1) and *n*-hexadecane (2). There are no association sites on either molecule, so $a^{\mathrm{assoc}} = 0$ in equation (3.65).

### 4.4.1 Test Problem 1

**Table 4.7** Results for Ethene - *n*-Eicosane Mixture at 423 K, 20 bar

| Quantities | DE with Gradient-Based | | DE | | Xu et al., 2002 | |
|---|---|---|---|---|---|---|
| | Vapor | Liquid | Vapor | Liquid | Vapor | Liquid |
| Ethene | 0.39115 | 0.10885 | 0.32551 | 0.17252 | 0.37995 | 0.11904 |
| *n*-Eicosane | 0.00013 | 0.49987 | 0.46286 | 0.03546 | 0.00005 | 0.50096 |
| $\rho$ (mol/L) | 0.58670 | 2.81560 | 3.54005 | 4.33759 | Not report | Not report |
| $\varphi$ | 0.39128 | 0.60872 | 0.79 | 0.21 | 0.38 | 0.62 |
| $F$ (mol$^{-1}$) | -101.66254 | | -100.97967 | | Not report | |
| *NFE* | 68982 | | 426804 | | Not report | |
| *CV* | $10^{-15}$ | | $8.8 \times 10^{-3}$ | | Not report | |

### 4.4.1 Test Problem 1 (continued)

**Table 4.8** Results for Ethene - *n*-Eicosane Mixture at 423 K, 250 bar

| Quantities | DE with Gradient-Based | | DE | | Xu et al., 2002 | |
|---|---|---|---|---|---|---|
| | Vapor | Liquid | Vapor | Liquid | Vapor | Liquid |
| Ethene | 0.29139 | 0.65861 | 0.46450 | 0.48559 | 0.28908 | 0.66129 |
| *n*-Eicosane | 0.03861 | 0.01139 | 0.02462 | 0.02539 | 0.04092 | 0.00871 |
| $\rho$ (mol/L) | 7.946 | 8.431 | 8.558 | 8.560 | Not report | Not report |
| $\varphi$ | 0.330 | 0.670 | 0.49 | 0.51 | 0.330 | 0.670 |
| $F$ (mol$^{-1}$) | -94.05916 | | -94.06743 | | Not report | |
| *NFE* | 191702 | | 274386 | | Not report | |
| *CV* | $10^{-15}$ | | $2.0 \times 10^{-4}$ | | Not report | |

### 4.4.2 Test Problem 2

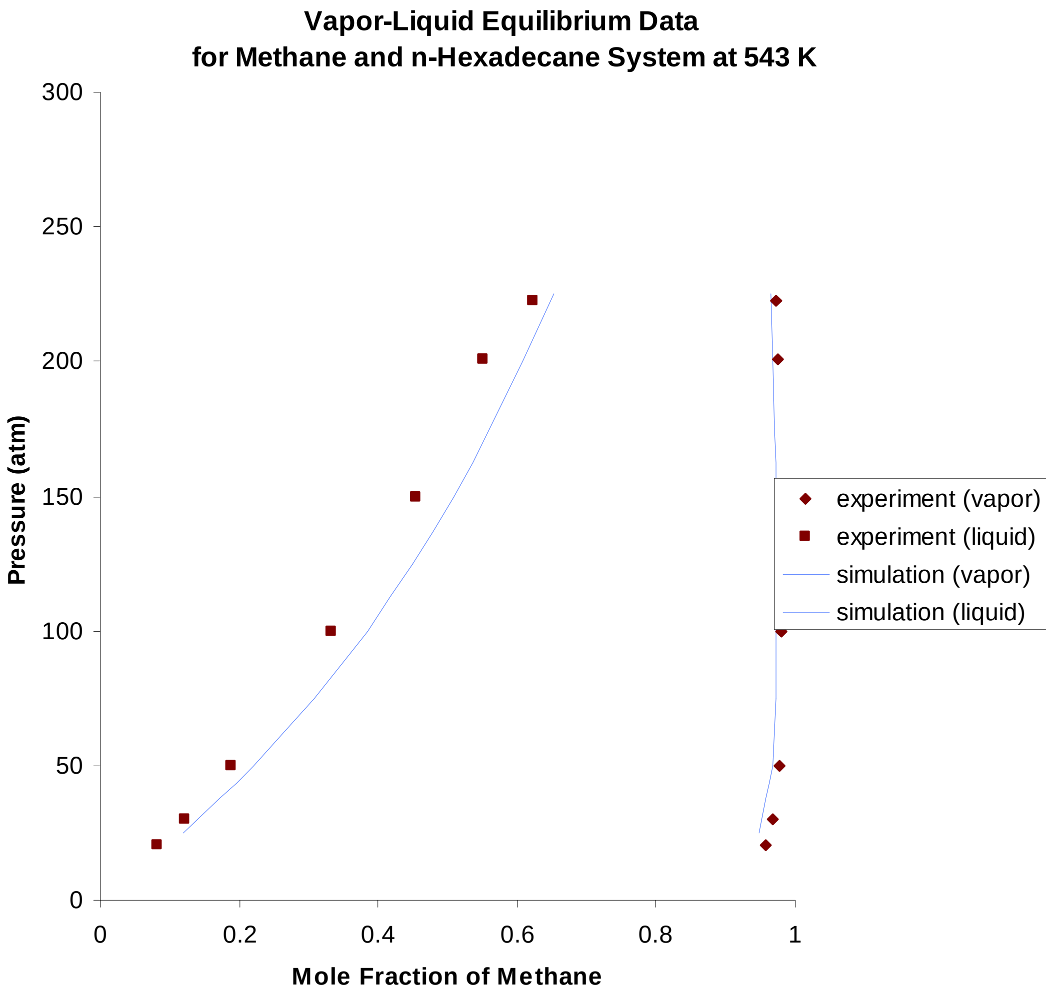

**Figure 4.7** Results for Methane - *n*-Hexadecane Mixture at 543 K

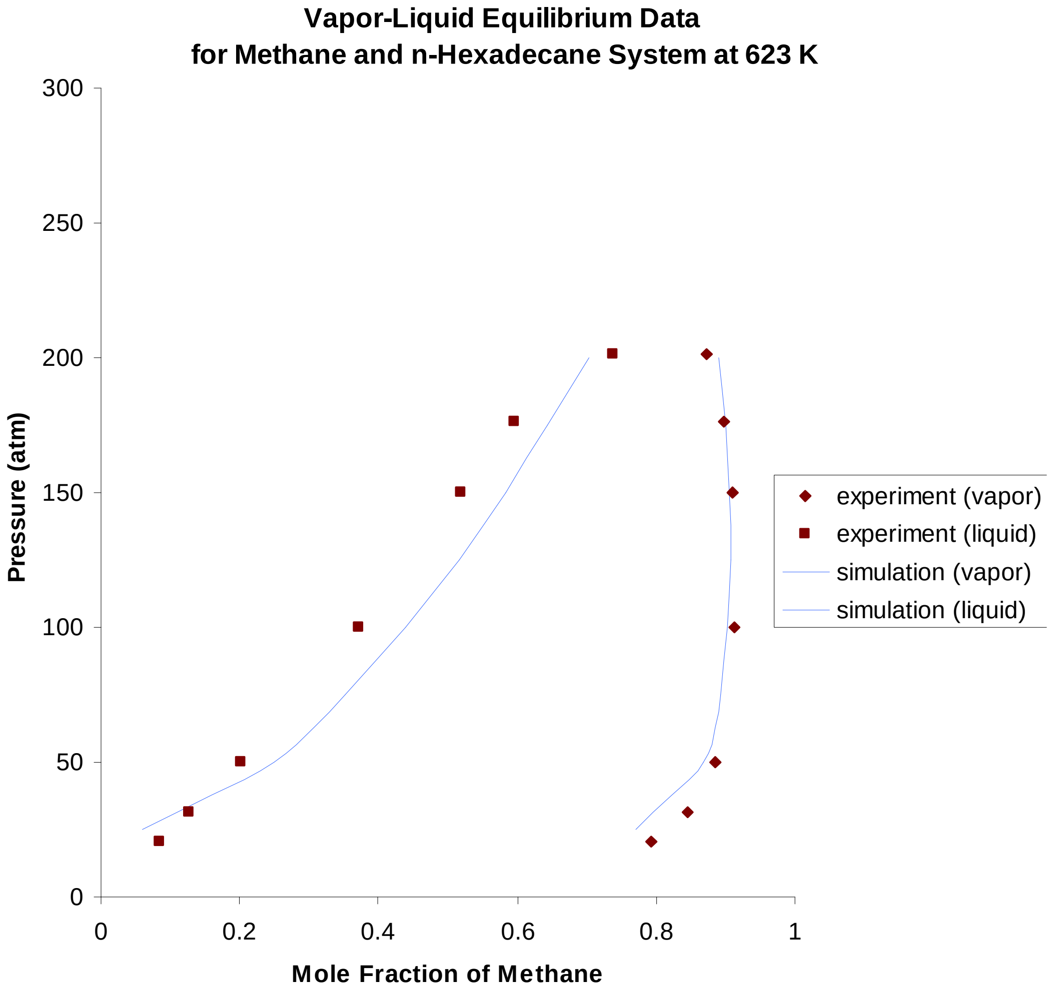

**Figure 4.8** Results for Methane - *n*-Hexadecane Mixture at 623 K

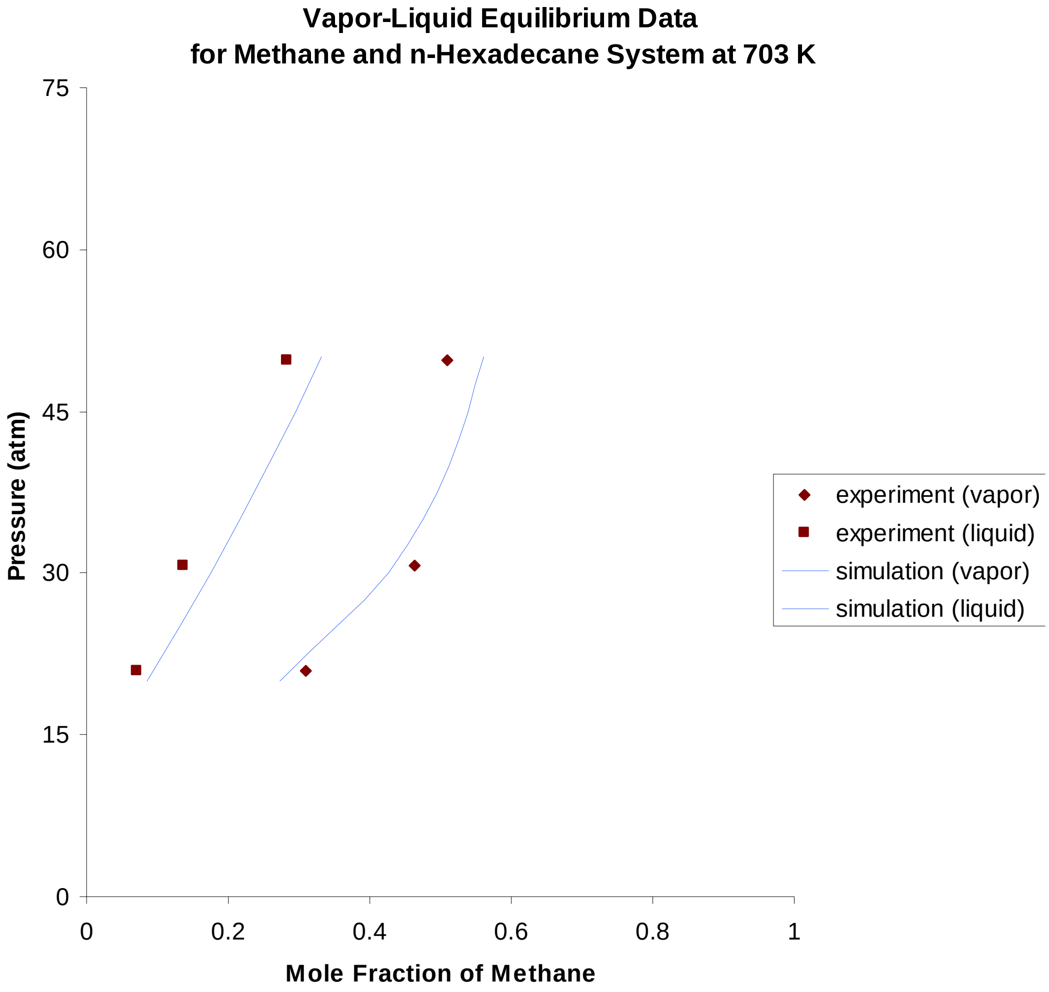

**Figure 4.9** Results for Methane - *n*-Hexadecane Mixture at 703 K

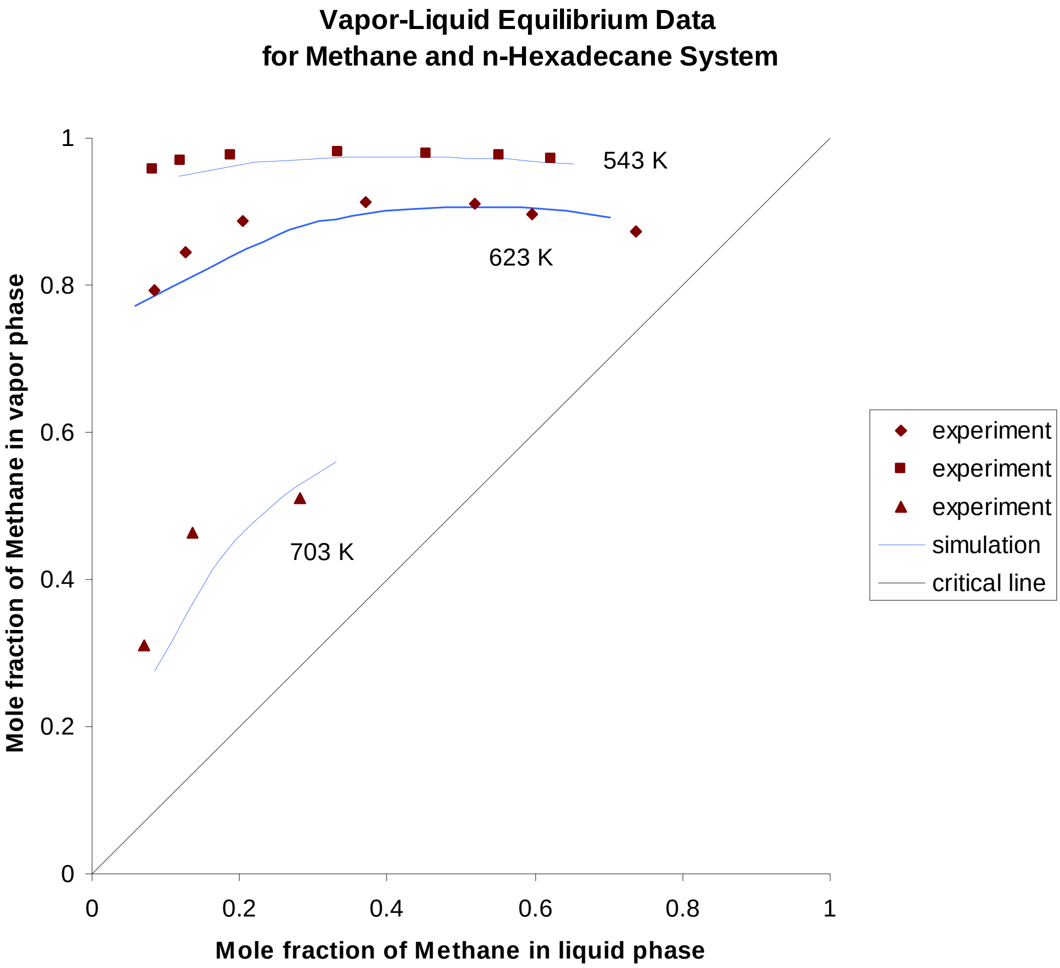

**Figure 4.10** Simulation Results for Methane - *n*-Hexadecane Mixture

**Table 4.9** Feed mole for test problem 1

| Components | Feed (mole) |
|---|---|
| $C_6H_{12}O_2$ | 0.5 |
| $H_2O$ | 0.5 |

**Table 4.10** Feed mole for test problem 2

| Components | Feed (mole) |
|---|---|
| $C_6H_6$ | 0.34483 |
| $CH_3N$ | 0.31034 |
| $H_2O$ | 0.34843 |

**Table 4.11** Feed mole for test problem 3

| Components | Feed (mole) |
|---|---|
| $C_2H_5OH$ | 0.5 |
| $CH_3COOH$ | 0.5 |
| $CH_3COOC_2H_5$ | - |
| $H_2O$ | - |

**Table 4.12** Feed mole for test problem 4

| Components | Feed (mole) |
|---|---|
| Methane | 0.594904600 |
| Ethane | 0.099399451 |
| Propane | 0.048299665 |
| *i*-Butane | 0.008700722 |
| *n*-Butane | 0.020501924 |
| *i*-Pentane | 0.006995458 |
| *n*-Pentane | 0.011500843 |
| *n*-Hexane | 0.013903715 |
| *i*-Pentadecane | 0.164693622 |

**Table 4.13** Feed mole for test problem 5

| Components | Feed (mole) |
|---|---|
| CO | 0.75 |
| $CO_2$ | - |
| $H_2$ | 0.75 |
| $O_2$ | 0.50 |
| $H_2O$ | - |
| Fe | 1.00 |
| FeO | 2.00 |

**Table 4.14** Feed mole for test problem 6

| Conditions | Components | Feed (mole) |
|---|---|---|
| 423 K, 20 bar | Ethene | 0.50 |
| | *n*-Eicosane | 0.50 |
| 423 K, 250 bar | Ethene | 0.95 |
| | *n*-Eicosane | 0.05 |

**Table 4.15** Equilibrium data for test problem 7 (Lin et al., 1980)

| Pressure (atm) | Mole fraction of methane in liquid phase | Mole fraction of methane in vapor phase |
|---|---|---|
| | 543 K | |
| 20.50 | 0.0831 | 0.9580 |
| 30.23 | 0.1208 | 0.9687 |
| 50.0 | 0.1884 | 0.9765 |
| 99.5 | 0.3322 | 0.9808 |
| 149.9 | 0.4539 | 0.9798 |
| 200.6 | 0.5512 | 0.9754 |
| 222.5 | 0.6229 | 0.9719 |
| | 623 K | |
| 20.71 | 0.0836 | 0.7930 |
| 31.39 | 0.1265 | 0.8453 |
| 50.0 | 0.2032 | 0.8865 |
| 99.7 | 0.3716 | 0.9132 |
| 150.3 | 0.5178 | 0.9097 |
| 176.1 | 0.5968 | 0.8970 |
| 201.3 | 0.7371 | 0.8733 |
| | 703 K | |
| 20.87 | 0.0697 | 0.3097 |
| 30.77 | 0.1363 | 0.4632 |
| 49.8 | 0.2822 | 0.5099 |

# CHAPTER V

# CONCLUDING REMARKS

## 5.1 Conclusion

This study has proposed a constraint handling technique that can effectively repair the infeasible solutions based on the gradient of the constraint set. Such gradient information can be derived directly from the constraints or indirectly by the finite difference scheme. Coupled with a real-coded DE, experimental results clearly illustrate the attractiveness of the method for handling several types of constraint. It can produce competitive, if not better, solutions compared to the stochastic ranking method, which appears to be the most promising constraint-handling technique reported thus far in the literature. In addition, as indicated by the results of several test runs, the method proposed here is quite robust; similar solutions are always obtained (i.e., indicated by a small standard deviation of the objective value). Experiments were also conducted to examine the effects of repair probability, which is the only parameter in the proposed method, on the computational requirements and solution quality.

## 5.2 Recommendation

For the future work, the binary interaction parameters for the SAFT equation of state will be estimated from the developed DE. This DE in the dissertation will be developed for more efficient algorithm to solve the engineering optimization problems

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Mr. Phichit Tungtharawiwat was born in Saraburi, Thailand, on Febuary 22, 1983. He received a Bachelor of Science (Biochemistry) from Chulalongkorn University in academic year 2004 and then continued his education in chemical engineering department at Chulalongkorn University. The degree of Master of Engineering in Chemical Engineering will be conferred in academic year 2008.