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Phase Equilibrium Data Reconciliation Using Multi-Objective Differential Evolution with Tabu List

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10.1 Introduction

Data processing and reconciliation are focused on the problem of improving process knowledge to enhance plant operations and general management planning (Romagnoli and Sanchez, 2000). In particular, data reconciliation is a statistical approach applied in process systems engineering to improve process performance based on more accurate data (Romagnoli and Sanchez, 2000; de Andrade Lima, 2006). Experimental measurements contain uncertainties (i.e., experimental errors) and, consequently, it is necessary to reduce the effect of these errors via the statistical correction of experimental data. This correction of experimental measurements is fundamental to establish correctly the status of the system under study. Data reconciliation is the classical statistical approach used to perform this measurement error adjustment, and it has been employed in several applications including mineral, petrochemical, biochemical, chemical and metallurgical processes. In the chemical engineering context, Kuehn and Davidson (1961) reported the pioneer study of data reconciliation in the process industry and, to date, it has found many applications for process monitoring, design, control and optimization (Martinez *et al.*, 2009).

The development of accurate models for design and optimization in process systems engineering relies particularly on reliable phase equilibrium data. The statistical regression of phase equilibrium data is a common and fundamental task for determining appropriate values of parameters for any thermodynamic model to be used in process simulation (Marcilla *et al.*, 2011). The objective of this data regression is to determine parameters of the thermodynamic model for obtaining the best fit to a set of experimental measurements. In the classical approach for modeling phase equilibrium data, it is considered that the experimental data do not contain measurement errors (Englezos and Kalogerakis, 2001). However, phase equilibrium data can include different types of errors (e.g., random and systematic) due to random inherent variations in equipment operation and incorrect calibration or malfunction of the measurement instruments. It is therefore necessary to employ a statistical technique to rectify or reconcile these experimental data for process modeling purposes.

As stated, data reconciliation allows the adjustment of the measured values so that the corrected measurements (i.e., reconciled values) are consistent with the corresponding equations that describe the phenomenon under study. In particular, error-in-variable methods are commonly used for data reconciliation. In this approach, it is assumed that the state variables in the experiments of the system to be modeled may contain measurement errors, and both the model parameters and the reconciled data are simultaneously determined (Esposito and Floudas, 1998; Romagnoli and Sanchez, 2000; Gau and Stadtherr, 2002a). Note that unbiased estimates of model parameters can be obtained if the measurement errors in both independent and dependent variables are considered during data regression, and the reconciled data become an accurate estimate of the system state. As a consequence, the tasks of process systems engineering (e.g., simulation, optimization and control) are based on reliable information and more accurate models (Romagnoli and Sánchez, 2000).

Even though data reconciliation is a well known statistical technique, its application in thermodynamic modeling has received little attention. Recently, some studies have been performed on the simultaneous parameter estimation and data reconciliation for phase equilibrium data processing (Esposito and Floudas, 1998; Gau and Stadtherr, 2002a; 2002b; Srinivas and Rangaiah, 2006; Bonilla-Petriciolet *et al.*, 2007; Bonilla-Petriciolet *et al.*, 2010; Zhang *et al.*, 2011b). Data reconciliation for phase equilibrium modeling is particularly challenging even for relatively simple thermodynamic models (e.g., activity coefficient models) because we have to solve a large-scale global optimization problem, which has the following characteristics: (i) the optimization problem for data reconciliation is non-convex and has several local minima, (ii) there are discontinuities in the objective function and flat regions in the solution domain of decision variables (i.e., model parameters and state variables), and (iii) the range of values for determining the model parameters may be very large.

Incorrect parameter estimation from phase equilibrium data may cause erroneous conclusions about model performance due to incorrect qualitative and quantitative predictions of phase behavior, including uncertainties and errors in process design and calculations, for example, the equipment size (Bollas *et al.*, 2009). In fact, results reported by several studies have noted the importance of using reliable numerical tools for phase equilibrium data modeling and parameter estimation (Esposito and Floudas, 1998; Gau and Stadtherr, 2002a; 2002b; Bollas *et al.*, 2009; Bonilla-Petriciolet *et al.*, 2010; Zhang *et al.*, 2011a &

2011b). The development of reliable methods for performing data reconciliation in phase equilibrium modeling is therefore still a challenge and a current research topic.

Until now, a few deterministic and stochastic global optimization approaches for simultaneous parameter estimation and data reconciliation in phase equilibrium modeling can be found in the literature (Zhang *et al.*, 2011a). For example, Esposito and Floudas (1998) have used a branch-and-bound procedure and convex underestimating functions to solve the data reconciliation problem using vapor-liquid equilibrium (VLE) equations. Global optimality is guaranteed using this approach but, in general, problem reformulation, including the development of specific convex underestimators, is required for each new application. Gau and Stadtherr (2002a, 2002b) used an interval-Newton method to solve data reconciliation problems in the VLE modeling of binary systems. On the other hand, several meta-heuristics (i.e., stochastic global optimization techniques) have been used to solve the data reconciliation problem in phase equilibrium modeling of binary systems especially for VLE, and they include genetic algorithm, simulated annealing, differential evolution with and without tabu list, random tunneling algorithm, particle swarm optimization, harmony search, ant colony optimization and bare-bones particle swarm optimization (Srinivas and Rangaiah, 2006; Bonilla-Petriciolet *et al.*, 2007; Bonilla-Petriciolet *et al.*, 2010; Zhang *et al.*, 2011a & 2011b). In general, these studies have showed the challenging nature of phase equilibrium data reconciliation and have highlighted the need for alternative, reliable methods for solving this type of optimization problems (Zhang *et al.*, 2011a).

In this context, recall that the traditional approach used for performing reconciliation of phase equilibrium data employs a single objective function, where the differences between the adjusted and measured values of several state variables are integrated into a single objective function using weight factors. In reality, data reconciliation is a multi-objective optimization (MOO) problem because it involves conflicting objectives to be satisfied simultaneously. Recently, MOO approaches have been applied for parameter estimation in chemical engineering and other scientific fields (e.g., Wang and Sheu, 2000; Martinez *et al.*, 2009; Kohne *et al.*, 2011). However, to the best of the authors' knowledge, MOO has not been used for performing simultaneous parameter estimation and data reconciliation using phase equilibrium data.

This chapter therefore focuses on the application of MOO to perform phase-equilibrium data reconciliation. In particular, we have analyzed the advantages of MOO for data processing and reconciliation of VLE data using activity coefficient models. Two experimental sets of VLE data are used to illustrate the advantages and capabilities of the proposed MOO procedure. In both examples, the reconciliation of data and estimation of thermodynamic model parameters were performed with a MOO method based on differential evolution with tabu list (Sharma and Rangaiah, 2010). Finally, some criteria are discussed to characterize the solutions obtained from the Pareto-optimal front of the multi-objective data reconciliation. In summary, this study shows that MOO is an alternative approach for performing the data reconciliation of experimental data in thermodynamics.

This chapter is organized as follows: a brief description of the data reconciliation problem and its formulation for phase equilibrium data modeling are presented in section 10.2. Section 10.3 contains the description of a MOO method based on differential evolution with tabu list, which has been used for VLE data reconciliation. Results of multi-objective data reconciliation of VLE models are discussed in section 10.4. Finally, conclusions are provided in the last section of this chapter.

10.2 Formulation of the Data Reconciliation Problem for Phase Equilibrium Modeling

10.2.1 Data Reconciliation Problem

In general, data reconciliation is a large-scale global optimization problem with a non-convex objective function subject to linear and nonlinear equality/inequality constraints derived from physical relationships of the application (Romagnoli and Sanchez, 2000; Andrade Lima, 2006). Usually, the data reconciliation is performed using the criterion of weighted least squares; this problem can be defined formally as:

$$\min_{\hat{x}} F_{obj}(\hat{x}) = (\hat{x} - \bar{x})W^{-1}(\hat{x} - \bar{x}) \quad (10.1)$$

subject to

$$\begin{aligned} \bar{h}(\hat{x}) &= 0 \\ \bar{g}(\hat{x}) &\geq 0 \\ \hat{x}_l &\leq \hat{x} \leq \hat{x}_u \end{aligned} \quad (10.2)$$

where \bar{x} corresponds to the vector of the measured variables, \hat{x} is the vector of adjusted (i.e., reconciled) variables, W is a covariance-variance matrix where its diagonal contains the measurement variance ($\sigma_{x_i}^2$) and all off-diagonal elements are assumed to be zero, \bar{h} and \bar{g} are the equality and inequality constraints, and \hat{x}_l and \hat{x}_u are respectively the lower and upper bounds of \hat{x} . In this formulation, it is assumed that the measurements are affected by errors that follow Gaussian (normal) distribution of zero average and covariance W (Andrade Lima, 2006). Therefore, Equation (10.1) can be rewritten as follows:

$$F_{obj}(\hat{x}) = \sum_i (\hat{x}_i - x_i)^2 \frac{1}{\sigma_{x_i}^2} \quad (10.3)$$

Note that the traditional method of Lagrange multipliers can be used to solve this data-reconciliation problem without inequality constraints (Andrade Lima, 2006).

In the context of data modeling, the error-in-variable (EIV) approach is the standard procedure for simultaneous parameter estimation and data reconciliation (Romagnoli and Sánchez, 2000; Gau and Stadtherr, 2002a). In this case, the state variables z_{ij} for the experiments of the system to be modeled contain measurement errors, and the EIV formulation is the global optimization problem for data reconciliation. Consider the problem of estimating the parameters $\vec{\theta} = (\theta_1, \theta_2, \dots, \theta_{npar})^T$ in a model $\vec{h}(\vec{\theta}, z_{ij}) = \mathbf{0}$, where \vec{h} is a vector of np model equations (Gau and Stadtherr, 2002a). Then, EIV formulation is defined as follows:

$$\min_{\theta, z^t} F_{obj} = \sum_{j=1}^{ndat} \sum_{i=1}^{ne} \frac{(z_{ij}^t - z_{ij})^2}{\sigma_i^2} \quad (10.4)$$

subject to

$$\vec{h}(z_{ij}^t, \vec{\theta}) = 0 \quad i = 1, \dots, ne \quad j = 1, \dots, ndat \quad (10.5)$$

where $ndat$ corresponds to the number of experiments used in data modeling, ne is the overall number of state variables, z_{ij}^t is the known “true” value of i^{th} state variable in j^{th}

experiment, and σ_i is the standard deviation for the experimental measurements of i^{th} state variable.

The set of z_{ij}^f and the model parameters $\vec{\theta}$ are the decision variables of EIV formulation. This optimization problem is considered large scale; its dimensionality depends on the number of state variables and experiments. As suggested by Gau and Stadtherr (2002a), in several applications, the solution of np state variables is obtained by solving np model equations. We can then formulate an unconstrained optimization problem for EIV approach by substitution of these state variables into the objective function. This procedure reduces the problem dimensionality and can improve the computational efficiency of numerical methods used for solving the optimization problem. However, the reduced optimization problem is not necessarily easier to solve because the reduced space of decision variables may be more complex than the original space (Gau and Stadtherr, 2002a).

10.2.2 Data Reconciliation for Phase Equilibrium Modeling

In the case of phase equilibrium modeling, data reconciliation is usually performed for the following state variables: temperature (T), pressure (P) and phase equilibrium compositions. In particular, experimental VLE data are necessary for the development of accurate models and for the design of industrial separation processes. The parameter estimation in thermodynamic models for VLE data processing has therefore been an important topic in the chemical engineering literature (Bollas *et al.*, 2009), and so this study focuses on solving VLE data reconciliation problem.

Classical thermodynamics establishes that the necessary condition for VLE in a multi-component system requires that P , T and the component fugacities must be the same in both phases. This condition is sufficient for a stable equilibrium if this solution corresponds to the global minimum of the Gibbs free energy (Zhang *et al.*, 2011a). The thermodynamic modeling of VLE can be performed using equations of state or activity coefficient (local composition) models where the parameters of these models are determined via experimental data fitting. Poynting corrections are usually very close to unity, and the pure component fugacity coefficients nearly cancel each other at low pressure. Under these conditions, the VLE condition is given by:

$$x_i P_i^0 \gamma_i = y_i P \quad i = 1, \dots, c \quad (10.6)$$

where y_i and x_i are the mole fractions of VLE for component i , c corresponds to the number of components in the VLE system, γ_i is the component activity coefficient calculated with the thermodynamic model, and P_i^0 is the pure component vapor pressure at the system temperature T .

For the case of VLE data (i.e., x - y - T at constant P , or x - y - P at constant T), local composition models based on excess Gibbs free energy equations (e.g., Wilson, NRTL and UNIQUAC models) are commonly used to model phase equilibrium, which is known as the activity coefficient approach. So, the excess Gibbs free energy G^E is used to calculate the activity coefficients γ_i employing the relationship:

$$\ln \gamma_i = \left[\frac{\partial \left(\frac{nG^E}{RT} \right)}{\partial n_i} \right]_{T, P, n_j \neq i} \quad (10.7)$$

where n_i is the mole number of component i and R is the universal gas constant. Under this scenario, state variables of VLE are the equilibrium mole fractions, pressure and temperature (x, y, P, T) with standard deviations ($\sigma_x, \sigma_y, \sigma_P$ and σ_T), and the VLE model can be reformulated as follows:

$$P = \sum_{i=1}^c \gamma_i x_i P_i^0 \quad (10.8)$$

$$y_i = \frac{\gamma_i x_i P_i^0}{\sum_{j=1}^c \gamma_j x_j P_j^0} \quad i = 1, \dots, c \quad (10.9)$$

Then, the objective function for VLE data reconciliation using the EIV approach is commonly defined by:

$$F_{obj} = \sum_{j=1}^{ndat} \sum_{i=1}^{c-1} \left[\frac{(x_{ij}^t - x_{ij})^2}{\sigma_{x_i}^2} + \frac{(y_{ij}^t - y_{ij})^2}{\sigma_{y_i}^2} \right] + \sum_{j=1}^{ndat} \left[\frac{(T_j^t - T_j)^2}{\sigma_T^2} + \frac{(P_j^t - P_j)^2}{\sigma_P^2} \right] \quad (10.10)$$

This objective function must be globally optimized with respect to $n_{par} + 2c \times ndat$ decision variables subject to constraints/model Equations (10.8) and (10.9). These equations are used to eliminate P^t and y_j^t in the EIV objective function (Equation 10.10), and the VLE data-reconciliation problem is solved as an unconstrained optimization problem. Note that the independent variables are the set of $\vec{z} = (\vec{x}_{ij}, \vec{T})$ for all measurements, while the optimization variables are the reduced set of $\vec{z}^t = (\vec{x}_{ij}^t, \vec{T}^t)$ and $\vec{\theta} = (\theta_1, \dots, \theta_{n_{par}})^T$ subject to $0 \leq \vec{x}^t \leq 1$.

Objective function given by Equation (10.10) is nonlinear and potentially non-convex with several local minima due to the nonlinear nature of the thermodynamic models used in data reconciliation (Esposito and Floudas, 1998; Gau and Stadtherr, 2002a; 2002b; Bonilla-Petriciolet *et al.*, 2010; Zhang *et al.*, 2011a). The dimension of this optimization problem is also large, especially for data sets with many measurements (i.e., phase compositions, temperature and pressure). The VLE data treatment therefore involves the solution of a large-scale reconciliation problem. Under these conditions, traditional local optimizers (e.g., Newton-like optimization methods) require a good set of initial values of both model parameters and state variables. For this reason, these methods frequently fail to identify the global solution and may converge to a local minimum. In order to find the proper values of the adjustable parameters of thermodynamic models and the reconciled data we must employ global optimization techniques for minimizing the EIV objective function. In summary, studies have shown that the simultaneous data reconciliation and parameter estimation using traditional thermodynamic equations for VLE data modeling requires the solution of a challenging global optimization problem (Esposito and Floudas, 1998; Gau and Stadtherr, 2002a & 2002b; Bonilla-Petriciolet *et al.*, 2010; Zhang *et al.*, 2011b).

In fact, data reconciliation for VLE modeling is a MOO problem because Equation (10.10) involves conflicting objectives for each state variable. Note that each objective for the VLE state variables is weighted using the standard deviation of experimental measurements. However, the incorporation of all optimization targets into Equation (10.10) increases the possibility of missing some optimal solutions if the integrated objective function shows

a duality gap due to its nonconvexity (Silva and Biscaia, 2003). Rather than obtaining a unique solution to the overall problem, MOO can provide a family of optimal solutions (i.e., Pareto-optimal front) for VLE data reconciliation, where each Pareto-optimal solution improves the value of some objective causing a simultaneous deterioration in at least one other objective, compared to another Pareto-optimal solution. Since the Pareto-optimal front represents tradeoffs among different objectives, we can obtain a better understanding of the capabilities and limitations of the thermodynamic model used for VLE data reconciliation. Here, the application of MOO is illustrated for data reconciliation in VLE data modeling.

In this study, a VLE data-reconciliation problem is solved for three and four objectives and we have compared the results obtained from both the approaches. Specifically, the data-reconciliation problem comprising three objectives is formulated as follows:

$$\text{Approach 1: } \begin{cases} \min F_P = \sum_{j=1}^{ndat} \left[\frac{\left(P_j^t \left\{ \vec{\theta}, x_{ij}^t, T_j^t \right\} - P_j \right)^2}{\sigma_P^2} \right] \\ \min F_T = \sum_{j=1}^{ndat} \left[\frac{(T_j^t - T_j)^2}{\sigma_T^2} \right] \\ \min F_{xy} = \sum_{j=1}^{ndat} \sum_{i=1}^{c-1} \left[\frac{(x_{ij}^t - x_{ij})^2}{\sigma_{x_i}^2} + \frac{\left(y_{ij}^t \left\{ \vec{\theta}, x_{ij}^t, T_j^t \right\} - y_{ij} \right)^2}{\sigma_{y_i}^2} \right] \end{cases} \quad (10.11)$$

And the problem formulation for four objectives is given by:

$$\text{Approach 2: } \begin{cases} \min F_P = \sum_{j=1}^{ndat} \left[\frac{\left(P_j^t \left\{ \vec{\theta}, x_{ij}^t, T_j^t \right\} - P_j \right)^2}{\sigma_P^2} \right] \\ \min F_T = \sum_{j=1}^{ndat} \left[\frac{(T_j^t - T_j)^2}{\sigma_T^2} \right] \\ \min F_x = \sum_{j=1}^{ndat} \sum_{i=1}^{c-1} \left[\frac{(x_{ij}^t - x_{ij})^2}{\sigma_{x_i}^2} \right] \\ \min F_y = \sum_{j=1}^{ndat} \sum_{i=1}^{c-1} \left[\frac{\left(y_{ij}^t \left\{ \vec{\theta}, x_{ij}^t, T_j^t \right\} - y_{ij} \right)^2}{\sigma_{y_i}^2} \right] \end{cases} \quad (10.12)$$

Note that the MOO formulation given by Equation (10.12) is useful to identify the tradeoffs of all state variables on data reconciliation. In addition, separate objectives are used for T and P because these variables usually have different magnitudes and their experimental uncertainties may differ significantly during VLE measurements.

The above two MOO problems have been formulated without constraints, where the decision variables are $npar + c \cdot ndat$ based on the fact that $\sum_{i=1}^c x_{ij} = 1$ and $\sum_{i=1}^c y_{ij} = 1$.

These unconstrained MOO problems are solved for the domain defined by the lower and upper limits of the reduced set of decision variables: $\bar{\theta}$ and $\bar{z} = (\bar{x}_{ij}^t, \bar{T}^t)$. In particular, we emphasize VLE data reconciliation problems with many decision variables to illustrate the application of MOO. In the following section, a brief description of the MOO method used for phase equilibrium data reconciliation is provided.

10.3 Multi-Objective Optimization using Differential Evolution with Tabu List

The literature suggests that population-based multi-objective algorithms offer a better performance for solving MOO problems involved in engineering applications (Rangaiah, 2009). The characteristics of these methods (e.g., reliability, easy implementation, general use) are desirable and suitable for solving MOO problems. Several variants of population-based meta-heuristics were proposed for solving MOO problems during the 2000s. In particular, evolutionary MOO methods have been widely used for solving engineering problems. In this study, we have applied a MOO method based on differential evolution (Sharma and Rangaiah, 2010).

Storn and Price (1997) introduced differential evolution (DE) to solve optimization problems with continuous decision variables. It works with a population of individuals (i.e., solutions), and employs mutation, crossover, and selection operations in each iteration. Adaptation of DE for multiple objectives (MODE) requires modification in the selection step. Additionally, Srinivas and Rangaiah (2007) have found that use of tabu list (TL) can avoid the revisit of search space by keeping record of recently visited points, which can avoid unnecessary function evaluations. So, TL is also included in the MODE algorithm (MODE-TL) used in this study. Specifically, MODE-TL includes classical DE steps, adaptation for multiple objectives (selection of individuals for subsequent generations), TL and tabu check, and a convergence criterion based on maximum number of generations (see the flowchart in Figure 10.1). A brief description of MODE-TL is given below.

In MODE-TL, a population of NP individuals with D -dimension (number of decision variables) is initialized randomly inside the bounds on decision variables. Values of objectives and constraints are calculated for each individual of the initial population. The size of the TL is half of the population size, and the TL is randomly filled with 50% individuals from the initial population. Individuals in the population are also referred to as target individuals. A trial individual is generated for each target individual by mutation and crossover on three randomly selected individuals from initial/current/parent population. DE/rand/1 mutation strategy and binomial crossover (Price *et al.*, 2005) are used to generate a trial individual, see Figure 10.2. Note that the elements of the mutant vector (\mathbf{v}) compete with those of target vector (\mathbf{x}), with probability Cr to generate trial vector (\mathbf{u}).

As stated, the TL concept of TS has been included in MODE-TL to avoid the revisit of search space. The TL is continuously updated with the newly generated trial individuals. A tabu check is implemented in the trial vector generation step, and the trial individual is generated repeatedly until it is away from each individual in the TL by a specified distance (TR). The Euclidean distance between trial individual and each individual in TL is calculated in the normalized decision variables space for accepting the trial individual (Figure 10.3). After that, objectives and constraints are calculated for the temporarily

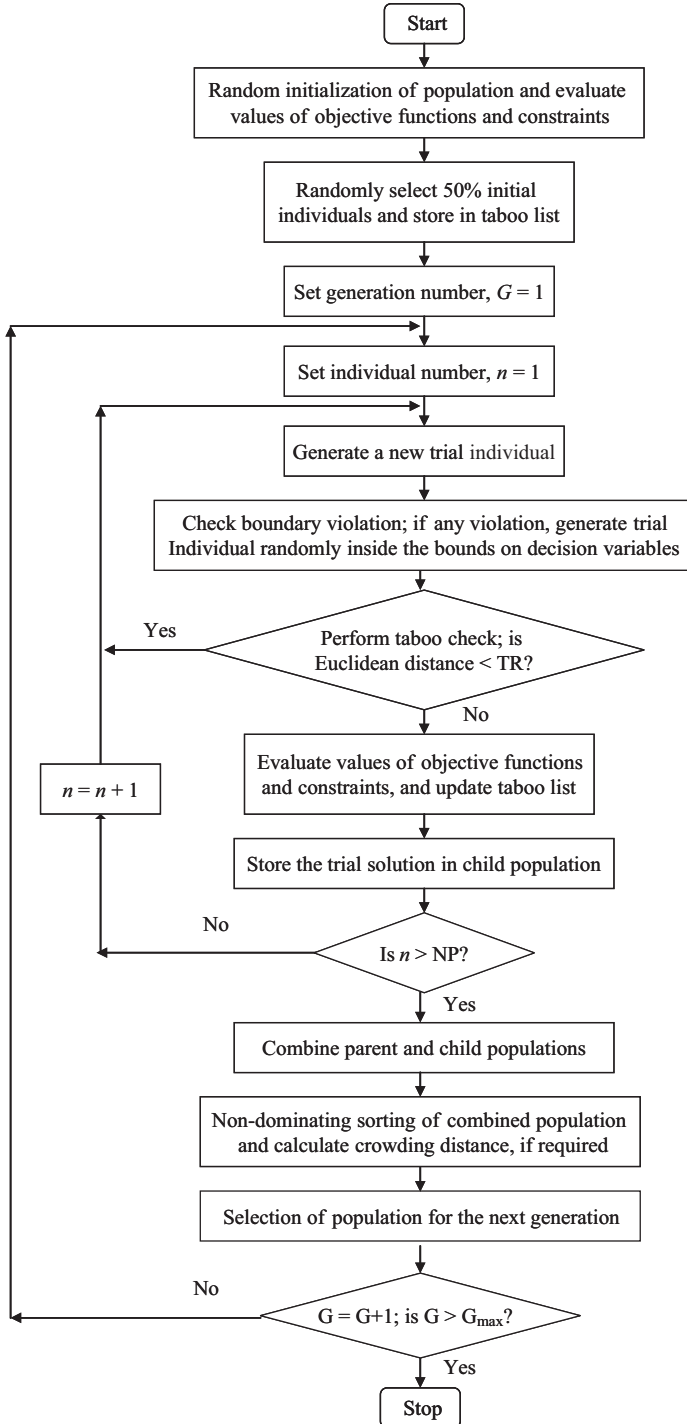


Figure 10.1 Flowchart of the MODE-TL algorithm.

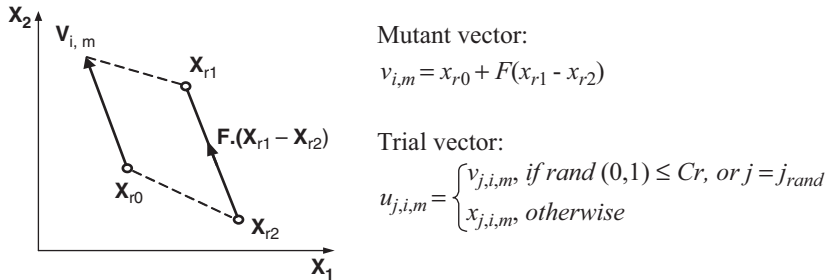


Figure 10.2 Generation of a trial vector using MODE-TL.

accepted trial individual. The trial individual is stored in the child population, and also added to TL.

After generating trial individuals for all the target individuals of current population, non-dominated sorting of the combined current and child populations followed by crowding distance calculation, if required, is performed to select individuals for the next generation (Deb, 2001). The first (best) NP individuals are used as the population in the subsequent generation. The MODE-TL algorithm handles inequality constraints by feasibility approach (constrained dominance) of Deb *et al.* (2002). Results reported by Sharma and Rangaiah (2010) show that MODE-TL is reliable for solving multimodal optimization problems due to the synergy from the integration of multi-objective DE with TL.

MS Excel has been used to implement the MODE-TL algorithm. Excel worksheets are used to calculate the values of objective functions and constraints, for program interface, and linking between cells. A program in Visual Basic for Applications (VBA) is used to implement MODE-TL algorithm steps. In this study on VLE data reconciliation, parameters of MODE-TL are: $NP = 100$, crossover probability = 0.3 and mutation probability = 0.5, and maximum number of generations, $G_{\max} = 5000$ is used as the search termination criterion. These parameters were determined using the results of preliminary calculations. CPU time required for solving selected data reconciliation problems may range from 2 to 3 hours.

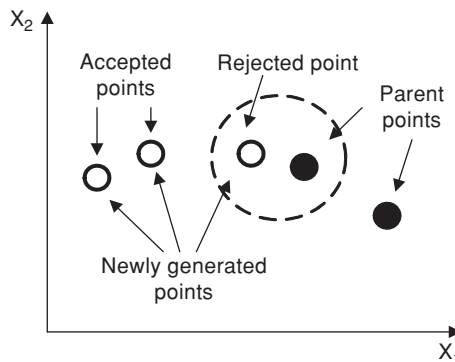


Figure 10.3 Use of TL in MODE-TL to accept or reject newly generated solution points.

10.4 Data Reconciliation of Vapor-Liquid Equilibrium by MOO

10.4.1 Description of the Case Study

In this study, the data reconciliation for modeling the VLE of the binary benzene (1) – hexafluorobenzene (2) system is considered. Note that the simultaneous parameter estimation and data reconciliation of this binary system has been performed in earlier studies. These studies have used a single EIV objective function and stochastic or deterministic global optimization method (see for instance, Gau and Stadtherr, 2002a & 2002b; Srinivas and Rangaiah, 2006; Bonilla-Petriciolet *et al.*, 2010; Zhang *et al.*, 2011b). However, until now, this binary system has not been investigated using the MOO approach

Here, the liquid-phase activity coefficients are calculated using the Wilson model and an ideal gas behavior is assumed for the vapor phase. So, these activity coefficients are given by:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (10.13)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (10.14)$$

where the Wilson binary parameters Λ_{12} and Λ_{21} are given by:

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(-\frac{\theta_1}{RT}\right) \quad (10.15)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(-\frac{\theta_2}{RT}\right) \quad (10.16)$$

In the above equations, v_1 and v_2 are the liquid molar volumes of pure components, θ_1 and θ_2 are the energy parameters in cal/mol, subscripts 1 and 2 refer to components 1 and 2, respectively, and $R = 1.98721$ cal/(K·mol). The Antoine equation is employed to calculate the vapor pressures of pure components:

$$\log_{10} P_i^0 = a_i - \frac{b_i}{c_i + T} \quad (10.17)$$

where T is in °C and P_i^0 in mmHg. Table 10.1 gives the model parameters for pure components used in the calculations.

Data reconciliation using MODE-TL is performed for two VLE data sets, reported in Table 10.2. All the experimental data used in this study are those reported in DECHEMA collection (Gmehling *et al.*, 1977–1990). Each data set contains measurements of the state

Table 10.1 Pure component parameters used in VLE data reconciliation of benzene–hexafluorobenzene system.

Component	v_i , cm ³ /mol	a	b	c
Benzene	89.41	6.87987	1196.76	219.161
Hexafluorobenzene	115.79	7.03295	1227.98	215.491

Table 10.2 Experimental VLE data of benzene (1) – hexafluorobenzene (2) system used in MOO based data reconciliation.

Example	$T_j, ^\circ\text{C}$	P_j, mmHg	x_{1j}	y_{1j}
1	40	167.17	0.1039	0.1
	40	167.1	0.2148	0.2199
	40	168.19	0.3108	0.3306
	40	170.12	0.3988	0.4318
	40	172.29	0.4736	0.515
	40	174.7	0.5464	0.5913
	40	177.63	0.6355	0.6772
	40	180.26	0.726	0.7571
	40	182.2	0.8151	0.8316
	40	183.21	0.9057	0.908
2	50	253.5	0.05	0.0475
	50	252.3	0.1	0.097
	50	251.8	0.2	0.21
	50	253.2	0.3	0.316
	50	256.3	0.4	0.425
	50	260	0.5	0.5295
	50	263.5	0.6	0.629
	50	267.3	0.7	0.7215
	50	270.4	0.8	0.8125
	50	272.9	0.9	0.9005
50	272.1	0.95	0.948	

variables: (x_1, y_1, P, T) . For data reconciliation, standard deviation of (0.003, 0.0029, 1.7, 0.083) is assumed for the vector of state variables (x_1, y_1, P, T) in both the examples; these values have been selected from the previous studies using global optimization (e.g., Gau and Stadtherr, 2000; Bonilla-Petriciolet *et al.*, 2010). As stated, Equations (10.11) and (10.12) are the objective functions for MOO. The bounds on the independent state variables $\vec{z} = (\vec{x}_{ij}, \vec{T})$ are set using $\pm 3\sigma$; that is, $x'_{1j} \in [x_{1j} - 3\sigma_x, x_{1j} + 3\sigma_x]$ and $T'_j \in [T_j - 3\sigma_T, T_j + 3\sigma_T]$. Finally, the bounds for the Wilson model parameters are $\theta_1, \theta_2 \in (-10000, 200000)$, which cover the range of physical interest (Gau and Stadtherr, 2000).

10.4.2 Data Reconciliation Results

10.4.2.1 Example 1: VLE Data of Benzene–Hexafluorobenzene System at 40 °C

In the first example, VLE data at 40 °C were used; these include ten experiments ($n_{dat} = 10$). Data reconciliation is performed with respect to 22 decision variables. Figures 10.4 and 10.5 show the Pareto-optimal fronts of VLE data reconciliation for three and four objectives, respectively, using MODE-TL. As expected, the objective functions used for data reconciliation are conflicting and are affected in opposing ways by changes in the decision variables, where an improvement in one objective can only be achieved at the cost of some deterioration in the other objectives. In general, MODE-TL gave Pareto-optimal fronts

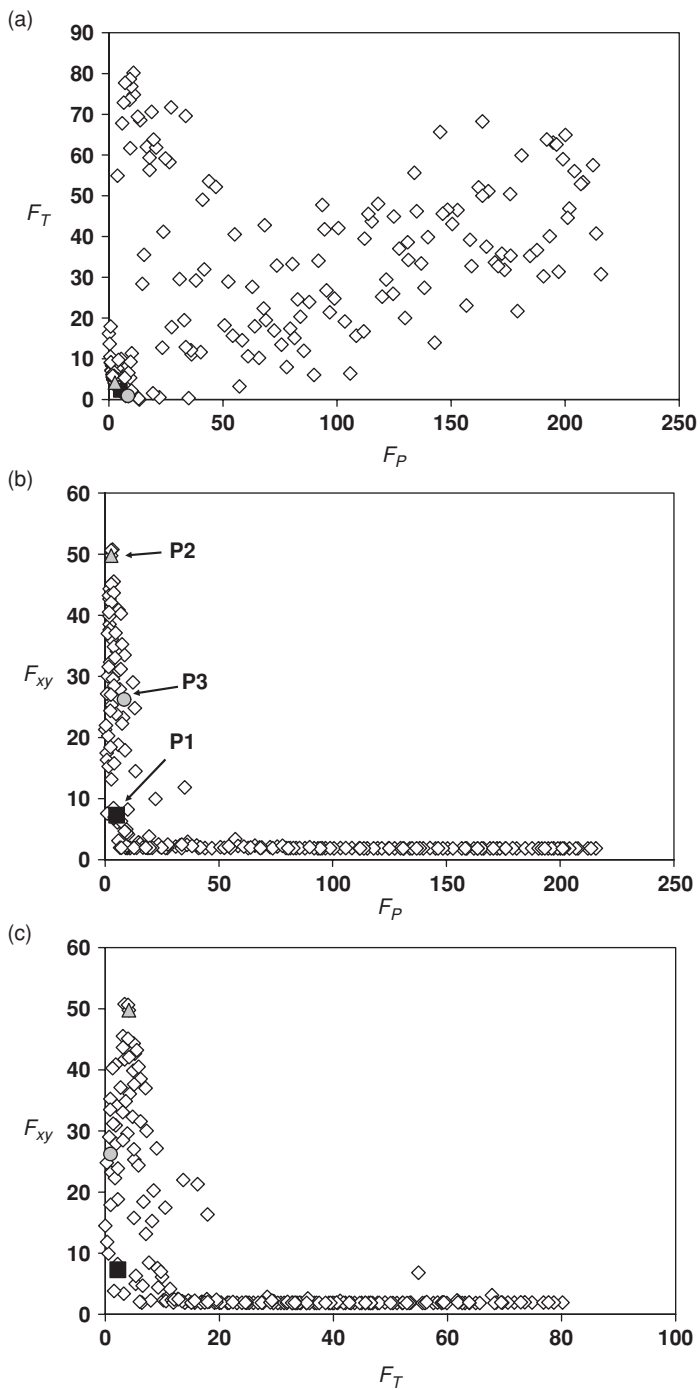


Figure 10.4 Pareto-optimal front for VLE data reconciliation of the benzene-hexafluorobenzene system at 40°C using three-objective optimization.

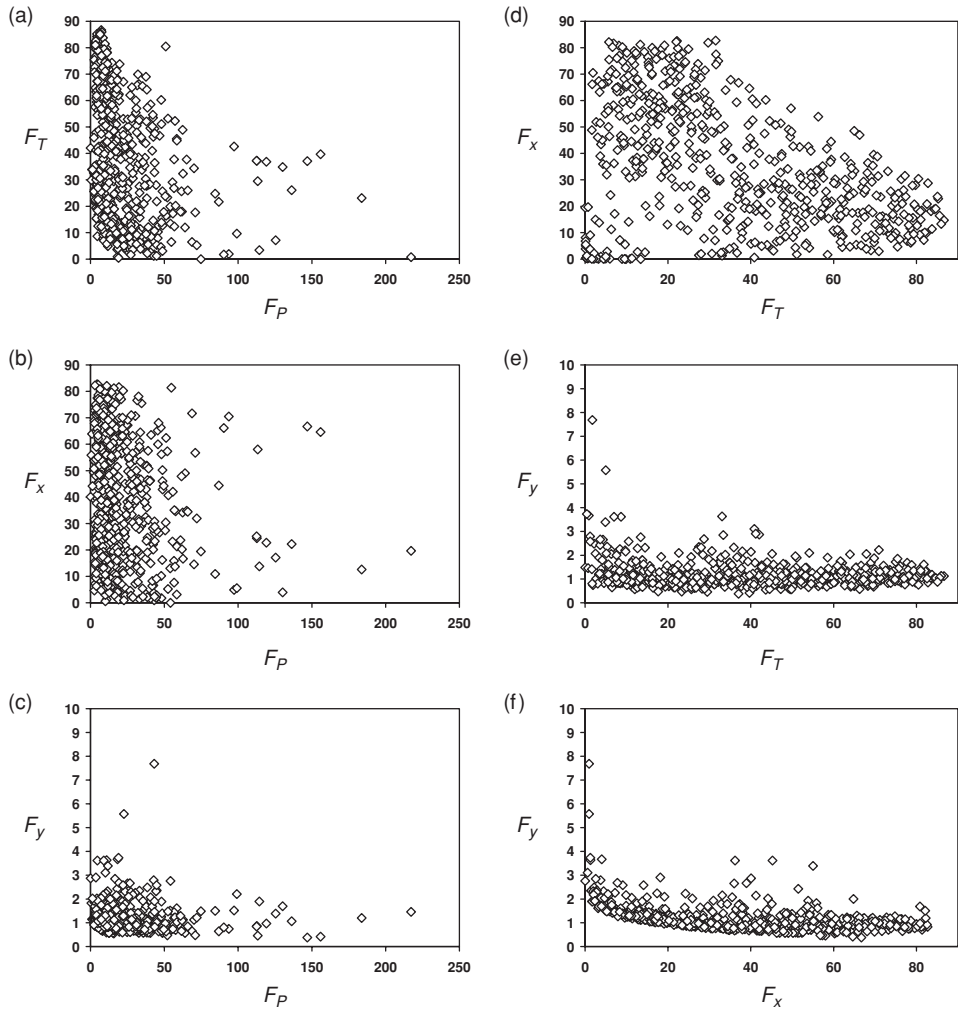


Figure 10.5 Pareto-optimal front for VLE data reconciliation of the benzene–hexafluorobenzene system at 40 °C using four-objective optimization.

with a good distribution of points. The fronts of the four-objective optimization problem seem to be more scattered than those for three-objective optimization. This is expected due to the increase in the number of objectives used in MOO, as has been reported for other MOO applications (e.g., Babu *et al.*, 2005; Agrawal *et al.*, 2007). We tried to improve the results of four-objective data reconciliation by using different values of G and NP for MODE-TL; but the scatter could not be significantly reduced. Results reported in Figure 10.5, for illustration, correspond to $NP = 600$ and $G = 5000$ used in MODE-TL.

Overall, many sets of reconciled VLE data and optimal values of model parameters can be obtained from the Pareto-optimal fronts. The fronts in Figures 10.4 and 10.5 largely depend on the reconciled values of states variables in contrast to the parameters of the Wilson model

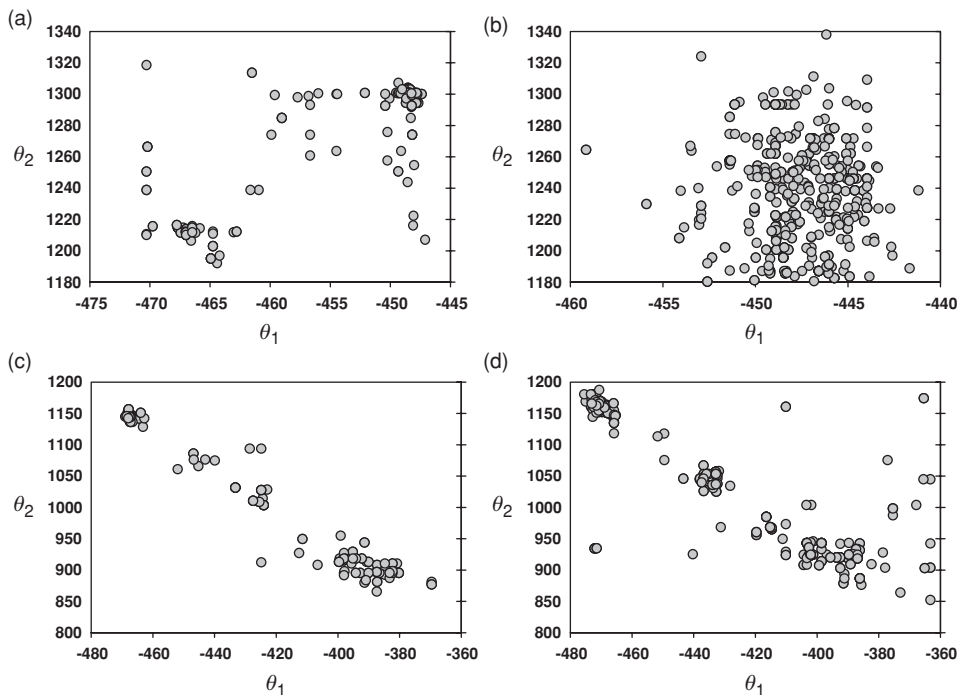


Figure 10.6 Wilson model parameters obtained from multi-objective data reconciliation of VLE of benzene–hexafluorobenzene system at (a, b) 40°C and (c, d) 50°C using MODE-TL.

because small variations in these variables may cause significant changes in the values of objective functions. In other words, this indicates that the objective functions used for the state variables T , P and x_1 play an important role and have more impact on VLE data reconciliation at 40°C. For illustration, Figure 10.6 shows the Wilson model parameters obtained from data reconciliation using three and four objectives. It is clear that the Pareto solutions for model parameters (θ_1, θ_2) have small variability in this example. Therefore, in this system, a Pareto-optimal solution should be chosen based on the reconciled values of state variables, especially x_1 and T , for better modeling of VLE data.

Additional knowledge of the application under study is required in order to identify the best solution for the conflicting objectives. In the literature, there are some methods to rank the Pareto-optimal solutions based on the user's preferences (e.g., Thibault, 2009). However, alternative criteria can be applied in multi-objective VLE data reconciliation to perform this selection without ranking. In particular, the capability of the thermodynamic model to reproduce and to fit properly the phase equilibrium behavior and the measured data is of special interest in thermodynamic modeling. So, the model accuracy for the prediction of a specific equilibrium condition (e.g., azeotrope point) and the characteristics of error residual distributions of state variables can be used as criteria to identify a more appropriate solution from the Pareto-optimal solutions obtained.

To illustrate the application of these criteria, three solutions (P1, P2 and P3) were chosen arbitrarily from results obtained from three-objective data reconciliation at 40°C

(see Figure 10.4). For these solutions, objective function values of both F_P and F_T are very close but they vary with respect to F_{xy} . Reconciled data of state variables for these solutions are reported in Table 10.3. First, analysis is focused on the distribution of error residuals between measured and reconciled data: $\Delta z = z_j^t - z_j$, shown in Figure 10.7 for the selected solutions P1, P2 and P3. These results indicate that the distributions are not similar for the solutions selected from the Pareto-optimal front. For example, when one goes from point P1 to point P2 on the Pareto front (see Figure 10.4), the error distribution changes significantly for some state variables, namely, x and T . For good data reconciliation, all residuals should be well spread out within their respective standard deviation (Gau and Stadtherr, 2002b). MOO results can be used to select the Pareto-optimal solution that provides more satisfactory error distribution of state variables for the desired application.

Next, consider the effect of the choice of the Pareto-optimal solution on the prediction of homogeneous azeotropes. As indicated by Gau *et al.* (2000), inappropriate parameter estimation affects the capability of thermodynamic models for homogeneous azeotropy prediction. In particular, an improper prediction of the presence of azeotropes can cause serious design problems in separation processes. This criterion is therefore important to characterize the solutions obtained from multi-objective VLE data reconciliation. Literature indicates that the benzene–hexafluorobenzene system has two homogeneous azeotropes at 40 °C and 50 °C (Gmehling *et al.*, 1977–1990). Gau *et al.* (2000) have shown that the Wilson model may fail to predict the presence of both these azeotropes in this system if inappropriate parameters are used (e.g., using a local optimum of the parameter estimation problem).

The P1, P2 and P3 solutions selected from the Pareto-optimal front at 40 °C were therefore employed for homogenous azeotropy calculations using the method suggested by Bonilla-Petriciolet *et al.* (2009), and the predictions are compared with the experimental data in Table 10.4. Using the model parameters obtained from MOO, two homogeneous azeotropes are predicted by Wilson model for the three solutions tested. These results are in agreement with the experimental data for this system. In this case, the azeotrope pressure predicted by the Wilson model is less sensitive to the binary parameters, whereas the composition of both azeotropes depends on the selected Pareto solution. In conclusion, the diverse solutions obtained from Pareto-optimal front can be employed to identify the capabilities and limitations of the thermodynamic model for modeling and predicting VLE. For this VLE data set, the agreement between experimental and calculated values of state variables and azeotropic conditions can be used to choose the best Pareto solution. Overall, P1 appears to be a good choice for this data reconciliation problem because it provides more satisfactory error distribution of state variables and better reconciled data.

10.4.2.2 *Example 2: VLE Data for the Benzene–Hexafluorobenzene System at 50 °C*

In this example, data reconciliation of VLE data at 50 °C ($ndat = 11$) is performed with respect to 24 decision variables using three- and four-objective optimization. Results of data reconciliation and Pareto-optimal fronts are reported in Figures 10.8 and 10.9. Again, a relatively smoother front is obtained in the case of three-objective data reconciliation, and scatter of Pareto-optimal fronts increases with the number of objectives. This is not surprising because the complexity of MOO problem for data reconciliation increases both

Table 10.3 Reconciled data of selected solutions from the Pareto-optimal front of three-objective optimization of VLE data reconciliation of benzene (1) – hexafluorobenzene (2) system at 40 °C (Figure 10.4).

P_j^i	P1			P2			P3				
	T_j^i	x_{1j}^i	y_{1j}^i	P_j^i	T_j^i	x_{1j}^i	y_{1j}^i	P_j^i	T_j^i	x_{1j}^i	y_{1j}^i
167.65	39.94	0.1048	0.1041	167.66	39.94	0.1066	0.1060	167.95	39.98	0.1061	0.1054
167.93	39.95	0.2147	0.2195	167.62	39.91	0.2147	0.2196	168.23	39.99	0.2147	0.2194
168.54	39.93	0.3104	0.3238	168.72	39.95	0.3095	0.3228	168.83	39.97	0.3100	0.3232
170.24	39.99	0.3992	0.4221	170.23	39.99	0.3959	0.4184	170.30	40.00	0.3986	0.4214
172.02	40.02	0.4736	0.5042	172.15	40.03	0.4765	0.5074	171.94	40.01	0.4736	0.5042
174.06	40.04	0.5476	0.5844	174.15	40.04	0.5483	0.5852	173.84	40.01	0.5485	0.5854
176.89	40.06	0.6355	0.6759	177.15	40.08	0.6381	0.6785	176.72	40.03	0.6384	0.6789
179.83	40.04	0.7259	0.7633	180.07	40.07	0.7259	0.7633	179.75	40.03	0.7262	0.7636
182.26	39.98	0.8150	0.8411	182.27	39.98	0.8142	0.8403	182.46	40.01	0.8142	0.8404
183.97	39.94	0.9057	0.9122	183.51	39.88	0.9028	0.9099	183.78	39.92	0.9042	0.9111
$\theta_1 = -466.99$				$\theta_1 = -466.91$				$\theta_1 = -467.44$			
$\theta_2 = 1210.13$				$\theta_2 = 1211.87$				$\theta_2 = 1211.63$			

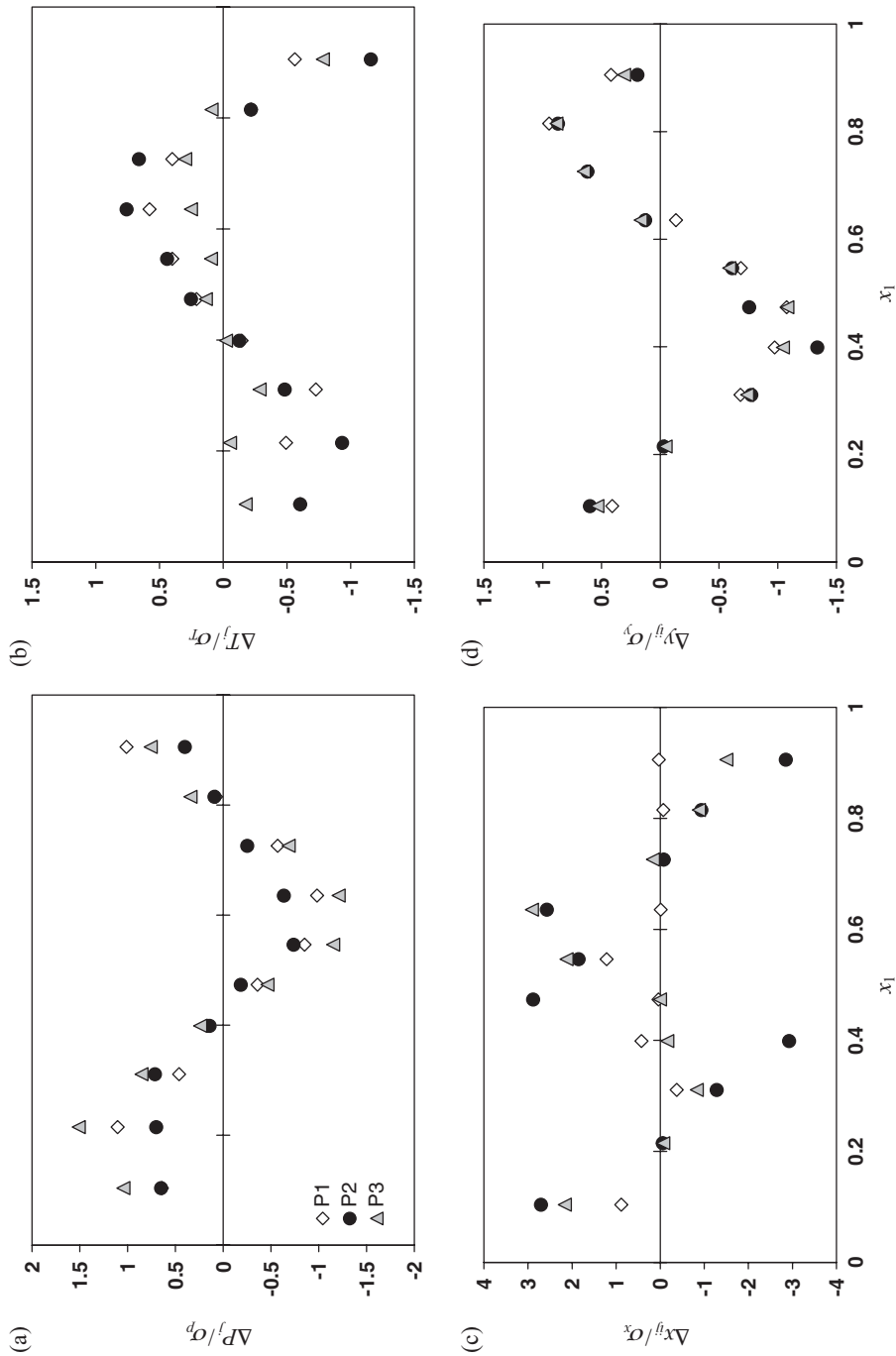


Figure 10.7 Error residuals ($\Delta z = z^i - z$) in state variables (x_1, y_1, P, T) for selected solutions from the Pareto-optimal front for VLE data reconciliation of the benzene–hexafluorobenzene system at 40 °C using three-objective optimization.

Table 10.4 Results of homogeneous azeotrope prediction using selected solutions from Pareto fronts of VLE data reconciliation of benzene (1) – hexafluorobenzene (2) system.

$T, ^\circ\text{C}$	Solution	Model parameters, cal/mol		Homogeneous azeotrope Calculated values		Experimental data	
		θ_1	θ_2	x^{azeo}	$P, \text{ mmHg}$	x^{azeo}	$P, \text{ mmHg}$
40	P1	-466.99	1210.13	(0.1265, 0.8735)	168.09	(0.16, 0.84)	167
				(0.9348, 0.0652)	184.70	(0.93, 0.07)	183
	P2	-466.91	1211.87	(0.1252, 0.8748)	168.10		
50	P1	-387.39	865.73	(0.9345, 0.0655)	184.73		
				(0.1277, 0.8723)	168.08		
	P2	-467.44	1211.63	(0.9350, 0.0650)	184.70		
50	P1	-387.39	865.73	(0.0130, 0.9870)	255.64	(0.17, 0.83)	254
				(0.9213, 0.0787)	273.06	(0.90, 0.10)	273
	P2	-380.25	895.51	No azeotrope			
50	P3	-468.03	1144.58	(0.8960, 0.1040)	274.36		
				(0.1951, 0.8049)	254.18		
				(0.9347, 0.0653)	273.62		

with the number of decision variables and conflicting objectives. However, four-objective optimization allows us to identify and understand the contribution and effect of all state variables on VLE data modeling.

Figure 10.10 shows error residual distributions for three arbitrary solutions (P1, P2 and P3) selected from the results in Figure 10.8, while Table 10.5 reports their reconciled data and model parameters. Note that these solutions show significant differences in the values of objective functions. It is clear that different reconciled data and error residual distributions will be obtained depending on the solution selected from the Pareto-optimal front (Figure 10.10). Results in this case show that larger errors are observed in the state variables x and P , and the objective functions of phase equilibrium compositions are more sensitive to changes on values of state variables. Figures 10.6c and 10.6d show the values of the Wilson model parameters obtained from Pareto-optimal fronts using three and four objectives in data reconciliation at 40 °C. In this example, the model parameters have wider ranges in comparison to the results obtained at 40 °C. An almost linear relationship between the Wilson model parameters (θ_1, θ_2) can be seen for the Pareto-optimal solutions obtained from both three- and four-objective optimization of data reconciliation of VLE data at 50 °C (Figure 10.6). This is different from the scattered results for data reconciliation of VLE data at 40 °C.

Azeotropy calculations using the solutions selected from the Pareto-optimal front are given in Table 10.4. It is interesting to observe that, depending on the solution, the Wilson model may fail to predict the presence and location of homogeneous azeotropes. There are cases in which only one azeotrope is found when in fact this system shows the presence of several azeotropes (see Table 10.4). In this example, the P2 solution can be discarded because its Wilson model parameters are improper for predicting the physical reality of this system. Using the solutions P1 and P3, the Wilson model is capable of predicting the two azeotropes but with different accuracy for composition and pressure. Based on the VLE results of solutions P1 and P3, solution P3 appears to be better.

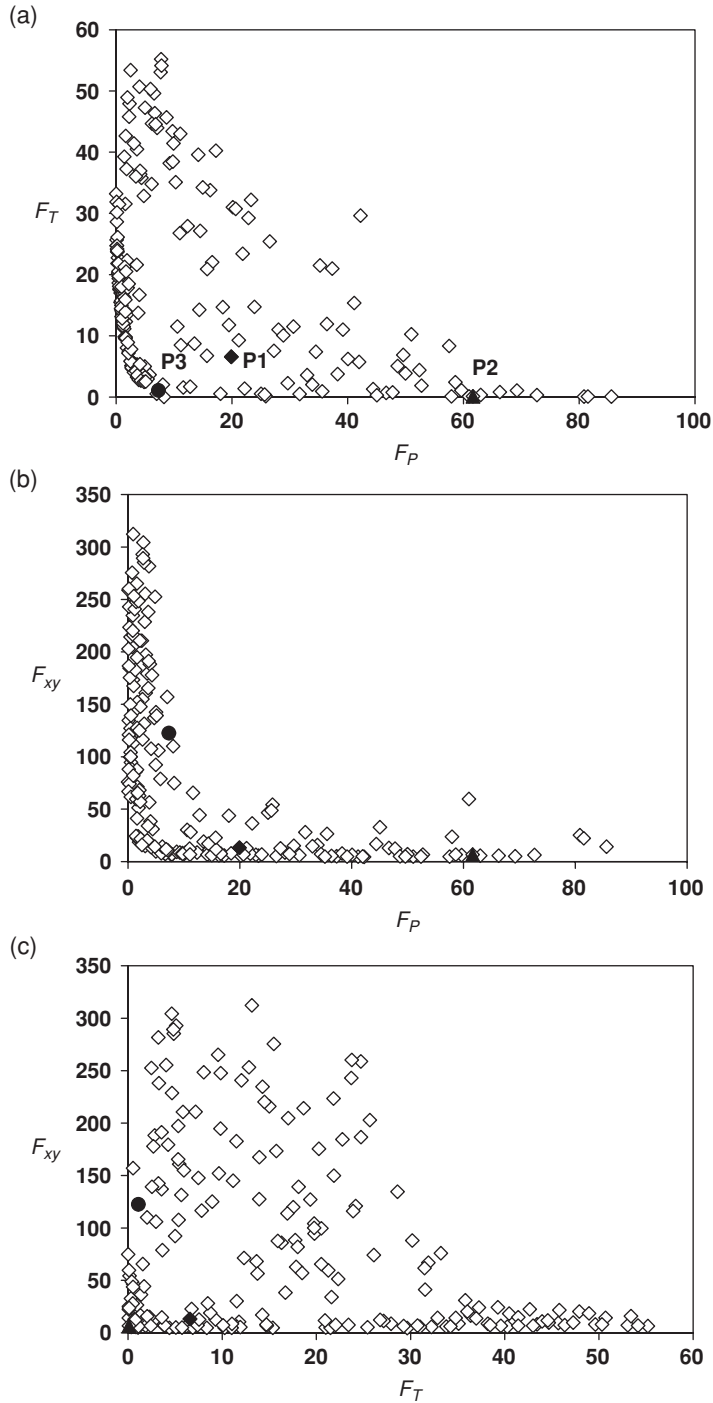


Figure 10.8 Pareto-optimal front for VLE data reconciliation of the benzene–hexafluorobenzene system at 50°C using three-objective optimization.

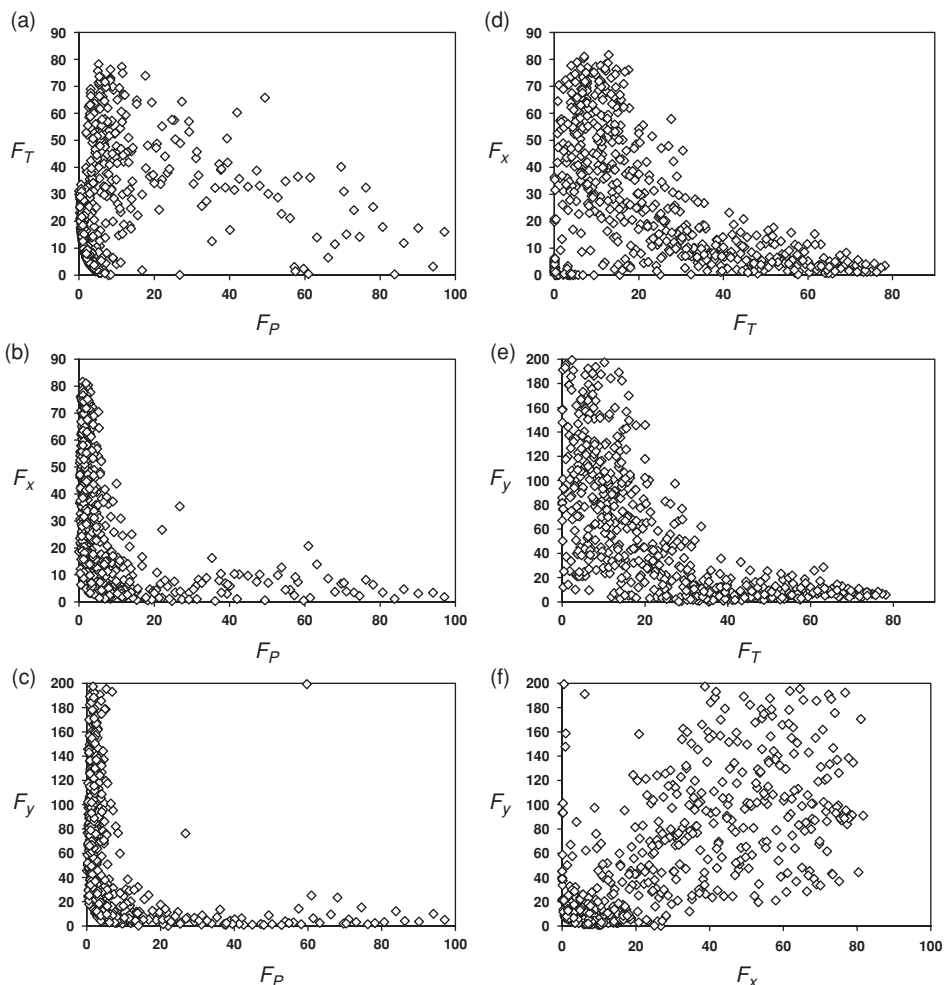


Figure 10.9 Pareto-optimal front for VLE data reconciliation of the benzene – hexafluorobenzene system at 50°C using four-objective optimization.

In summary, a solution that provides good agreement between measured and reconciled VLE data, a good distribution of residuals, and predicts experimental data such as azeotropes, can be selected from the MOO results. The user can use only the relevant and meaningful part of the Pareto-optimal set obtained from data reconciliation for process design and modeling. The MOO approach offers flexibility to identify several alternatives for the model parameters and the reconciled state variables and, as a consequence, it can provide a deeper level of analysis of model performance in phase equilibrium modeling.

10.5 Conclusions

Multi-objective optimization of the VLE data reconciliation using activity coefficient (local composition) models and EIV formulation, was studied. Pareto-optimal fronts for this data

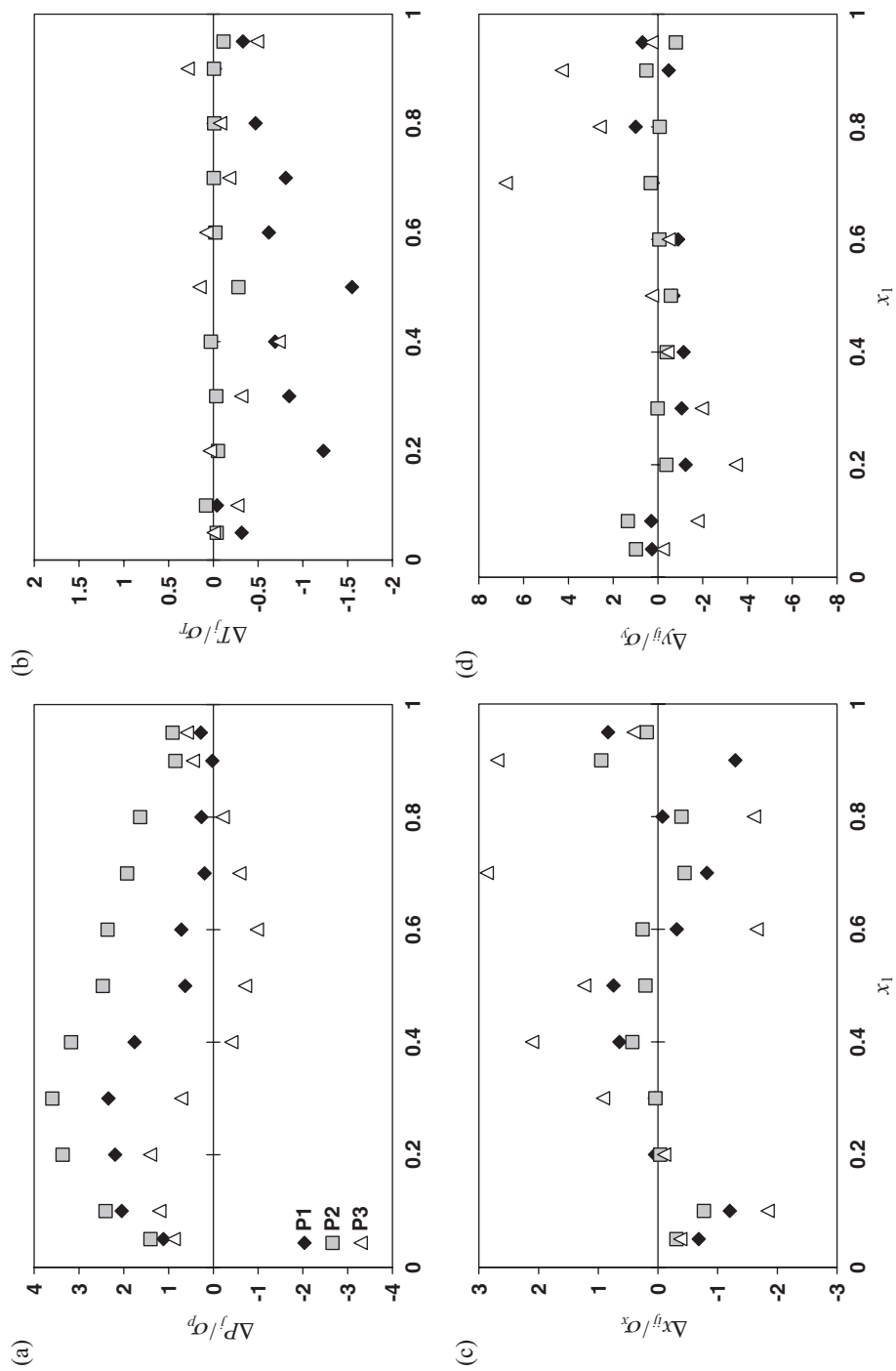


Figure 10.10 Error residuals ($\Delta z = z^t - z$) in state variables (x_1, y_1, P, T) for selected solutions from the Pareto-optimal front for VLE data reconciliation of the benzene – hexafluorobenzene system at 50°C using three-objective optimization.

Table 10.5 Reconciled data of selected solutions from Pareto front of three-objective optimization of VLE data reconciliation of benzene (1) – hexafluorobenzene (2) system at 50 °C (Figure 10.8).

P1			P2			P3					
P_j^t	T_j^t	x_{1j}^t	y_{1j}^t	P_j^t	T_j^t	x_{1j}^t	y_{1j}^t	P_j^t	T_j^t	x_{1j}^t	y_{1j}^t
255.39	49.97	0.0480	0.0483	255.88	50.00	0.0491	0.0503	255.01	50.00	0.0489	0.0469
255.78	50.00	0.0964	0.0979	256.39	50.01	0.0977	0.1009	254.35	49.98	0.0945	0.0919
255.53	49.90	0.2002	0.2064	257.52	50.00	0.1999	0.2089	254.20	50.00	0.1997	0.1999
257.18	49.93	0.3002	0.3129	259.31	50.00	0.3001	0.3160	254.42	49.97	0.3028	0.3103
259.29	49.94	0.4019	0.4217	261.70	50.00	0.4013	0.4239	255.61	49.94	0.4063	0.4238
261.07	49.87	0.5022	0.5275	264.19	49.98	0.5006	0.5278	258.79	50.01	0.5037	0.5303
264.71	49.95	0.5991	0.6264	267.51	50.00	0.6008	0.6288	261.85	50.01	0.5950	0.6276
267.63	49.93	0.6975	0.7222	270.57	50.00	0.6987	0.7224	266.31	49.99	0.7086	0.7412
270.85	49.96	0.7998	0.8154	273.18	50.00	0.7988	0.8123	270.05	49.99	0.7952	0.8201
272.94	50.00	0.8961	0.8991	274.34	50.00	0.9028	0.9020	273.68	50.02	0.9081	0.9130
272.57	49.97	0.9525	0.9500	273.65	49.99	0.9506	0.9457	273.10	49.96	0.9512	0.9488
$\theta_1 = -387.39$				$\theta_1 = -380.25$				$\theta_1 = -468.03$			
$\theta_2 = 865.73$				$\theta_2 = 895.51$				$\theta_2 = 1144.58$			

reconciliation problem were successfully obtained using the MODE-TL. Multi-objective optimization results are useful to identify different alternatives for model parameters and reconciled data in VLE modeling. In particular, MOO results allow the determination of the capabilities and limitations of thermodynamic models for VLE data reconciliation including its flexibility for modeling the phase equilibrium behavior. The MOO approach described in this chapter is general, can be applied with any thermodynamic model, and can be extended for modeling other types of phase equilibrium data, such as liquid-liquid equilibrium.

Exercises

- 10.1.** The results of data reconciliation depend on the assumed standard deviation of state variables and a change in these values can modify the characteristics of a MOO problem. Consider a standard deviation vector of (0.0025, 0.0025, 1.2, 0.07) for the vector of VLE state variables (x_1, y_1, P, T) at 50 °C. Perform VLE data reconciliation using this standard deviation vector and the Wilson model. Compare and discuss the results with those reported in this chapter.
- 10.2.** Study the VLE data reconciliation of benzene–hexafluorobenzene system at 40 °C using both NRTL and UNIQUAC models to calculate the liquid-phase activity coefficients. Use a standard deviation vector of (0.003, 0.0029, 1.7, 0.083) for the vector of state variables (x_1, y_1, P, T). Compare and discuss the results with those obtained using the Wilson model in this chapter.

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