

# **Part III**

## **Chemical Engineering Applications**

# 9

## Parameter Estimation in Phase Equilibria Calculations Using Multi-Objective Evolutionary Algorithms

*Sameer Punnapala<sup>1</sup>, Francisco M. Vargas<sup>1</sup> and Ali Elkamel<sup>1,2</sup>*

*<sup>1</sup>Department of Chemical Engineering, The Petroleum Institute, Abu Dhabi, UAE*

*<sup>2</sup>Department of Chemical Engineering, University of Waterloo, Canada*

### 9.1 Introduction

Multi-objective optimization has recently been gaining interest among the chemical engineering community. It is applied to numerous areas such as process design, biotechnology, petroleum refining, pharmaceuticals and polymerization [1]. In the field of thermodynamics, the use of multi-objective optimization has not yet been reported, to the best of our knowledge.

Accurate simultaneous predictions of phase equilibrium and thermophysical properties are crucial for the design and simulation of chemical processes. Equations of state (EOS) are extensively used in process industries and also in the academic community. The characteristic parameters in most EOS are exclusively tuned to the phase equilibrium data in order to obtain the best possible representation of Vapor-liquid equilibrium (VLE). Although VLE predictions are of primary importance for practical purposes, it is found that these fitted parameters give very poor estimates for other thermophysical properties like excess enthalpy, heat capacities, Joule Thomson coefficient, and so forth. The predictions

of second-derivative properties like isobaric heat capacity, speed of sound, thermal expansivity or isothermal compressibility using parameters tuned to phase equilibrium show large deviations from the actual value. The contrary also happens, i.e. parameters tuned to thermophysical properties cannot simultaneously describe the phase equilibrium. For most of the thermodynamic models, the objective functions are highly nonlinear and non-convex. This calls for the use of global optimization strategies for parameter estimation. Performances of genetic algorithms, simulated annealing, particle swarm optimization, harmonic search, and so forth, have been studied for VLE modeling since the early 2000s. There are a number of publications devoted to parameter estimation for phase equilibria calculations [2, 3, 4, 5]. However, all these formulate only a single objective function for optimization, with the usual practice of minimizing the error between experimental and model predictions. In this chapter, we illustrate the use of multi-objective optimization that can be applied when two or more conflicting objectives are addressed simultaneously.

Multi-objective (MO) optimization problems can be solved by different techniques among which evolutionary algorithms are particularly suited because they are capable of finding multiple optimal solutions in one single simulation run [6, 7]. Genetic algorithm (GA)-based algorithms such as the non-dominated sorting genetic algorithm (NSGA, NSGA-II, etc.) have found many applications in the field of chemical engineering. Particle swarm optimization (PSO) is a population-based stochastic optimization technique developed by Eberhart and Kennedy in 1995. It is inspired by the coordinated behavior in a flock of birds, swarm of bees, or a school of fish [8]. Particle swarm optimization can be easily implemented and has only few parameters to adjust which makes it a better candidate than genetic algorithms. Extensive studies on using PSO for MO applications have been carried out by different researchers and as such specialized variants of PSO are available [9]. The scope of this chapter is not to illustrate all the different techniques—rather the authors intend to explore the application of MO technique for phase equilibrium calculations.

## 9.2 Particle Swarm Optimization (PSO)

For the sake of readers who are unfamiliar with the PSO technique, we briefly revisit the important concepts of single objective PSO. The basic idea is that a number of particles (solutions) are used, which constitute a swarm moving around the search space with a velocity, looking for the best solution. Suppose the search space is  $n$ -dimensional, then the  $i^{\text{th}}$  particle of the swarm can be represented as  $x_i = (x_{i1}, x_{i2}, \dots, x_{in})$  and the velocity of this particle is given by  $v_i = (v_{i1}, v_{i2}, \dots, v_{in})$ . The best previous position (personal best) of the  $i^{\text{th}}$  particle (i.e. the position giving the best function value) is recorded as  $p_i = (p_{i1}, p_{i2}, \dots, p_{in})$  and the global best position obtained by any particle in the entire swarm can be represented as  $p_{gn}$ . For each time step, the particle compares its current position with the personal best and also the global best and manipulates the velocity for the next iteration accordingly. The particles adjust its velocity and position according to Equations (9.1) and (9.2):

$$v_m^{k+1} = w^* v_m^k + c_1 r_1 (p_m^k - x_m^k) + c_2 r_2 (p_{gn}^k - x_m^k) \quad (9.1)$$

$$x_m^{k+1} = x_m^k + v_m^{k+1} \quad (9.2)$$

Where  $k$  represents the time step,  $c_1$  and  $c_2$  are the cognitive and social parameters respectively (normally,  $c_1 = c_2 = 2$ ),  $r_1$  and  $r_2$  are random numbers within the interval  $[0,1]$  and  $w$  is known as inertia, which influences convergence to either a local (smaller  $w$ ) or global (larger  $w$ ) optimum. Linearly decreasing the inertia weight from a relatively large value to a small value through the course of the PSO run gives the best PSO performance compared with fixed inertia weight settings.

A pseudocode for the algorithm is given below [10]:

### ***PSO Algorithm***

*For each particle:*

*Initialize particle*

*End*

*Do*

*For each particle*

*Calculate fitness value*

*If the fitness value is better than its personal best*

*set current value as the new pbest*

*End*

*Choose the particle with the best fitness value of all as gbest*

*For each particle*

*Calculate particle velocity according to equation (9.1)*

*Update particle position according to equation (9.2)*

*End*

*While maximum iterations or minimum error criteria is not attained*

There are different variants of PSO available and a good number of references can be found in the literature [11]. The performance of single-objective PSO for parameter estimation in phase equilibrium calculations, phase stability analyses, and so forth, provides very promising results [12, 13]. The relative simplicity of PSO and its population based approach have made it a potential candidate to be extended to multi-objective optimization. Many different strategies for solving MO problems using PSO have been published since 2002 [14].

### **9.2.1 Multi-Objective Particle Swarm Optimization (MO-PSO)**

There are two approaches to solve multi-objective problems using PSO [11, 15]. The first method involves either combining all objective functions into a single one or considering each objective function separately. In these approaches, each particle is evaluated with only one objective function at a time and the standard algorithm for single objective PSO is followed. The main limitation with this procedure is in defining a protocol for the proper manipulation of objective functions to ensure their convergence to the actual Pareto front. This traditional category to solve MO problems includes weighted aggregation, objective function ordering, and non-Pareto vector evaluated approaches. The second category consists of approaches that evaluate all objective functions for each particle, and, based on the concept of Pareto optimality, produce non-dominated best positions (often called leaders) to guide the particles. The determination of leaders is nontrivial, as they have to be selected

among a plethora of non-dominated solutions in the neighborhood of a particle. This is the main challenge related to the second category.

A general MO-PSO algorithm is given below [16]:

### **MO-PSO Algorithm**

*Start*

*Initialize swarm, velocities and best positions.*

*Set an empty set as the external archive.*

*While (stopping criteria not satisfied) Do*

*For each particle of the swarm*

*Select a leader from the external archive (if applicable).*

*Update particle velocity and position.*

*Evaluate new particle position.*

*Update best position and external archive.*

*End For*

*End While*

*End*

Some of the commonly used MO-PSO approaches are briefly discussed below [14].

- (i) **Weighted-sum approach:** This technique combines all the objective functions into a single one. In other words, the multi-objective problem is transformed to a single objective function. A function  $F(x)$  can be expressed as a linear combination of non-negative weights ( $w_i$ ):

$$F(x) = \sum_{i=1}^n w_i f_i(x) \quad (9.3)$$

such that

$$\sum_{i=1}^n w_i = 1 \quad (9.4)$$

Parsopoulos and Vrahatis adopted three types of weighting/aggregating functions:

- Conventional weighted aggregation (CWA) where the weights are fixed during the run.
- Bang-bang weighted aggregation (BWA) where the weights abruptly change during the run. For a bi-objective problem, the weights are adapted as follows:

$$\begin{aligned} w_1(t) &= \text{sign}(\sin(2t\pi/a)) \\ w_2(t) &= 1 - w_1(t) \end{aligned} \quad (9.5)$$

where:  $a$  is user-defined adaptation frequency and  $t$  stands for the iteration number.

- Dynamic weighted aggregation (DWA) where the weights are gradually modified during the run. For a bi-objective problem, the weights are adapted as follows:

$$\begin{aligned} w_1(t) &= |\sin(2t\pi/a)| \\ w_2(t) &= 1 - w_1(t) \end{aligned} \quad (9.6)$$

- (ii) The lexicographic approach: In this approach, the user ranks the objective functions in increasing order of priority. The optimum solution is then obtained by minimizing the objective functions separately, starting with the most important one. Hu and Eberhart [14] proposed such an ordering scheme.
- (iii) Non-Pareto vector evaluated approaches: Parsopoulos and Vrahatis [16] also proposed the vector evaluated PSO (VEPSO) scheme, which employs one swarm per objective function and evaluates it only with this function. The best positions of one swarm are used to update the velocity of another swarm corresponding to a different objective function.
- (iv) Pareto-based approaches: These approaches use the concept of Pareto dominance to determine the best positions (leaders) that guide the swarm during the search. There are several schemes to select the leader, making it an active area for research. Coello Coello and his group [9, 17] proposed one of the first Pareto-based PSO approaches. The basic idea in this proposal was to create an external archive (repository) that will store the non-dominated solutions and a geographically based approach to maintain diversity. Works from several other evolutionary multi-objective researchers can be found in the reference.

### 9.3 Parameter Estimation in Phase Equilibria Calculations

Phase-equilibria calculations play a vital role in the design, development, operation, optimization and control of chemical processes. Commercial process simulators like ASPEN, and so forth, use equations of state and / or activity coefficient models for thermodynamic modeling of vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE), and so forth. The phase behavior of the system is highly sensitive to the parameters used in these thermodynamic models. For instance, the predictive capability of an equation of state is highly dependent on the binary interaction parameters. These parameters are estimated by tuning the model to match certain observed properties. Using the correct set of parameters for these models is vital in order to obtain reliable results. Generally, the model parameters are obtained by fitting the data to different phase equilibrium properties like binary VLE/LLE data, critical points, vapor pressure, liquid density, etc. and the objective functions are formulated based on either the classical least squares (LS) or maximum likelihood approaches (ML). As mentioned above, simultaneous description of phase equilibrium and thermophysical properties is a very difficult task in applied thermodynamics. Here we illustrate one important example where the liquid phase is modeled by an activity coefficient model. The objective is to have a simultaneous prediction of both phase equilibrium (VLE) and the heat of mixing (excess enthalpy). A number of optimal solutions are obtained and the parameters are selected depending upon which prediction is more important. The idea presented here can be extended to solve other exercise problems listed at end of this chapter. Also the reader is free to choose any suitable MO optimization technique to find the optimal solutions.

### 9.4 Model Description

The nonrandom, two-liquid (NRTL) activity coefficient model can be used to describe the phase behavior of the ethyl formate (1)–methanol (2) system at 45 °C [18]. The model

parameters can be estimated by fitting to the phase equilibrium data (VLE, LLE, etc.) or the heat of mixing data [19]. The following sections illustrate the procedure.

### 9.4.1 Vapor Liquid Equilibrium

For equilibrium to exist, the temperature, pressure and fugacities of component  $i$  in all phases must be constant. At low pressures we can neglect the Poynting correction factor and ideal vapor phase can be assumed (fugacity coefficient in vapor phase is assumed unity). With these considerations, the experimental activity coefficient  $\gamma_i^{\text{exp}}$  can be written by:

$$\gamma_i^{\text{exp}} = \frac{y_i P}{x_i P_i^{\text{sat}}}, \quad i = 1, \dots, \quad (9.7)$$

where,  $x_i$  and  $y_i$  are experimental mole fractions of component  $i$  in liquid and vapor phases respectively at equilibrium, and  $P_i^{\text{sat}}$  is the pure component vapor pressure of component  $i$  at system temperature  $T$  and pressure  $P$ .

The NRTL model proposed by Renon and Prausnitz is used for the liquid phase to predict the VLE and excess enthalpy. The NRTL equation for the excess Gibbs energy is given by:

$$\frac{g^E}{RT} = x_1 x_2 \left[ \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \quad (9.8)$$

where:

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \quad \tau_{21} = \frac{g_{21} - g_{11}}{RT} \quad (9.9)$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}) \quad G_{21} = \exp(-\alpha_{12} \tau_{21}) \quad (9.10)$$

The parameter  $\alpha_{12}$  is related to the nonrandomness in the mixture, which is fixed at the typical value of 0.3 for our model. There are therefore two parameters namely,  $(g_{12}-g_{22})$  and  $(g_{21}-g_{11})$  that need to be estimated for the NRTL model. The activity coefficients are:

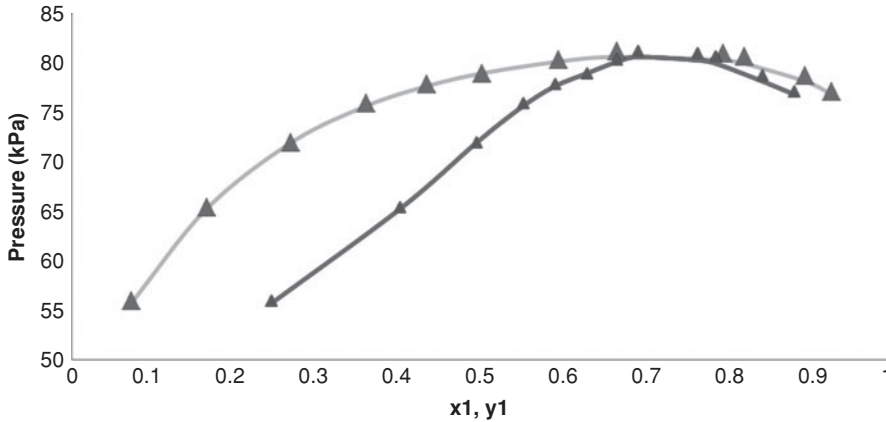
$$\begin{aligned} \ln(\gamma_1) &= x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \\ \ln(\gamma_2) &= x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \end{aligned} \quad (9.11)$$

The VLE data for the binary mixture at 45 °C is taken from the works of Nagata *et al.* [18]. We would like to determine the parameters for NRTL model to match the VLE data. The objective function can be formulated in terms of the difference between experimental and model predicted activity coefficients as:

$$f_1 = \sum_{j=1}^{ndat} \sum_{i=1}^c \left\{ 100 * \left( \frac{\gamma_{ij}^{\text{exp}} - \gamma_{ij}^{\text{cal}}}{\gamma_{ij}^{\text{exp}}} \right) \right\}^2 \quad (9.12)$$

where,  $ndat$  is the number of experimental VLE data points and  $c$  is the number of components in the mixture.

The above error function is minimized using single objective PSO and the parameters were calculated as  $(g_{12}-g_{22}) = 2246.1$  J/mol and  $(g_{21}-g_{11}) = 1178.14$  J/mol that best fit the VLE data (Figure 9.1).



**Figure 9.1** Vapor-liquid equilibria for the ethyl formate (1)–methanol(2) system at 45 °C.

### 9.4.2 Heat of Mixing

Heats of mixing determine the relative volatilities and consequently the temperature profile in a distillation column. Hence the heats of mixing data are needed for reliable and economic designs of industrial separation processes. In applied thermodynamics, the simultaneous prediction of vapor-liquid equilibrium (VLE) and excess enthalpies (heat of mixing) by either equations of state or activity coefficient models has always been a very difficult problem. The excess enthalpy ( $h^E$ ), which indicates the temperature dependence of excess Gibbs energy ( $g^E$ ), can be calculated using the Gibbs–Helmholtz equation:

$$\left(\frac{\partial(g^E/T)}{\partial T}\right)_{P,x} = -\left(\frac{h^E}{T^2}\right) \quad (9.13)$$

For the NRTL model, the expression for excess enthalpies can be derived to be as given below:

$$\frac{h^E}{RT} = \frac{g^E}{RT} - x_1 x_2 \alpha_{12} \left[ \frac{x_1 \tau_{21}^2 G_{21}}{(x_1 + x_2 G_{21})^2} + \frac{x_2 \tau_{12}^2 G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (9.14)$$

where,  $(g^E/RT)$  is calculated from Equation (9.8).

Experimental heats of mixing for the binary system of Ethyl formate - methanol are also reported by Nagata *et al.* [18]. Using the set of parameters obtained by fitting to VLE data, the excess enthalpies are calculated from Equation (9.14) and shown in Figure 9.2.

The NRTL model does not give good predictions for the heat of mixing with the set of parameters obtained from VLE fitting. If we define a second objective function that minimizes the error in heat of mixing as:

$$f_2 = \sum_{i=1}^{ndat} \left\{ 100 * \left( \frac{h_i^{\text{exp}} - h_i^{\text{cal}}}{h_i^{\text{exp}}} \right) \right\}^2 \quad (9.15)$$

Optimizing the above function  $f_2$  gives a good fit for the excess enthalpy (Figure 9.3) but at the expense of degrading the VLE predictions (Figure 9.4). The parameters obtained



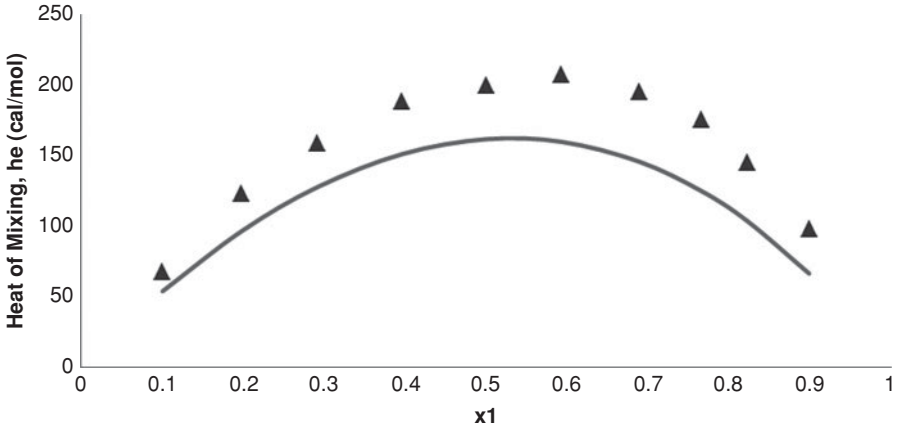


Figure 9.2 Heats of mixing for ethyl formate(1)-methanol(2) system at 45°C.

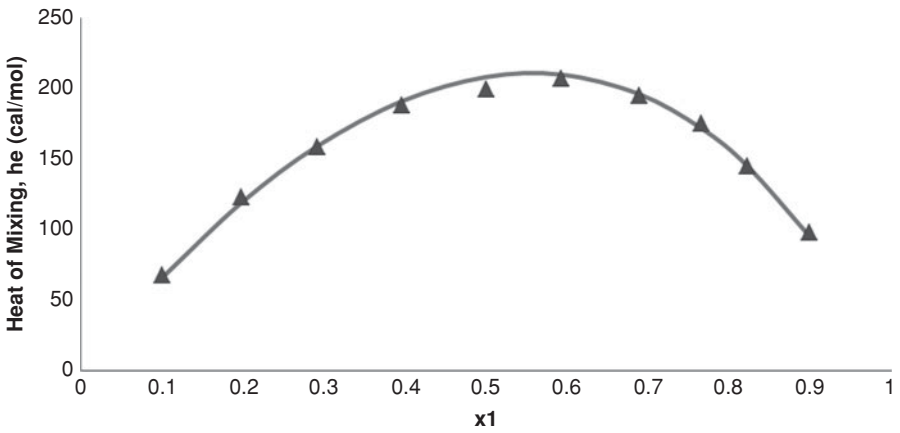


Figure 9.3 Heats of mixing when the parameters are fit to excess enthalpies.

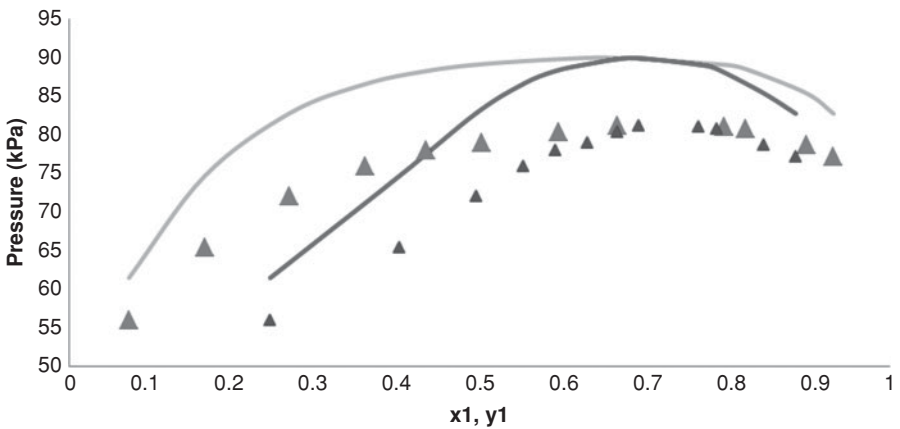


Figure 9.4 VLE predictions when the parameters are fit to excess enthalpies.

in this case were  $(g_{12}-g_{22}) = 3596.07.1$  J/mol and  $(g_{21}-g_{11}) = 1602.71$  J/mol. This shows that the simultaneous prediction of vapor-liquid equilibrium and heat of mixing using one set of parameters for the NRTL model is not possible. The decision-maker has to make a compromise on one of the objectives based on the final requirement.

## 9.5 Multi-Objective Optimization Results and Discussion

In order to solve the two conflicting objective functions  $f_1$  and  $f_2$  formulated in the preceding section, the multi-objective particle swarm optimization technique (MO-PSO) is used. To illustrate, we adopt the weighted-sum approach strategy. The problem is converted to a single objective function by using different weights and the Pareto front is developed. To validate the MO-PSO code, it was used on a test-function initially.

The following two-objective functions are considered:

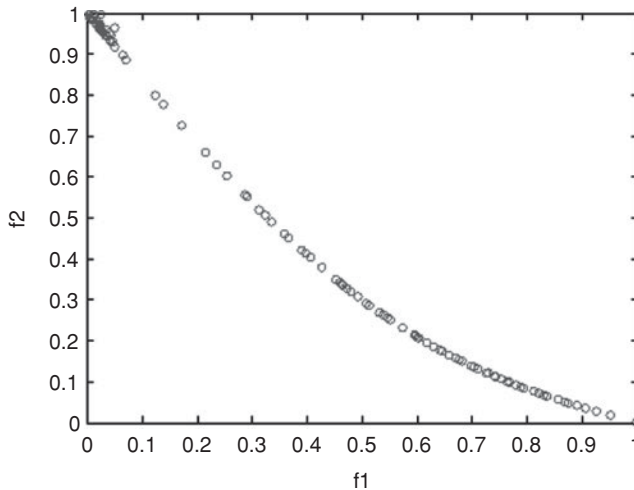
$$\text{Minimize : } f_1(x) = x_1 \quad (9.16)$$

$$f_2(x) = 1 + x_2^2 - x_1 - \alpha \sin(b\pi x_1)$$

$$\text{Subject to : } 0 \leq x_1 \leq 1, \quad -2 \leq x_2 \leq 2$$

The problem has two parameters,  $a$  and  $b$ , which control the convexity of the search space. The complete Pareto-optimal front is shown in Figure 9.5, which is consistent with the one reported by Deb [20].

The parameters used for the MO-PSO are given in Table 9.1 [21].



**Figure 9.5** Pareto-optimal set for Test function using MO-PSO.

**Table 9.1** PSO parameters used.

Parameter	Value
$c_1$	2
$c_2$	2
$w$	Initially 0.9, gradually reduced to 0.4 over time
No. of particles	40
Max Iterations	10 000

After validating the code, MO-PSO is used to optimize the two objective functions  $f_1$  and  $f_2$  for the parameter estimation problem. The combined objective function can be formulated as:

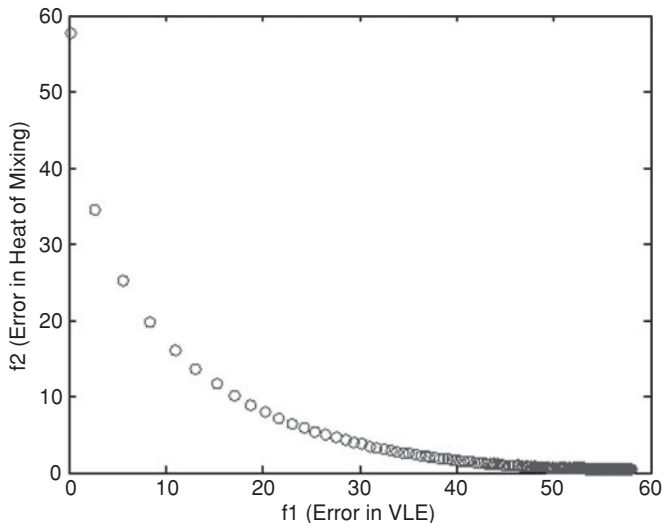
$$F(x) = w_1 f_1(x) + w_2 f_2(x) \quad (9.17)$$

where:  $f_1$  and  $f_2$  represent the sum of errors for VLE and heat of mixing prediction respectively as explained in previous section. The function  $F(x)$  is solved using the standard PSO algorithm for different weights  $w_1$  and  $w_2$ , where

$$w_2 = 1 - w_1 \quad (9.18)$$

The same parameters given in Table 9.1 are used for the MO-PSO. The complete Pareto-front (Figure 9.6) and the errors with respect to different parameters are shown below (Figures 9.7 and 9.8).

The bi-objective function is solved using Particle Swarm Optimization (coded in MATLAB 7.11) for different weights. Figures 9.7 and 9.8 help to select the optimum parameters

**Figure 9.6** Pareto-optimal set for fitting VLE and excess enthalpy.

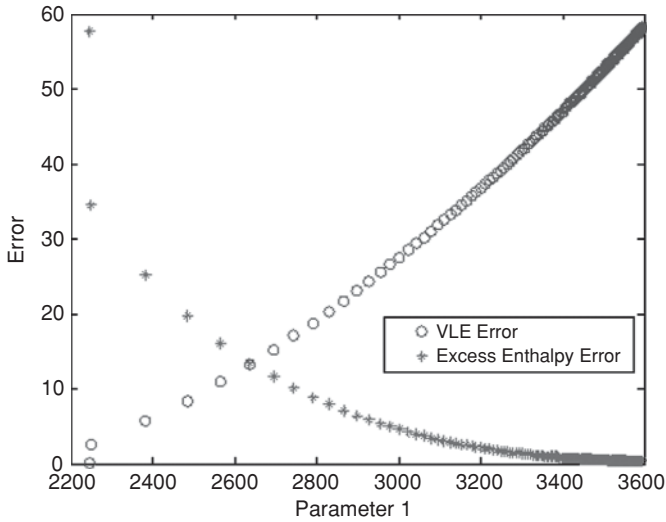


Figure 9.7 Error in VLE and heat of mixing w.r.t. parameter 1 ( $g_{12}-g_{22}$ ).

for the NRTL model depending on the final outcome of the problem. For instance, in cases where accurate prediction of VLE is the sole objective, the parameters are selected that make the error  $f_1$  as low as possible and vice-versa for heat of mixing calculations. If both the predictions are equally important (e.g. in a distillation column), tradeoff solutions should be used (which minimizes both  $f_1$  and  $f_2$  simultaneously). In the example presented in this chapter, only two objective functions have been used (VLE and heat of mixing).

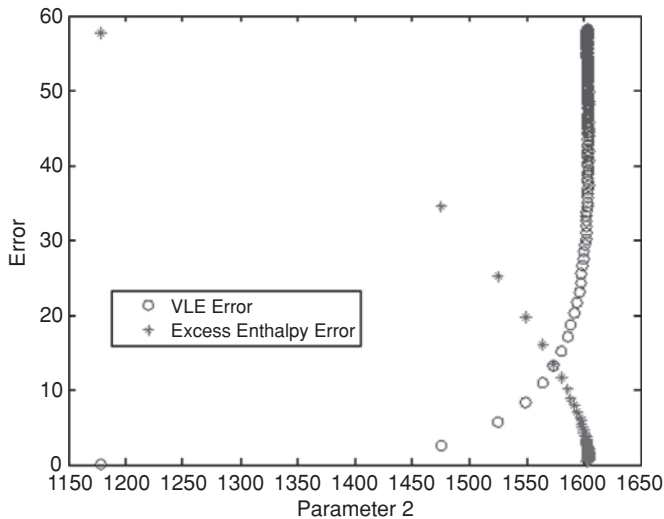


Figure 9.8 Error in VLE and heat of mixing w.r.t. parameter 2 ( $g_{21}-g_{11}$ )

There may be instances where additional objectives must be formulated to determine the best solutions for the process under study; therefore detailed knowledge of the application is required to make a final decision. The selected parameters should be able to predict other thermodynamic phenomena like existence of azeotropes, retrograde condensation, and so forth. Decision-making depends on the user preference and there exist some methods in the literature to rank the Pareto-optimal solutions [22]. The computational time for the weighted-aggregation technique is quite high as the objectives are solved for a number of weights to obtain a good Pareto-front.

## 9.6 Conclusions

This chapter introduced the application of multi-objective optimization for phase equilibria calculations, which is one of the most important areas in the field of chemical engineering. There are numerous instances where the user has to make a decision based on number of factors. Using the correct set of parameters is crucial for all the process simulators; incorrect values lead to large errors in prediction, affecting the design, operation and optimization of the process. Simultaneous description of phase equilibrium and thermophysical properties using equations of state models is a very difficult task. The parameters fitted for phase equilibrium are not able to predict the thermophysical properties and vice-versa. Evolutionary algorithms like PSO promise to be the best approach for solving multi-objective problems as these can give the optimal solutions in one single simulation run. The weighted-aggregation technique illustrated in this chapter is the easiest way to solve the multi-objective problem, although it suffers from crucial limitations like difficulty in fixing the weights, finding the Pareto-optimal solutions in non-convex objective space, and increased computational cost.

## Acknowledgments

The authors would like to thank Dr. Hatem Zeineldin (Masdar Institute) and Professor Walter Chapman (Rice University) for helpful discussions.

## Nomenclature

$a$	user-defined adaptation frequency in DWA and BWA.
$BWA$	Bang-bang weighted aggregation.
$c$	number of components in mixture.
$c_1$	cognitive parameter in PSO.
$c_2$	social parameter in PSO.
$CWA$	conventional weighted aggregation.
$DWA$	dynamic weighted aggregation.
$g_{12}$ - $g_{22}$	NRTL parameter.
$G_{12}$ , $G_{21}$	NRTL parameters.
$g_{21}$ - $g_{11}$	NRTL parameter.

<i>GA</i>	genetic algorithm.
$g^E$	excess Gibb's energy.
$h^E$	excess enthalpy (heat of mixing).
<i>k</i>	time step.
<i>LLE</i>	liquid-liquid equilibrium.
<i>LS</i>	least squares.
<i>ML</i>	maximum likelihood.
<i>MO</i>	multi-objective.
<i>MO-PSO</i>	multi-objective particle swarm optimization.
<i>n</i>	search space dimension.
<i>ndat</i>	number of experimental points.
<i>NRTL</i>	nonrandom two liquid theory (activity coefficient model).
<i>NSGA</i>	non-dominated sorting genetic algorithm.
<i>P</i>	total pressure.
$p_{gn}$	global best position.
$p_i$	personal best position of the $i^{th}$ particle.
$P^{sat}$	vapor pressure of the pure component.
<i>PSO</i>	particle swarm optimization.
<i>R</i>	universal gas constant.
$r_1, r_2$	random numbers between 0 and 1.
<i>t</i>	iteration number.
<i>T</i>	temperature.
<i>VEPSO</i>	vector evaluated PSO.
$v_i$	velocity of the $i^{th}$ particle.
<i>VLE</i>	vapor-liquid equilibrium.
<i>w</i>	inertia factor in PSO.
$w_1, w_2$	weights in a bi-objective function.
$x_i$	mole fraction in liquid phase.
$x_i$	position of the $i^{th}$ particle.
$y_i$	mole fraction in vapor phase.

## Greek Characters

$\alpha_{12}$	NRTL parameter
$\gamma$	activity coefficient
$\tau_{12}, \tau_{21}$	NRTL parameters

## Exercises

Generate Pareto-optimal solutions for the following problems:

- 9.1.** Fit the parameters for the NRTL Activity coefficient model for ethanol (1) – cyclohexane (2) binary mixture at 298.15 K to:
- (a) VLE and excess enthalpy.

(b) Excess enthalpy and excess heat capacity which is related to the excess enthalpy

$$\text{by } c_p^E = \left( \frac{\partial h^E}{\partial T} \right)_{P,x}.$$

(c) VLE, excess enthalpy and excess heat capacity.

The experimental data for the binary mixture are given below.

Experimental VLE data for the binary mixture at 298.15 K [23]:

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$x_1$	0.0128	0.1511	0.2701	0.4129	0.5355	0.6766	0.7598	0.8364	0.9175	0.9697
$y_1$	0.213	0.3212	0.3345	0.3448	0.3534	0.3712	0.3924	0.4321	0.5332	0.714

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Binary excess molar enthalpies  $h^E$  in  $\text{J mol}^{-1}$  at 298.15 K [24]:

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$x_1$	0.1020	0.1708	0.3166	0.4427	0.5526	0.6495	0.9434
$h^E$	426.2	520.2	617.5	639.8	617.9	564.7	147.4

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Binary excess molar heat capacities  $c_p^E$  in  $\text{J mol}^{-1} \text{K}^{-1}$  at 298.15 K [24]:

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$x_1$	0.0195	0.149	0.244	0.300	0.343	0.413	0.558	0.657	0.762	0.877	0.958
$c_p^E$	4.60	9.19	10.10	9.94	9.80	8.95	7.50	5.88	3.84	1.93	0.67

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**9.2.** Equations of state can be fit to speed of sound data that finds important application for reservoir fluids as it would help to determine the properties of fluids under reservoir conditions without any PVT measurements. However, cubic equations like SRK and PR does not give good predictions for the speed of sound when the parameters are tuned to the critical properties. Using multi-objective optimization, estimate the parameters for Peng–Robinson EOS for the methane (1) -butane (2) mixture in the supercritical region ( $x_1 = 0.894$ ) that can give a fairly good description of both phase equilibrium and other thermophysical properties. The experimental data for velocity of sound is given below:

Experimental data for speed of sound for methane (1) + butane (2),  $x_1 = 0.894$  [25]:

P (MPa)	u (m/s)
17.237	438.0
16.547	428.4
15.858	419.4
15.168	410.8
14.479	402.9
13.79	395.6
13.10	388.9
12.411	383.1
11.721	378.0
11.032	373.7
10.342	370.3
9.653	367.8
8.963	366.0
8.274	365.1
7.584	364.8
6.895	365.2
6.205	366.4
5.516	368.0
4.826	370.1
4.137	372.7
3.447	375.5
2.758	378.5
2.068	381.6

The velocity of sound using PR EOS can be calculated using the following expressions:

$$c^2 = - \left( \frac{V^2}{M} \right) \left[ \frac{RT}{(v-b)^2} + \frac{2a(V+b)}{(v^2+2bV-b^2)^2} - T \left( \frac{R}{V-b} - \frac{a_1}{V^2+2bV-b^2} \right)^2 \right. \\ \left. \times \left( C_p^o - R - \frac{Ta_2}{2\sqrt{2}} \ln \frac{V+b-\sqrt{2b}}{V+b+\sqrt{2b}} \right)^{-1} \right]$$

$$a_1 = \frac{da}{dT}, \quad a_2 = \frac{d^2a}{dT^2}$$

Other symbols have the usual meaning and van-der Waals mixing rules can be used to calculate the mixture coefficients.



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