Handbook of Test Problems in Local and Global Optimization

Nonconvex Optimization and Its Applications

Volume 33

The titles published in this series are listed at the end of this volume.

Handbook of Test Problems in Local and Global Optimization

by

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Preface

Significant research activities have taken place in the areas of local and global optimization in the last two decades. Many new theoretical, computational, algorithmic, and software contributions have resulted. It has been realized that despite these numerous contributions, there does not exist a systematic forum for thorough experimental computational testing and evaluation of the proposed optimization algorithms and their implementations.

Well-designed nonconvex optimization test problems are of major importance for academic and industrial researchers interested in algorithmic and software development. It is remarkable that even though nonconvex models dominate all the important application areas in engineering and applied sciences, there is only a limited class of reported representative test problems. This book reflects our long term efforts in designing a benchmark database and it is motivated primarily from the need for nonconvex optimization test problems. The present collection of benchmarks includes test problems from literature studies and a large class of applications that arise in several branches of engineering and applied science.

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Chapter 1

Introduction

During the last two decades, a significant growth has taken place in algorithmic and software development of local and global optimization methods for a variety of classes of nonlinear, discrete, and dynamic mathematical problems. These problems include (i) multi-quadratic programming, (ii) bilinear and biconvex, (iii) generalized geometric programming, (iv) general constrained nonlinear optimization, (v) bilevel optimization, (vi) complementarity, (vii) semidefinite programming, (viii) mixed-integer nonlinear optimization, (ix) combinatorial optimization, and (x) optimal control problems. Relative to these advances there have been very limited efforts in establishing a systematic benchmark framework for the evaluation of the algoritms and their implementations (Hock and Schittkowski (1981); Floudas and Pardalos (1990); Bongartz et al. (1995)). A well-designed experimental computational testing framework is of primary importance in identifying the merits of each algorithm and implementation.

The principal objective of this book is to present a collection of challenging test problems arising in literature studies and a wide spectrum of applications. These applications include : pooling/blending operations, heat exchanger network synthesis, phase and chemical reaction equilibrium, robust stability analysis, batch plant design under uncertainty, chemical reactor network synthesis, parameter estimation and data reconcilliation, conformational problems in clusters of atoms and molecules, pump network synthesis, trim loss minimization, homogeneous azeotropic separation system, dynamic optimization problems in parameter estimation and in reactor network synthesis, and optimal control problems.

This book reflects our long term efforts in establishing a benchmark database of nonconvex optimization problems. These efforts started a decade ago with the book by Floudas and Pardalos (1990) which introduced the first collection of nonconvex test problems for constrained global optimization algorithms.

Several approaches have been proposed to address the challenging task of testing and benchmarking local and global optimization algorithms and software. In regard to the test problems presented in this book, the following

C. A. Floudas et al., *Handbook of Test Problems in Local and Global Optimization*

approaches have been considered.

Collections of randomly generated test problems with known solution.

Problem instances with certain characteristics that have been used to test some aspects of specific algorithms.

Collection of *real-world* problems, that is, problems that model a variety of practical applications.

Furthermore, there exist different types of specific problem instances that are used to test some aspects of an algorithm. Such types of test problems include :

Worst case test problems : For example a global optimization test problem with an exponential number of local minima can be used to check the efficiency of an algorithm based on local searches or simulated annealing methods.

Standard test problems : A test problem becomes standard if it is used frequently. Standard test problems are usually small dimension problems published in papers to illustrate the main steps of a particular algorithm. Most of the references listed at the end of this book contain standard test problems.

This book contains many nonconvex optimization test problems that model a diverse range of practical applications. The main criteria in selecting such test problems have been (a) the size (ranging from small to medium to large), (b) the mathematical properties (exhibiting different types of nonconvexities), and (c) the degree of difficulty (resulting from the wide range of applications).

Chapter 2 presents test problems in quadratic programming. Chapter 3 discusses multi-quadratic programming problems, and Chapter 4 presents univariate polynomial test problems. Chapter 5 deals with bilinear problems and their applications in pooling/blending operations, distillation column sequencing, and heat exchanger networks. Chapter 6 addresses biconvex and (D.C.) optimization problems with applications in phase and chemical reaction equilibrium. Chapter 7 introduces generalized geometric programming problems with applications in design and robust stability analysis. Chapter 8 focuses on the large class of twice-continuously differentiable NLPs and presents literature test problems and applications in the areas of batch design under uncertainty, chemical reactor networks, parameter estimation, phase and chemical equilibrim with equations of state, and clusters of atoms and molecules. Chapter 9 presents test problems for bilevel optimization and focuses on bilevel linear and bilevel quadratic programming problems. Chapter 10 discusses test problems for linear and nonlinear complementarity. Chapter 11 introduces test problems in the area of semidefinite programming. Chapter 12 addresses mixed-integer nonlinear optimization test problems and presents literature test problems and applications in heat exchanger network synthesis, pump network synthesis, and trim loss minimization problems. Chapter 13 introduces several combinatorial optimization problems. Chapter 14 presents test problems of nonlinear constrained systems of equations with applications in homogeneous azeotropic systems. Finally, Chapter 15 introduces dynamic optimization test problems with applications in reactor networks, parameter estimation, and optimal control.

The input files of the algebraic test problems presented in this book are available in the GAMS modeling language format, while the input files of the differential-algebraic test problems are available in the MINOPT modeling language format. Both types of input files of the aforementioned test problems are at the following internet address :

`http://titan.princeton.edu/TestProblems`

These input files can also be accessed via anonymous ftp as follows :

```
ftp titan.princeton.edu <enter>
name: anonymous <enter>
password: (your e-mail address) <enter>
cd pub/TestProblems <enter>
get filename.gms
quit
```

Chapter 2

Quadratic Programming Problems

2.1 Introduction

In this chapter nonconvex quadratic programming test problems are considered. These test problems have a quadratic objective function and linear constraints. Quadratic programming has numerous applications (Pardalos and Rosen (1987), Floudas and Visweswaran (1995)) and plays an important role in many nonlinear programming methods. Recent methods of generating challenging quadratic programming test problems and disjointly constrained bilinear programming test problems can be found in the work of Vicente et al. (1992) and Calamai et al. (1993). Furthermore, a very broad class of difficult combinatorial optimization problems such as integer programming, quadratic assignment, and the maximum clique problem can be formulated as nonconvex quadratic programming problems.

2.2 Test Problem 1

Objective function

$$\min_{\boldsymbol{x}} \ f(\boldsymbol{x}) = \boldsymbol{c}^T\boldsymbol{x} - 0.5\boldsymbol{x}^T\boldsymbol{Q}\boldsymbol{x}$$

Constraints

$$20x_1 + 12x_2 + 11x_3 + 7x_4 + 4x_5 \quad \leq \quad 40$$

Variable bounds

$$0 \leq \boldsymbol{x} \leq 1$$

Data

$$\boldsymbol{c} = (42, 44, 45, 47, 47.5)^T$$

$$\boldsymbol{Q} = 100\boldsymbol{I}$$

where $\boldsymbol{I}$ is the identity matrix.

Problem Statistics

No. of continuous variables	5
No. of linear inequalities	1
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

- Objective function: -17
- Continuous variables

$$\boldsymbol{x} = (1, 1, 0, 1, 0)^T.$$

2.3 Test Problem 2

Objective function

$$\min_{\boldsymbol{x},y} f(\boldsymbol{x}, y) = \boldsymbol{c}^T\boldsymbol{x} - 0.5\boldsymbol{x}^T\boldsymbol{Q}\boldsymbol{x} + dy$$

Constraints

$$\begin{aligned} 6x_1 + 3x_2 + 3x_3 + 2x_4 + x_5 &\leq 6.5 \\ 10x_1 + 10x_3 + y &\leq 20 \end{aligned}$$

Variable bounds

$$0 \leq \boldsymbol{x} \leq 1$$
$$0 \leq y$$

Data

$$\boldsymbol{c} = (-10.5, -7.5, -3.5, -2.5, -1.5)^T$$

$$d = -10$$

$$\boldsymbol{Q} = 100\boldsymbol{I}$$

where $\boldsymbol{I}$ is the identity matrix.

Problem Statistics

No. of continuous variables	6
No. of linear inequalities	2
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

- Objective function: -413
- Continuous variables

$$\boldsymbol{x} = (0, 1, 0, 1, 1)^T$$

$$y = 20.$$

2.4 Test Problem 3

Objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} f(\boldsymbol{x}, \boldsymbol{y}) = \boldsymbol{c}^T\boldsymbol{x} - 0.5\boldsymbol{x}^T\boldsymbol{Q}\boldsymbol{x} + \boldsymbol{d}^T\boldsymbol{y}$$

Constraints

$$\begin{aligned}
2x_1 + 2x_2 + y_6 + y_7 &\leq 10 \\
2x_1 + 2x_3 + y_6 + y_8 &\leq 10 \\
2x_2 + 2x_3 + y_7 + y_8 &\leq 10 \\
-8x_1 + y_6 &\leq 0 \\
-8x_2 + y_7 &\leq 0 \\
-8x_3 + y_8 &\leq 0 \\
-2x_4 - y_1 + y_6 &\leq 0 \\
-2y_2 - y_3 + y_7 &\leq 0 \\
-2y_4 - y_5 + y_8 &\leq 0
\end{aligned}$$

Variable bounds

$$\begin{aligned} 0 &\leq \boldsymbol{x} \leq 1 & \\ 0 &\leq y_i \leq 1 & i = 1,2,3,4,5,9 \\ 0 &\leq y_i \leq 3 & i = 6,7,8 \end{aligned}$$

Data

$$\boldsymbol{c} = (5,5,5,5)^T$$

$$\boldsymbol{d} = (-1,-1,-1,-1,-1,-1,-1,-1,-1)^T$$

$$\boldsymbol{Q} = 100\boldsymbol{I}$$

where $\boldsymbol{I}$ is the identity matrix.

Problem Statistics

No. of continuous variables	13
No. of linear inequalities	9
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

- Continuous variables

$$\boldsymbol{x} = (1,1,1,1)^T$$

$$\boldsymbol{y} = (1,1,1,1,1,3,3,3,1)^T.$$

2.5 Test Problem 4

Objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} f(x,\boldsymbol{y}) = 6.5x - 0.5x^2 - y_1 - 2y_2 - 3y_3 - 2y_4 - y_5$$

Constraints

$$\begin{aligned} \boldsymbol{Az} &\leq \boldsymbol{b} \\ \boldsymbol{z} &= (x, \boldsymbol{y})^T \end{aligned}$$

Variable bounds

$$\begin{aligned} 0 \leq \boldsymbol{x} &\leq 1 \\ y_i &\leq 1 \qquad\qquad i = 3,4 \\ y_5 &\leq 2 \end{aligned}$$

Data

$\boldsymbol{A}$ is the following (5x6) matrix :

$$\boldsymbol{A} = \begin{pmatrix} 1 & 2 & 8 & 1 & 3 & 5 \\ -8 & -4 & -2 & 2 & 4 & -1 \\ 2 & 0.5 & 0.2 & -3 & -1 & -4 \\ 0.2 & 2 & 0.1 & -4 & 2 & 2 \\ -0.1 & -0.5 & 2 & 5 & -5 & 3 \end{pmatrix}$$

$$\boldsymbol{b} = (16, -1, 24, 12, 3)^T$$

Problem Statistics

No. of continuous variables	6
No. of linear inequalities	5
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

- Objective function: -11.005
- Continuous variables

$$x = 0$$

$$\boldsymbol{y} = (6, 0, 1, 1, 0)^T.$$

2.6 Test Problem 5

Objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} f(\boldsymbol{x},\boldsymbol{y}) = \boldsymbol{c}^T\boldsymbol{x} - 0.5\boldsymbol{x}^T\boldsymbol{Q}\boldsymbol{x} + \boldsymbol{d}^T\boldsymbol{y}$$

Constraints

$$\begin{aligned} \boldsymbol{A}\boldsymbol{z} &\leq \boldsymbol{b} \\ \boldsymbol{z} &= (\boldsymbol{x},\boldsymbol{y})^T \end{aligned}$$

Variable bounds

$$0 \leq \boldsymbol{z} \leq 1$$

Data

$\boldsymbol{A}$ is the following (11x10) matrix :

$$\boldsymbol{A} = \begin{pmatrix} -2 & -6 & -1 & 0 & -3 & -3 & -2 & -6 & -2 & -2 \\ 6 & -5 & 8 & -3 & 0 & 1 & 3 & 8 & 9 & -3 \\ -5 & 6 & 5 & 3 & 8 & -8 & 9 & 2 & 0 & -9 \\ 9 & 5 & 0 & -9 & 1 & -8 & 3 & -9 & -9 & -3 \\ -8 & 7 & -4 & -5 & -9 & 1 & -7 & -1 & 3 & -2 \\ -7 & -5 & -2 & 0 & -6 & -6 & -7 & -6 & 7 & 7 \\ 1 & -3 & -3 & -4 & -1 & 0 & -4 & 1 & 6 & 0 \\ 1 & -2 & 6 & 9 & 0 & -7 & 9 & -9 & -6 & 4 \\ -4 & 6 & 7 & 2 & 2 & 0 & 6 & 6 & -7 & 4 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ -1 & -1 & -1 & -1 & -1 & -1 & -1 & -1 & -1 & -1 \end{pmatrix}$$

$$\boldsymbol{b} = (-4, 22, -6, -23, -12, -3, 1, 12, 15, 9, -1)^T$$

$$\boldsymbol{d} = (10, 10, 10)^T$$

$$\boldsymbol{c} = (-20, -80, -20, -50, -60, -90, 0)^T$$

$$\boldsymbol{Q} = 10\boldsymbol{I}$$

where $\boldsymbol{I}$ is the identity matrix.

Problem Statistics

No. of continuous variables	10
No. of linear inequalities	11
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

- Objective function: -268.01463
- Continuous variables

$$\boldsymbol{x} = (1, 0.90755, 0, 1, 0.71509, 1, 0)^T$$

$$\boldsymbol{y} = (0.91698, 1, 1)^T.$$

2.7 Test Problem 6

Objective function

$$\min_{\boldsymbol{x}} \ f(\boldsymbol{x}) = \boldsymbol{c}^T\boldsymbol{x} - 0.5\boldsymbol{x}^T\boldsymbol{Q}\boldsymbol{x}$$

Constraints

$$\begin{aligned} \boldsymbol{A}\boldsymbol{x} &\leq \boldsymbol{b} \\ \boldsymbol{x} &\in \Re^{10} \end{aligned}$$

Variable bounds

$$0 \leq \boldsymbol{x} \leq 1$$

Data

$\boldsymbol{A}$ is the following (5x10) matrix :

$$\boldsymbol{A} = \begin{pmatrix} -2 & -6 & -1 & 0 & -3 & -3 & -2 & -6 & -2 & -2 \\ 6 & -5 & 8 & -3 & 0 & 1 & 3 & 8 & 9 & -3 \\ -5 & 6 & 5 & 3 & 8 & -8 & 9 & 2 & 0 & -9 \\ 9 & 5 & 0 & -9 & 1 & -8 & 3 & -9 & -9 & -3 \\ -8 & 7 & -4 & -5 & -9 & 1 & -7 & -1 & 3 & -2 \end{pmatrix}$$

$$\boldsymbol{b} = (-4, 22, -6, -23, -12)^T$$

$$\boldsymbol{c} = (48, 42, 48, 45, 44, 41, 47, 42, 45, 46)^T$$

$$\boldsymbol{Q} = 100\boldsymbol{I}$$

where $\boldsymbol{I}$ is the identity matrix.

Problem Statistics

No. of continuous variables	10
No. of linear inequalities	5
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

- Objective function: -39
- Continuous variables

$$\boldsymbol{x} = (1, 0, 0, 1, 1, 1, 0, 1, 1, 1)^T.$$

2.8 Test Problem 7

This class of the test problems belongs to separable concave quadratic programming problems.

Objective function

$$\min_{\boldsymbol{x}} f(\boldsymbol{x}) = -0.5 \sum_i \lambda_i (x_i - \alpha_i)^2$$

Constraints

$$\begin{aligned} \boldsymbol{Ax} &\leq \boldsymbol{b} \\ \boldsymbol{x} &\in \Re^{20} \end{aligned}$$

Variable bounds

$$0 \leq \boldsymbol{x}$$

Data

$$b = (-5, 2, -1, -3, 5, 4, -1, 0, 9, 40)^T$$

The sets of parameters involve the λ's which correspond to a set of non-negative eigenvalues, and the α's. These parameter values will be provided for five cases along with the corresponding best known optimum solutions in the following sections.

$\boldsymbol{A}$ is a (10x20) matrix and $\boldsymbol{A}^T$ is the following (20x10) matrix :

$$\boldsymbol{A} = \begin{pmatrix}
-3 & 7 & 0 & -5 & 1 & 1 & 0 & 2 & -1 & 1 \\
7 & 0 & -5 & 1 & 1 & 0 & 2 & -1 & -1 & 1 \\
0 & -5 & 1 & 1 & 0 & 2 & -1 & -1 & -9 & 1 \\
-5 & 1 & 1 & 0 & 2 & -1 & -1 & -9 & 3 & 1 \\
1 & 1 & 0 & 2 & -1 & -1 & -9 & 3 & 5 & 1 \\
1 & 0 & 2 & -1 & -1 & -9 & 3 & 5 & 0 & 1 \\
0 & 2 & -1 & -1 & -9 & 3 & 5 & 0 & 0 & 1 \\
2 & -1 & -1 & -9 & 3 & 5 & 0 & 0 & 1 & 1 \\
-1 & -1 & -9 & 3 & 5 & 0 & 0 & 1 & 7 & 1 \\
-1 & -9 & 3 & 5 & 0 & 0 & 1 & 7 & -7 & 1 \\
-9 & 3 & 5 & 0 & 0 & 1 & 7 & -7 & -4 & 1 \\
3 & 5 & 0 & 0 & 1 & 7 & -7 & -4 & -6 & 1 \\
5 & 0 & 0 & 1 & 7 & -7 & -4 & -6 & -3 & 1 \\
0 & 0 & 1 & 7 & -7 & -4 & -6 & -3 & 7 & 1 \\
0 & 1 & 7 & -7 & -4 & -6 & -3 & 7 & 0 & 1 \\
1 & 7 & -7 & -4 & -6 & -3 & 7 & 0 & -5 & 1 \\
7 & -7 & -4 & -6 & -3 & 7 & 0 & -5 & 1 & 1 \\
-7 & -4 & -6 & -3 & 7 & 0 & -5 & 1 & 1 & 1 \\
-4 & -6 & -3 & 7 & 0 & -5 & 1 & 1 & 0 & 1 \\
-6 & -3 & 7 & 0 & -5 & 1 & 1 & 0 & 2 & 1
\end{pmatrix}$$

Problem Statistics

No. of continuous variables	20
No. of linear inequalities	10
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

Case 1 : $\lambda_i = 1$, $\alpha_i = 2$ for $i = 1, \ldots, 20$

- Objective function: -394.7506

- Continuous variables

$$\boldsymbol{x} = (0, 0, 28.8024, 0, 0, 4.1792, 0, 0, 0, 0, 0, 0, 0, 0, \\ 0.6188, 4.0933, 0, 2.3064, 0, 0)^T$$

Case 2 : $\lambda_i = 1$, $\alpha_i = -5$ for $i = 1, \ldots, 20$

- Objective function: -884.75058
- Continuous variables

$$\boldsymbol{x} = (0, 0, 28.8024, 0, 0, 4.1792, 0, 0, 0, 0, 0, 0, 0, 0, \\ 0.6188, 4.0933, 0, 2.3064, 0, 0)^T$$

Case 3 : $\lambda_i = 20$, $\alpha_i = 0$ for $i = 1, \ldots, 20$

- Objective function: -8695.01193
- Continuous variables

$$\boldsymbol{x} = (0, 0, 28.8024, 0, 0, 4.1792, 0, 0, 0, 0, 0, 0, 0, 0, \\ 0.6188, 4.0933, 0, 2.3064, 0, 0)^T$$

Case 4 : $\lambda_i = 1$, $\alpha_i = 8$ for $i = 1, \ldots, 20$

- Objective function: -754.75062
- Continuous variables

$$\boldsymbol{x} = (0, 0, 28.8024, 0, 0, 4.1792, 0, 0, 0, 0, 0, 0, 0, 0, \\ 0.6188, 4.0933, 0, 2.3064, 0, 0)^T$$

Case 5 : $\lambda_i = i$, $\alpha_i = 2$ for $i = 1, \ldots, 20$

- Objective function: -4150.4101
- Continuous variables

$$\boldsymbol{x} = (0, 0, 1.04289, 0, 0, 0, 0, 0, 0, 0, 1.74674, 0, 0.43147, 0, 0, \\ 4.43305, 0, 15.85893, 0, 16.4889)^T.$$

2.9 Test Problem 8

This class of global optimization problems belongs to minimum concave cost trasportation problems.

Objective function

$$\min_{\boldsymbol{x}} f(\boldsymbol{x}) = \sum_{i=1}^{m}\sum_{j=1}^{n}(c_{ij}x_{ij} + d_{ij}x_{ij}^2)$$

Constraints

$$\begin{aligned} \sum_{i=1}^{m} x_{ij} &= b_j \quad j = 1, \ldots, n \\ \sum_{j=1}^{n} x_{ij} &= a_i \quad i = 1, \ldots, m \end{aligned}$$

Variable bounds

$$0 \leq \boldsymbol{x} \leq 1$$

Data

The parameters d_{ij}, a_i, and b_j satisfy the following conditions :

$$\begin{aligned} d_{ij} &\leq 0 & i = 1, \ldots, m, \quad j = 1, \ldots, n \\ \sum_{i=1}^{m} a_i &= \sum_{j=1}^{n} b_j & i = 1, \ldots, m, \quad j = 1, \ldots, n \end{aligned}$$

$$n = 4$$

$$m = 6$$

$$\boldsymbol{a} = (8, 24, 20, 24, 16, 12)^T$$

$$\boldsymbol{b} = (29, 41, 13, 21)^T$$

$\boldsymbol{C} = (c_{ij})$ is the following (6x4) matrix :

$$C = \begin{pmatrix} 300 & 270 & 460 & 800 \\ 740 & 600 & 540 & 380 \\ 300 & 490 & 380 & 760 \\ 430 & 250 & 390 & 600 \\ 210 & 830 & 470 & 680 \\ 360 & 290 & 400 & 310 \end{pmatrix}$$

$D = (d_{ij})$ is the following (6x4) matrix :

$$D = \begin{pmatrix} -7 & -4 & -6 & -8 \\ -12 & -9 & -14 & -7 \\ -13 & -12 & -8 & -4 \\ -7 & -9 & -16 & -8 \\ -4 & -10 & -21 & -13 \\ -17 & -9 & -8 & -4 \end{pmatrix}$$

Problem Statistics

No. of continuous variables	24
No. of linear equalities	10
No. of convex inequalities	–
No. of nonlinear equalities	–

The resulting model contains $(n+m)$ equality constraints and $(n \times m)$ variables. There is exactly one redundant equality constraint. When any one of the constraints is dropped the remaining constraints form a linearly independent system of constraints, which results in a basic vector for the trasportation problem consisting of $(n+m-1)$ basic variables. Furthermore, if all the a_i's, and b_j's are positive integers, then every basic solution is an integer solution.

Global Solution

- Objective function: 15639
- Continuous variables

$$\begin{array}{lllll} x_{11} = 6 & x_{12} = 2 & x_{22} = 3 & x_{24} = 21 & x_{31} = 20 \\ x_{41} = 24 & x_{51} = 3 & x_{53} = 13 & x_{62} = 12. & \end{array}$$

2.10 Test Problem 9

Given an undirected graph $G(V, E)$ where V is a set of vertices and E is a set of edges, a clique is defined to be a set of vertices that is completely interconnected. The maximum clique problem consists of determining a clique of maximum cardinality.

The maximum clique problem can be stated as a nonconvex quadratic programming problem over the unit simplex (Pardalos and Phillips (1990)) and its general formulation is :

$$\min_{\boldsymbol{x}} f(\boldsymbol{x}) = \sum_{(i,j)\in E} x_i x_j$$

$$\begin{aligned} s.t. \quad \sum_{i\in V} x_i &= 1 \\ x_i &\geq 0 \quad i = 1,\ldots,|V| \end{aligned}$$

If k is the size of the maximum clique of G, then $f(\boldsymbol{x}^*) = 0.5(1-(1/k))$. The global maximum $\boldsymbol{x}^*$ is defined by $x_i^* = (1/k)$ if the vertex i belongs to the clique and zero otherwise.

In the following, a specific instance of this general formulation is presented.

<u>Objective function</u>

$$\min_{\boldsymbol{x}} f(\boldsymbol{x}) = \sum_{i=1}^{n-1} x_i x_{i+1} + \sum_{i=1}^{n-2} x_i x_{i+2} + x_1 x_9 + x_1 x_{10} + x_2 x_{10} + x_1 x_5 + x_4 x_7$$

<u>Constraints</u>

$$\sum_{i=1}^{n} x_i = 1$$

<u>Variable bounds</u>

$$0 \leq \boldsymbol{x} \quad i = 1,\ldots,n$$

Data

$$n = 10$$

Problem Statistics

No. of continuous variables	10
No. of linear equalities	1
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

- Objective function: 0.375
- Continuous variables

$$\boldsymbol{x} = (0, 0, 0, 0.25, 0.25, 0.25, 0.25, 0, 0)^T.$$

2.11 Test Problem 10

This test problem has a separable quadratic objective function where there exists a convex part (i.e., the summation multiplied by +0.5) and a concave part (i.e., the summation multiplied by −0.5).

Objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} f(\boldsymbol{x}, \boldsymbol{y}) = -0.5 \sum_{i}^{10} \lambda_i (x_i - \alpha_i)^2 + 0.5 \sum_{i}^{10} \mu_i (y_i - \beta_i)^2$$

Constraints

$$\begin{array}{rcl} \boldsymbol{A}_1 \boldsymbol{x} + \boldsymbol{A}_2 \boldsymbol{y} & \leq & \boldsymbol{b} \\ \boldsymbol{x} & \in & \Re^{10} \\ \boldsymbol{y} & \in & \Re^{10} \end{array}$$

Variable bounds

$$\begin{array}{c} 0 \leq \boldsymbol{x} \\ 0 \leq \boldsymbol{y} \end{array}$$

Data

$$\lambda = (63, 15, 44, 91, 45, 50, 89, 58, 86, 82)^T$$

$$\mu = (42, 98, 48, 91, 11, 63, 61, 61, 38, 26)^T$$

$$\alpha = (-19, -27, -23, -53, -42, 26, -33, -23, 41, 19)^T$$

$$\beta = (-52, -3, 81, 30, -85, 68, 27, -81, 97, -73)^T$$

$\boldsymbol{A}_1$, which corresponds to the concave variables, is the (10x10) matrix :

$$A_1 = \begin{pmatrix} 3 & 5 & 5 & 6 & 4 & 4 & 5 & 6 & 4 & 4 \\ 5 & 4 & 5 & 4 & 1 & 4 & 4 & 2 & 5 & 2 \\ 1 & 5 & 2 & 4 & 7 & 3 & 1 & 5 & 7 & 6 \\ 3 & 2 & 6 & 3 & 2 & 1 & 6 & 1 & 7 & 3 \\ 6 & 6 & 6 & 4 & 5 & 2 & 2 & 4 & 3 & 2 \\ 5 & 5 & 2 & 1 & 3 & 5 & 5 & 7 & 4 & 3 \\ 3 & 6 & 6 & 3 & 1 & 6 & 1 & 6 & 7 & 1 \\ 1 & 2 & 1 & 7 & 8 & 7 & 6 & 5 & 8 & 7 \\ 8 & 5 & 2 & 5 & 3 & 8 & 1 & 3 & 3 & 5 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix}$$

A_2, that corresponds to the convex variables, is the following (10x10) matrix :

$$A_2 = \begin{pmatrix} 8 & 4 & 2 & 1 & 1 & 1 & 2 & 1 & 7 & 3 \\ 3 & 6 & 1 & 7 & 7 & 5 & 8 & 7 & 2 & 1 \\ 1 & 7 & 2 & 4 & 7 & 5 & 3 & 4 & 1 & 2 \\ 7 & 7 & 8 & 2 & 3 & 4 & 5 & 8 & 1 & 2 \\ 7 & 5 & 3 & 6 & 7 & 5 & 8 & 4 & 6 & 3 \\ 4 & 1 & 7 & 3 & 8 & 3 & 1 & 6 & 2 & 8 \\ 4 & 3 & 1 & 4 & 3 & 6 & 4 & 6 & 5 & 4 \\ 2 & 3 & 5 & 5 & 4 & 5 & 4 & 2 & 2 & 8 \\ 4 & 5 & 5 & 6 & 1 & 7 & 1 & 2 & 2 & 4 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix}$$

$$\boldsymbol{b} = (380, 415, 385, 405, 470, 415, 400, 460, 400, 200)^T$$

Problem Statistics

No. of continuous variables	20
No. of linear inequalities	10
No. of convex inequalities	–
No. of nonlinear equalities	–

Global Solution

- Objective function: 49318
- Continuous variables

$$\boldsymbol{x} = (0, 0, 0, 0, 0, 4.348, 0, 0, 0, 0)^T$$
$$\boldsymbol{y} = (0, 0, 0, 62.609, 0, 0, 0, 0, 0, 0)^T.$$

Chapter 3

Quadratically Constrained Problems

3.1 Introduction

In this chapter, we discuss nonconvex quadratically constrained test problems. These include problems with separable quadratic constraints, complementarity type constraints, and integer type constraints. Notice that every simple binary constraint of the form :

$$x \in \{0,1\}$$

can be written as :

$$\begin{aligned} -x^2 + x &\leq 0 \\ 0 \leq x &\leq 1 \end{aligned}$$

or

$$x^2 - x = 0$$

In the following sections, a number of standard test problems that are quadratically constrained are presented.

3.2 Test Problem 1

This test problem is taken from Hock and Schittkowski (1981) (Problem 106). Its objective function is linear while it features three linear inequalities and three nonconvex inequalities.

Objective function

$$\min_{\boldsymbol{x}} f(\boldsymbol{x}) = x_1 + x_2 + x_3$$

Constraints

$$\begin{aligned}
-1 + 0.0025(x_4 + x_6) &\leq 0 \\
-1 + 0.0025(-x_4 + x_5 + x_7) &\leq 0 \\
-1 + 0.01(-x_5 + x_8) &\leq 0 \\
100x_1 - x_1x_6 + 8333.33252x_4 - 83333.333 &\leq 0 \\
x_2x_4 - x_2x_7 - 1250x_4 + 1250x_5 &\leq 0 \\
x_3x_5 - x_3x_8 - 2500x_5 + 1250000 &\leq 0
\end{aligned}$$

Variable bounds

$$\begin{gathered}
100 \leq x_1 \leq 10000 \\
1000 \leq x_2 \leq 10000 \\
1000 \leq x_3 \leq 10000 \\
10 \leq x_4 \leq 1000 \\
10 \leq x_5 \leq 1000 \\
10 \leq x_6 \leq 1000 \\
10 \leq x_7 \leq 1000 \\
10 \leq x_8 \leq 1000
\end{gathered}$$

Problem Statistics

No. of continuous variables	8
No. of linear inequalities	3
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	3

Global Solution

- Objective function: 7049.25

- Continuous variables

$$\boldsymbol{x} = (579.19, 1360.13, 5109.92, 182.01, 295.60, 217.99, 286.40, 395.60)^T.$$

3.3 Test Problem 2

This problem consists of a nonconvex quadratic objective function subject to six nonconvex quadratic inequality constraints, and it is taken from Colville (1970).

Objective function

$$\min_{\boldsymbol{x}} f(\boldsymbol{x}) = 37.293239x_1 + 0.8356891x_1x_5 + 5.3578547x_3^2 - 40792.141$$

Constraints

$$\begin{array}{rcl}
-0.0022053x_3x_5 + 0.0056858x_2x_5 + 0.0006262x_1x_4 - 6.665593 & \leq & 0 \\
0.0022053x_3x_5 - 0.0056858x_2x_5 - 0.0006262x_1x_4 - 85.334407 & \leq & 0 \\
0.0071317x_2x_5 + 0.0021813x_3^2 + 0.0029955x_1x_2 - 29.48751 & \leq & 0 \\
-0.0071317x_2x_5 - 0.0021813x_3^2 - 0.0029955x_1x_2 + 9.48751 & \leq & 0 \\
0.0047026x_3x_5 + 0.0019085x_3x_4 + 0.0012547x_1x_3 - 15.699039 & \leq & 0 \\
-0.0047026x_3x_5 - 0.0019085x_3x_4 - 0.0012547x_1x_3 + 10.699039 & \leq & 0
\end{array}$$

Variable bounds

$$\begin{array}{l}
78 \leq x_1 \leq 102 \\
33 \leq x_2 \leq 45 \\
27 \leq x_3 \leq 45 \\
27 \leq x_4 \leq 45 \\
27 \leq x_5 \leq 45
\end{array}$$

Problem Statistics

No. of continuous variables	5
No. of linear inequalities	–
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	6

Global Solution

- Objective function: -30665.5387
- Continuous variables

$$\boldsymbol{x} = (78, 33, 29.9953, 45, 36.7758)^T.$$

3.4 Test Problem 3

This test problem is taken from Hesse (1973), and it features a concave quadratic objective function subject to linear and quadratic constraints. There exist 18 local minima, and this problem can be decomposed into three smaller independent problems.

Objective function

$$\begin{aligned}\min_{\boldsymbol{x}} \; f(\boldsymbol{x}) = & -25(x_1-2)^2-(x_2-2)^2-(x_3-1)^2 \\ & -(x_4-4)^2-(x_5-1)^2-(x_6-4)^2\end{aligned}$$

Constraints

$$\begin{aligned}(x_3-3)^2+x_4 &\geq 4 \\ (x_5-3)^2+x_6 &\geq 4 \\ x_1-3x_2 &\leq 2 \\ -x_1+x_2 &\leq 2 \\ x_1+x_2 &\leq 6 \\ x_1+x_2 &\geq 2\end{aligned}$$

Variable bounds

$$\begin{aligned}&0 \leq x_1 \\ &0 \leq x_2 \\ &1 \leq x_3 \leq 5 \\ &0 \leq x_4 \leq 6 \\ &1 \leq x_5 \leq 5 \\ &0 \leq x_6 \leq 10\end{aligned}$$

Problem Statistics

No. of continuous variables	6
No. of linear inequalities	4
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	2

Global Solution

- Objective function: -310

- Continuous variables

$$\boldsymbol{x} = (5, 1, 5, 0, 5, 10)^T.$$

3.5 Test Problem 4

This test problem is taken from Ben-Saad (1989), and it features a linear objective function subject to a single reverse convex inequality and three linear inequalities.

Objective function

$$\min_{\boldsymbol{x}} f(\boldsymbol{x}) = -2x_1 + x_2 - x_3$$

Constraints

$$\begin{aligned}
\boldsymbol{x}^T \boldsymbol{A}^T \boldsymbol{A}\boldsymbol{x} - 2\boldsymbol{y}^T \boldsymbol{A}\boldsymbol{x} + \| \boldsymbol{y} \|^2 - 0.25 \| \boldsymbol{b} - \boldsymbol{z} \|^2 &\geq 0 \\
x_1 + x_2 + x_3 - 4 &\leq 0 \\
3x_2 + x_3 - 6 &\leq 0 \\
\boldsymbol{x} &\in \Re^3
\end{aligned}$$

Variable bounds

$$\begin{aligned}
&0 \leq x_1 \leq 2 \\
&0 \leq x_2 \\
&0 \leq x_3 \leq 3
\end{aligned}$$

Data

$\boldsymbol{A}$ is the following (3x3) matrix :

$$\boldsymbol{A} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -2 & 1 & -1 \end{pmatrix}$$

$$\boldsymbol{b} = (3, 0, -4)^T$$

$$\boldsymbol{y} = (1.5, -0.5, -5)^T$$

$$\boldsymbol{z} = (0, -1, -6)^T$$

Problem Statistics

No. of continuous variables	1
No. of linear inequalities	3
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	1

Global Solution

- Objective function: -4
- Continuous variables

$$\boldsymbol{x} = (0.5, 0, 3)^T.$$

Chapter 4

Univariate Polynomial Problems

4.1 Introduction

In this chapter, we describe both unconstrained and constrained nonconvex univariate polynomial problems. The reported global solutions are from the studies of Visweswaran and Floudas (1992).

4.2 Test Problem 1

This test problem is taken from Wingo (1985).

Objective function

$$\min_{x} \; x^6 - \frac{52}{25}x^5 + \frac{39}{80}x^4 + \frac{71}{10}x^3 - \frac{79}{20}x^2 - x + \frac{1}{10}$$

Variable bounds

$$-2 \leq x \leq 11$$

Global Solution

- Objective function: -29763.233
- Continuous variables

$$x = 10.$$

C. A. Floudas et al., *Handbook of Test Problems in Local and Global Optimization*

4.3 Test Problem 2

This example concerns the minimization of a 50^{th} degree polynomial, and it is taken from Moore (1979).

Objective function

$$\min_x \sum_{i=1}^{50} a_i x^i$$

where

$$\begin{aligned} a = (&-500.0, 2.5, 1.666666666, 1.25, 1.0, 0.8333333, 0.714285714,\\ &0.625, 0.555555555, 1.0, -43.6363636, 0.41666666, 0.384615384,\\ &0.357142857, 0.3333333, 0.3125, 0.294117647, 0.277777777, 0.263157894,\\ &0.25, 0.238095238, 0.227272727, 0.217391304, 0.208333333, 0.2,\\ &0.192307692, 0.185185185, 0.178571428, 0.344827586, 0.6666666,\\ &-15.48387097, 0.15625, 0.1515151, 0.14705882, 0.14285712,\\ &0.138888888, 0.135135135, 0.131578947, 0.128205128, 0.125,\\ &0.121951219, 0.119047619, 0.116279069, 0.113636363, 0.1111111,\\ &0.108695652, 0.106382978, 0.208333333, 0.408163265, 0.8). \end{aligned}$$

Variable bounds

$$1 \leq x \leq 2$$

Global Solution

- Objective function: -663.5
- Continuous variables

$$x = 1.0911.$$

4.4 Test Problem 3

This example is taken from Wilkinson (1963).

Objective function

$$\min_x \; 0.000089248x - 0.0218343x^2 + 0.998266x^3 - 1.6995x^4 + 0.2x^5$$

Variable bounds

$$0 \leq x \leq 10$$

Global Solution

This problem has local minima at $x = 6.325, f = -443.67$, $x = 0.4573$, $f = -0.02062$, $x = 0.01256, f = 0.0$ and $x = 0.00246, f = 0$ amongst others.

4.5 Test Problem 4

This example is taken from Dixon and Szegö (1975).

Objective function

$$\min_{x} \; 4x^2 - 4x^3 + x^4$$

Variable bounds

$$-5 \leq x \leq 5$$

Global Solution

This problem has two global minima at $x = 0, f = 0$, and $x = 2, f = 0$. There is a local maximum at $x = 1$.

4.6 Test Problem 5

This example is taken from Dixon and Szegö (1975) and it is denoted as the three-hump camel-back function.

Objective function

$$\min_{\boldsymbol{x}} \; f(x) = 2x_1^2 - 1.05x_1^4 + \frac{1}{6}x_1^6 - x_1x_2 + x_2^2$$

Variable bounds

$$-5 \leq x_1, x_2 \leq 5$$

Global Solution

- Objective function: 0
- Continuous variables

$$\begin{aligned} x_1 &= 0 \\ x_2 &= 0. \end{aligned}$$

4.7 Test Problem 6

This example is taken from Goldstein and Price (1971).

Objective function

$$\min_{x} \; x^6 - 15x^4 + 27x^2 + 250$$

Variable bounds

$$-5 \le x \le 5$$

Global Solution

This function has a local minima at (0,250), and two global minima at (3,7) and (-3,7).

4.8 Test Problem 7

This example is taken from Dixon (1990).

Objective function

$$\min_{x} \; x^4 - 3x^3 - 1.5x^2 + 10x$$

Variable bounds

$$-5 \le x \le 5$$

Global Solution

This function has a global solution of -7.5 at $x = -1$.

4.9 Test Problem 8

This example is taken from Soland (1971).

Objective function

$$\min_{x} \; -12x_1 - 7x_2 + x_2^2$$

Constraints

$$-2x_1^4 + 2 - x_2 = 0$$

Variable bounds

$$0 \le x_1 \le 2$$
$$0 \le x_2 \le 3$$

Global Solution

- Objective function: -16.73889
- Continuous variables

$$\begin{aligned} x_1 &= 0.7175 \\ x_2 &= 1.47. \end{aligned}$$

4.10 Test Problem 9

This is a test example that has a feasible region consisting of two disconnected sub-regions.

Objective function

$$\min_{\boldsymbol{x}} \quad -x_1 - x_2$$

Constraints

$$\begin{aligned} x_2 &\leq 2 + 2x_1^4 - 8x_1^3 + 8x_1^2 \\ x_2 &\leq 4x_1^4 - 32x_1^3 + 88x_1^2 - 96x_1 + 36 \end{aligned}$$

Variable bounds

$$\begin{gathered} 0 \leq x_1 \leq 3 \\ 0 \leq x_2 \leq 4 \end{gathered}$$

Global Solution

- Objective function: -5.50796
- Continuous variables

$$\begin{aligned} x_1 &= 2.3295 \\ x_2 &= 3.17846. \end{aligned}$$

Chapter 5

Bilinear problems

5.1 Introduction

Bilinear problems are an important subclass of nonconvex quadratic programming problems whose applications encompass pooling and blending, separation sequencing, heat exchanger network design and multicommodity network flow problems. The general form of a bilinear problem is given by

$$
\begin{array}{ll}
\min\limits_{\boldsymbol{x},\boldsymbol{y}} & \boldsymbol{x}^T A_0 \boldsymbol{y} + \boldsymbol{c}_0^T \boldsymbol{x} + \boldsymbol{d}_0^T \boldsymbol{y} \\
s.t. & \boldsymbol{x}^T A_i \boldsymbol{y} + \boldsymbol{c}_i^T \boldsymbol{x} + \boldsymbol{d}_i^T \boldsymbol{y} \leq b_i, \;\; i = 1, \ldots, p \\
 & \boldsymbol{x}^T A_i \boldsymbol{y} + \boldsymbol{c}_i^T \boldsymbol{x} + \boldsymbol{d}_i^T \boldsymbol{y} = b_i, \;\; i = p+1, \ldots, p+q \\
 & \boldsymbol{x} \in \mathcal{R}^n \\
 & \boldsymbol{y} \in \mathcal{R}^m
\end{array}
$$

where $\boldsymbol{x}$ and $\boldsymbol{y}$ are n- and m-dimensional vectors respectively, A_i, $i = 1, \ldots, p+q$, are $n \times m$ matrices, $\boldsymbol{c}_i$, $i = 1, \ldots, p+q$, are n-dimensional real vectors, $\boldsymbol{d}_i$, $i = 0, \ldots, p+q$, are m-dimensional real vectors and $\boldsymbol{b}$ is a $(p+q)$-dimensional real vector.

Since the specific structure of this class leads to almost linear problems, it has attracted the attention of researchers in global optimization early on. The first methods to tackle these problems were proposed by Mangasarian (1964) and Mangasarian and Stone (1974). Since then, a large number of solution techniques have been presented in the literature (Altmann, 1968; Falk and Soland, 1969; Falk, 1973; Konno, 1976; McCormick, 1976; Vaish and Shetty, 1976; Gallo and Ulculü, 1977; Sherali and Shetty, 1980; Thieu, 1980; Al-Khayyal and Falk, 1983; Baker and Lasdon, 1985; Floudas and Visweswaran, 1990; Visweswaran and Floudas, 1991; Floudas and Visweswaran, 1993). In particular, McCormick (1976) derived the convex envelope of bilinear terms, providing the tightest possible convex relaxation. Reviews of techniques that address quadratic and bilinear problems can be found in Horst and Tuy (1993), Floudas and Visweswaran (1995) and in the forthcoming book by Floudas (2000).

C. A. Floudas et al., *Handbook of Test Problems in Local and Global Optimization*

Several examples of bilinear problems are listed in this chapter. They focus on three types of engineering design applications: pooling, separation sequencing and heat exchanger network design.

5.2 Pooling Problems

5.2.1 Introduction

Pooling and blending problems are very common in the chemical and petrochemical industries. Given several feeds with different properties and costs, the aim is to determine the optimum flowrates that yield intermediate and product streams of satisfactory quality. These problems have been studied by Haverly (1978), Lasdon et al. (1979), Baker and Lasdon (1985), Visweswaran and Floudas (1990), Floudas and Aggarwal (1990), Ben-Tal et al. (1994), Visweswaran and Floudas (1996b) and Androulakis et al. (1996).

5.2.2 Haverly Pooling Problem

Haverly (1978) formulated a series of pooling problems based on the flowsheet shown in Figure 5.1. Three feeds, A, B and C, with sulfur contents of 3%, 1% and 2% respectively, are combined to form two products streams x and y. The maximum sulfur content content for these two streams is 2.5% and 1.5% respectively. The bilinearities in the problem arise from the fact that A and B must be pooled together.

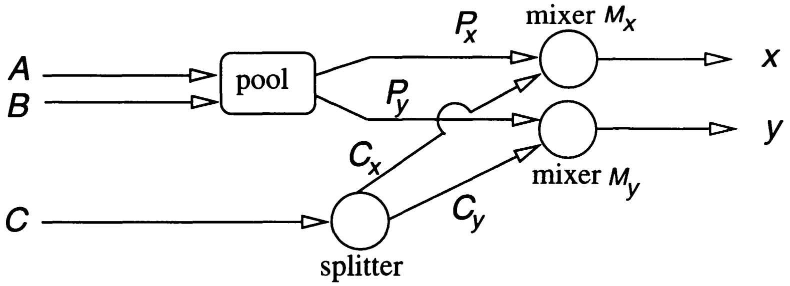


Figure 5.1: Schematic of the Haverly pooling problem.

Formulation

This problem is formulated as a profit maximization.

Objective function

$$\max_{x,y,A,B,p,C_x,C_y,P_x,P_y} \quad 9x + 15y - 6A - c_1B - 10(C_x + C_y)$$

Constraints

$$\begin{aligned} P_x + P_y - A - B &= 0 \\ x - P_x - C_x &= 0 \\ y - P_y - C_y &= 0 \\ pP_x + 2C_x - 2.5x &\leq 0 \\ pP_y + 2C_y - 1.5y &\leq 0 \\ pP_x + pP_y - 3A - B &= 0 \end{aligned}$$

Variable bounds

$$\begin{aligned} 0 \leq\ & x \leq c_2 \\ 0 \leq\ & y \leq 200 \\ 0 \leq\ & A, B, C_x, C_y, p, P_x, P_y \leq 500 \end{aligned}$$

Variable definitions
A and B are the flowrates for the two feeds to the pool; C is the flowrate of the feed to the splitter; p is the sulfur content of the streams coming out of the pool; P_x and P_y are the flowrates of the streams from the pool to mixers M_x and M_y, respectively; C_x and C_y are the flowrates of the streams from the splitter to mixers M_x and M_y, respectively; x and y are the flowrates of the two product streams. Three cases have been defined for different values of the parameters c_1 and c_2.

Data

- Case 1: $(c_1, c_2) = (16, 100)$.
- Case 2: $(c_1, c_2) = (16, 600)$.
- Case 3: $(c_1, c_2) = (13, 600)$.

Problem Statistics

No. of continuous variables	9
No. of linear equalities	3
No. of nonlinear equalities	1
No. of nonconvex inequalities	2
No. of known solutions – Case 1	1
No. of known solutions – Case 2	2
No. of known solutions – Case 3	1

Global Solution

- Objective function

Case 1	Case 2	Case 3
400	600	750

- Continuous variables

		Case 1		
$x = 0.0$	$A = 0.0$	$C_x = 0.0$	$P_x = 0.0$	$p = 1.0$
$y = 200.0$	$B = 100.0$	$C_y = 100.0$	$P_y = 100.0$	
		Case 2		
$x = 600.0$	$A = 300.0$	$C_x = 300.0$	$P_x = 300.0$	$p = 3.0$
$y = 0.0$	$B = 0.0$	$C_y = 0.0$	$P_y = 0.0$	
		Case 3		
$x = 0.0$	$A = 50.0$	$C_x = 0.0$	$P_x = 0.0$	$p = 1.5$
$y = 200.0$	$B = 150.0$	$C_y = 0.0$	$P_y = 200.0$	

5.2.3 Ben-Tal *et al.* (1994) Problems : General Formulation

Ben-Tal et al. (1994) proposed a more general formulation for pooling problems which can accomodate any number of feed streams, pools and products, and in which any feed stream may reach any pool and product. A graphical representation of a system involving three feeds, one pool and two products is shown in Figure 5.2. The $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$ vectors represent the flows between different units. Ben-Tal et al. (1994) suggested the substitution of flowrate x_{il}, denoting the flow from feed i to pool l, with a fractional flowrate, q_{il}, denoting the fraction of flow to pool l coming from feed i.

Objective function

$$\max_{\boldsymbol{q},\boldsymbol{y},\boldsymbol{z}} \sum_{j\in\mathcal{J}} \sum_{l\in\mathcal{L}} (d_j - \sum_{i\in\mathcal{I}} c_i q_{il}) y_{lj} + \sum_{i\in\mathcal{I}} \sum_{j\in\mathcal{J}} (d_j - c_i) z_{ij}$$

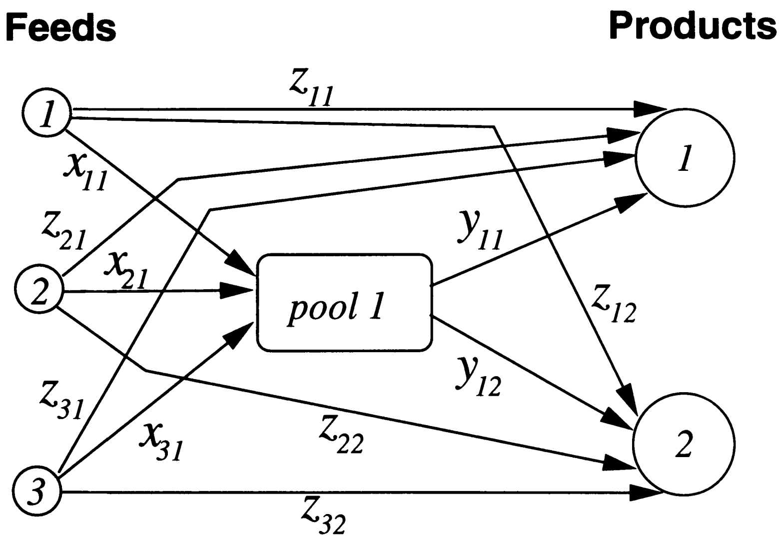


Figure 5.2: Schematic of a general pooling problem.

Constraints

$$
\begin{aligned}
\sum_{l\in\mathcal{L}}\sum_{j\in\mathcal{J}} q_{il}y_{lj} + \sum_{j\in\mathcal{J}} z_{ij} &\le A_i, \forall i \in \mathcal{I} \\
\sum_{j\in\mathcal{J}} y_{lj} &\le S_l, \forall l \in \mathcal{L} \\
\sum_{l\in\mathcal{L}} y_{lj} + \sum_{i\in\mathcal{I}} z_{ij} &\le D_j, \forall j \in \mathcal{J} \\
\sum_{l\in\mathcal{L}}\left(\sum_{i\in\mathcal{I}} C_{ik}q_{il} - P_{jk}\right) y_{lj} + \sum_{i\in\mathcal{I}}(C_{ik} - P_{jk})z_{ij} &\le 0, \forall j \in \mathcal{J}, \forall k \in \mathcal{K} \\
\sum_{i\in\mathcal{I}} q_{il} &= 1, \forall l \in \mathcal{L}
\end{aligned}
$$

Variable bounds

$$
\begin{array}{ll}
0 \le q_{il} \le 1, & \forall i \in \mathcal{I}, \forall l \in \mathcal{L} \\
0 \le y_{lj} \le D_j, & \forall l \in \mathcal{L}, \forall j \in \mathcal{J} \\
0 \le z_{ij} \le D_j, & \forall i \in \mathcal{I}, \forall j \in \mathcal{J}
\end{array}
$$

Variable definitions

The sets are defined as follows. $\mathcal{I}$ is the set of feeds, $\mathcal{J}$ is the set of products,

$\mathcal{L}$ is the set of pools and $\mathcal{K}$ is the set of components whose quality is being monitored.

The variables are q_{il}, the fractional flow from feed i to pool l; y_{lj}, the flow from pool l to product j; and z_{ij}, the flow from feed i directly to product j.

The parameters are A_i, the maximum available flow of feed i; D_j, the maximum demand for product j; S_l, the size of pool l; C_{ik}, the percentage of component k in feed i; P_{jk}, the maximum allowable percentage of component k in product j; c_i, the unit price of feed i; and d_j, the unit price of product j.

5.2.4 Ben-Tal *et al.* (1994) Problems : Test Problem 1

Ben-Tal et al. (1994) proposed a first instance of their general formulation consisting of four feeds, one pool and two products. The quality of only one component is monitored. The following restrictions are imposed on the problem: feeds 1, 2 and 4 can be sent to the pool and feed 3 cannot. Thus, there are only three q variables, q_{11}, q_{21} and q_{41}, and two z variables, z_{31} and z_{32}. The corresponding flowsheet is shown in Figure 5.3.

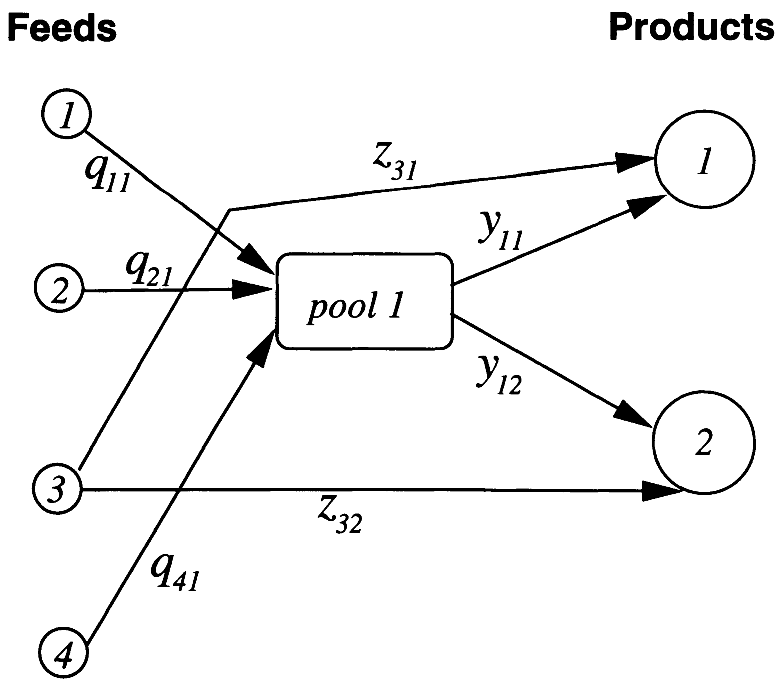


Figure 5.3: First instance of the Ben-Tal *et al.* (1994) pooling problems

Formulation

Objective function

$$\max_{q,y,z} \quad (9 - 6q_{11} - 16q_{21} - 15q_{41})y_{11} + (15 - 6q_{11} - 16q_{21} - 15q_{41})y_{12} - z_{31} + 5z_{32}$$

Constraints

$$\begin{aligned}
q_{41}y_{11} + q_{41}y_{12} &\leq 50 \\
y_{11} + z_{31} &\leq 100 \\
y_{12} + z_{32} &\leq 200 \\
(3q_{11} + q_{21} + q_{41} - 2.5)y_{11} - 0.5z_{31} &\leq 0 \\
(3q_{11} + q_{21} + q_{41} - 1.5)y_{12} + 0.5z_{32} &\leq 0 \\
q_{11} + q_{21} + q_{41} &= 1
\end{aligned}$$

Variable bounds

$$\begin{aligned}
0 \leq\ & q_{11} \leq 1 \\
0 \leq\ & q_{21} \leq 1 \\
0 \leq\ & q_{41} \leq 1 \\
0 \leq\ & y_{11} \leq 100 \\
0 \leq\ & y_{12} \leq 200 \\
0 \leq\ & z_{31} \leq 100 \\
0 \leq\ & z_{32} \leq 200
\end{aligned}$$

Data

$$\begin{array}{lll}
\boldsymbol{A} = (\infty, \infty, \infty, 50)^T & \boldsymbol{D} = (100, 200)^T & S_1 = \infty \\
\boldsymbol{C} = (3, 1, 2, 1)^T & \boldsymbol{P} = (2.5, 1.5)^T & \\
\boldsymbol{c} = (6, 16, 10, 15)^T & \boldsymbol{d} = (9, 15)^T &
\end{array}$$

Problem Statistics

No. of continuous variables	7
No. of linear equalities	1
No. of convex inequalities	2
No. of nonconvex inequalities	3
No. of known solutions	3

Global Solution

- Objective function: 450
- Continuous variables

$q_{11} = 0$	$q_{21} = 0.5$	$q_{41} = 0.5$
$y_{11} = 0$	$y_{12} = 100$	
$z_{31} = 0$	$z_{32} = 100$	

5.2.5 Ben-Tal *et al.* (1994) Problems : Test Problem 2

The second case suggested by Ben-Tal et al. (1994) consists of five feeds, three pools and five products. The quality of two components is monitored. The following restrictions are imposed on the problem: feeds 1, 2, 4 and 5 can be sent to the pool and feed 3 cannot. Thus, there are twelve q variables, and three z variables. The corresponding flowsheet is shown in Figure 5.4.

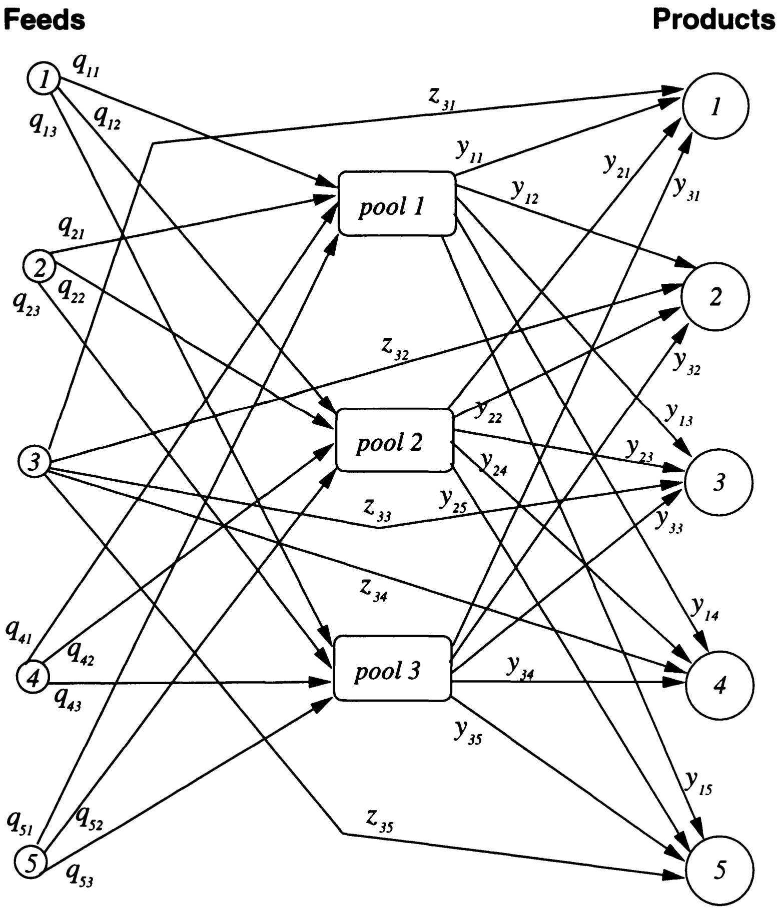


Figure 5.4: Second instance of the Ben-Tal *et al.* (1994) pooling problems

Formulation

Objective function

$$\begin{aligned}\max_{q,y,z}\quad & (18 - 6q_{11} - 16q_{21} - 15q_{41} - 12q_{51})y_{11} \\
& +(18 - 6q_{12} - 16q_{22} - 15q_{42} - 12q_{52})y_{21} \\
& +(18 - 6q_{13} - 16q_{23} - 15q_{43} - 12q_{53})y_{31} \\
& +(15 - 6q_{11} - 16q_{21} - 15q_{41} - 12q_{51})y_{12} \\
& +(15 - 6q_{12} - 16q_{22} - 15q_{42} - 12q_{52})y_{22} \\
& +(15 - 6q_{13} - 16q_{23} - 15q_{43} - 12q_{53})y_{32} \\
& +(19 - 6q_{11} - 16q_{21} - 15q_{41} - 12q_{51})y_{13} \\
& +(19 - 6q_{12} - 16q_{22} - 15q_{42} - 12q_{52})y_{23} \\
& +(19 - 6q_{13} - 16q_{23} - 15q_{43} - 12q_{53})y_{33} \\
& +(16 - 6q_{11} - 16q_{21} - 15q_{41} - 12q_{51})y_{14} \\
& +(16 - 6q_{12} - 16q_{22} - 15q_{42} - 12q_{52})y_{24} \\
& +(16 - 6q_{13} - 16q_{23} - 15q_{43} - 12q_{53})y_{34} \\
& +(14 - 6q_{11} - 16q_{21} - 15q_{41} - 12q_{51})y_{15} \\
& +(14 - 6q_{12} - 16q_{22} - 15q_{42} - 12q_{52})y_{25} \\
& +(14 - 6q_{13} - 16q_{23} - 15q_{43} - 12q_{53})y_{35} \\
& +8z_{31} + 5z_{32} + 9z_{33} + 6z_{34} + 4z_{35}\end{aligned}$$

Constraints

$$\begin{aligned}
q_{41}y_{11} + q_{41}y_{12} + q_{41}y_{13} + q_{41}y_{14} + q_{41}y_{15} + q_{42}y_{21} + q_{42}y_{22} + q_{42}y_{23} & \\
+q_{42}y_{24} + q_{42}y_{25} + q_{43}y_{31} + q_{43}y_{32} + q_{43}y_{33} + q_{43}y_{34} + q_{43}y_{35} & \le 50 \\
y_{11} + y_{21} + y_{31} + z_{31} & \le 100 \\
y_{12} + y_{22} + y_{32} + z_{32} & \le 200 \\
y_{13} + y_{23} + y_{33} + z_{33} & \le 100 \\
y_{14} + y_{24} + y_{34} + z_{34} & \le 100 \\
y_{15} + y_{25} + y_{35} + z_{35} & \le 100 \\
(3q_{11} + q_{21} + q_{41} + 1.5q_{51} - 2.5)y_{11} & \\
+(3q_{12} + q_{22} + q_{42} + 1.5q_{52} - 2.5)y_{21} & \\
+(3q_{13} + q_{23} + q_{43} + 1.5q_{53} - 2.5)y_{31} - 0.5z_{31} & \le 0 \\
(q_{11} + 3q_{21} + 2.5q_{41} + 2.5q_{51} - 2)y_{11} & \\
+(q_{12} + 3q_{22} + 2.5q_{42} + 2.5q_{52} - 2)y_{21} & \\
+(q_{13} + 3q_{23} + 2.5q_{43} + 2.5q_{53} - 2)y_{31} + 0.5z_{31} & \le 0 \\
(3q_{11} + q_{21} + q_{41} + 1.5q_{51} - 1.5)y_{12} & \\
+(3q_{12} + q_{22} + q_{42} + 1.5q_{52} - 1.5)y_{22} & \\
+(3q_{13} + q_{23} + q_{43} + 1.5q_{53} - 1.5)y_{32} + 0.5z_{32} & \le 0 \\
(q_{11} + 3q_{21} + 2.5q_{41} + 2.5q_{51} - 2.5)y_{12} & \\
+(q_{12} + 3q_{22} + 2.5q_{42} + 2.5q_{52} - 2.5)y_{22} & \\
+(q_{13} + 3q_{23} + 2.5q_{43} + 2.5q_{53} - 2.5)y_{32} & \le 0 \\
(3q_{11} + q_{21} + q_{41} + 1.5q_{51} - 2)y_{13} & \\
+(3q_{12} + q_{22} + q_{42} + 1.5q_{52} - 2)y_{23} & \\
+(3q_{13} + q_{23} + q_{43} + 1.5q_{53} - 2)y_{33} & \le 0
\end{aligned}$$

$$\begin{aligned}
&(q_{11} + 3q_{21} + 2.5q_{41} + 2.5q_{51} - 2.6)y_{13} \\
&\quad +(q_{12} + 3q_{22} + 2.5q_{42} + 2.5q_{52} - 2.6)y_{23} \\
&\quad +(q_{13} + 3q_{23} + 2.5q_{43} + 2.5q_{53} - 2.6)y_{33} - 0.1z_{33} && \leq 0 \\
&(3q_{11} + q_{21} + q_{41} + 1.5q_{51} - 2)y_{14} \\
&\qquad +(3q_{12} + q_{22} + q_{42} + 1.5q_{52} - 2)y_{24} \\
&\qquad +(3q_{13} + q_{23} + q_{43} + 1.5q_{53} - 2)y_{34} && \leq 0 \\
&(q_{11} + 3q_{21} + 2.5q_{41} + 2.5q_{51} - 2)y_{14} \\
&\quad +(q_{12} + 3q_{22} + 2.5q_{42} + 2.5q_{52} - 2)y_{24} \\
&\quad +(q_{13} + 3q_{23} + 2.5q_{43} + 2.5q_{53} - 2)y_{34} + 0.5z_{34} && \leq 0 \\
&(3q_{11} + q_{21} + q_{41} + 1.5q_{51} - 2)y_{15} \\
&\qquad +(3q_{12} + q_{22} + q_{42} + 1.5q_{52} - 2)y_{25} \\
&\qquad +(3q_{13} + q_{23} + q_{43} + 1.5q_{53} - 2)y_{35} && \leq 0 \\
&(q_{11} + 3q_{21} + 2.5q_{41} + 2.5q_{51} - 2)y_{15} \\
&\quad +(q_{12} + 3q_{22} + 2.5q_{42} + 2.5q_{52} - 2)y_{25} \\
&\quad +(q_{13} + 3q_{23} + 2.5q_{43} + 2.5q_{53} - 2)y_{35} + 0.5z_{35} && \leq 0 \\
&\qquad\qquad q_{11} + q_{21} + q_{41} + q_{51} && = 1 \\
&\qquad\qquad q_{12} + q_{22} + q_{42} + q_{52} && = 1 \\
&\qquad\qquad q_{13} + q_{23} + q_{43} + q_{53} && = 1
\end{aligned}$$

Variable bounds

$$\begin{array}{lll}
0 \leq q_{11} \leq 1 & 0 \leq q_{12} \leq 1 & 0 \leq q_{13} \leq 1 \\
0 \leq q_{21} \leq 1 & 0 \leq q_{22} \leq 1 & 0 \leq q_{23} \leq 1 \\
0 \leq q_{41} \leq 1 & 0 \leq q_{42} \leq 1 & 0 \leq q_{43} \leq 1 \\
0 \leq q_{51} \leq 1 & 0 \leq q_{52} \leq 1 & 0 \leq q_{53} \leq 1 \\
0 \leq y_{11} \leq 100 & 0 \leq y_{21} \leq 100 & 0 \leq y_{31} \leq 100 \\
0 \leq y_{12} \leq 200 & 0 \leq y_{22} \leq 200 & 0 \leq y_{32} \leq 200 \\
0 \leq y_{13} \leq 100 & 0 \leq y_{23} \leq 100 & 0 \leq y_{33} \leq 100 \\
0 \leq y_{14} \leq 100 & 0 \leq y_{24} \leq 100 & 0 \leq y_{34} \leq 100 \\
0 \leq y_{15} \leq 100 & 0 \leq y_{25} \leq 100 & 0 \leq y_{35} \leq 100 \\
0 \leq z_{31} \leq 100 & 0 \leq z_{32} \leq 200 & 0 \leq z_{33} \leq 100 \\
0 \leq z_{34} \leq 100 & 0 \leq z_{35} \leq 100 &
\end{array}$$

Data

$\boldsymbol{A} = (\infty, \infty, \infty, 50, \infty)^T \quad \boldsymbol{D} = (100, 200, 100, 100, 100)^T \quad \boldsymbol{S} = (\infty, \infty, \infty)^T$
$\boldsymbol{c} = (6, 16, 10, 15, 12)^T \quad \boldsymbol{d} = (18, 15, 19, 16, 14)^T$

$$\boldsymbol{C} = \begin{pmatrix} 3.0 & 1.0 \\ 1.0 & 3.0 \\ 2.0 & 2.5 \\ 1.5 & 2.5 \end{pmatrix} \quad \boldsymbol{P} = \begin{pmatrix} 2.5 & 2.0 \\ 1.5 & 2.5 \\ 2.0 & 2.6 \\ 2.0 & 2.0 \\ 2.0 & 2.0 \end{pmatrix}$$

Problem Statistics

No. of continuous variables	32
No. of linear equalities	3
No. of convex inequalities	5
No. of nonconvex inequalities	11
No. of known solutions	40

Global Solution

- Objective function: 3500
- Continuous variables: the variable values at the solution with the greatest objective function are reported here. The next best solution is very close, with a relative difference of only 1.5×10^{-8}.

$q_{11} = 1$	$q_{21} = 0$	$q_{41} = 0$	$q_{51} = 0$	
$q_{12} = 0$	$q_{22} = 0$	$q_{42} = 0$	$q_{52} = 1$	
$q_{13} = 0.2757$	$q_{23} = 0$	$q_{43} = 0$	$q_{53} = 0.7243$	
$y_{11} = 51.5527$	$y_{12} = 0$	$y_{13} = 0$	$y_{14} = 7.9609$	$y_{15} = 15.7866$
$y_{21} = 0$	$y_{22} = 200$	$y_{23} = 0$	$y_{24} = 0$	$y_{25} = 20.5622$
$y_{31} = 17.9504$	$y_{32} = 0$	$y_{33} = 0$	$y_{34} = 92.0391$	$y_{35} = 63.6512$
$z_{31} = 30.4969$	$z_{32} = 0$	$z_{33} = 100$	$z_{34} = 0$	$z_{35} = 0$

5.3 Distillation Column Sequencing Problems

5.3.1 Introduction

The separation of products from waste and recyclable material is a central part of chemical processes, in terms of both the technical challenges it presents and the capital and operating costs it entails. A common means of achieving separation is through the use of a series of distillation columns. The sequence in which different components in the initial feed are separated has a significant impact on the economics of the process. It is therefore beneficial to optimize this sequence in order to obtain the minimum annualized cost for the separation section of the plant. Research efforts have been directed towards this problem in the past three decades (Glinos et al., 1985; Westerberg, 1985; Floudas, 1987; Wehe and Westerberg, 1987; Floudas and Anastasiadis, 1988; Aggarwal and Floudas, 1990, 1992). While distillation columns are very complex, their operation can be approximated through bilinear models for the purpose of sequence design. Several examples of such models are given in this section. A particular difficulty of these problems, from the point of view of global optimization, is the presence of numerous equality constraints which, when relaxed, lead to a much enlarged feasible region and hence poor lower bounds on the global solution.

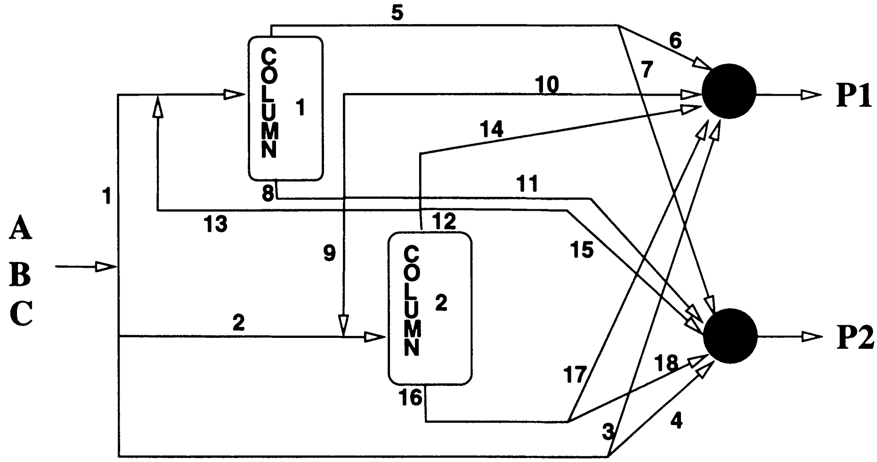


Figure 5.5: Distillation sequence superstructure for the separation of a propane, isobutane and n-butane mixture

5.3.2 Nonsharp separation of propane, isobutane and n-butane

The goal of this problem, taken from Aggarwal and Floudas (1990) and Adjiman et al. (1998b), is to identify the optimum design for the separation of a mixture of propane, isobutane and n-butane into two products: $P1$, with a total flow of 110 kgmol/h consisting of 30 kgmol/h of propane, 50 kgmol/h of isobutane and 30 kgmol/h of n-butane, and $P2$, with a total flow of 190 kgmol/h consisting of 70 kgmol/h of propane, 50 kgmol/h of isobutane and 70 kgmol/h of n-butane. Two distillation columns and a number of mixers and splitters can be used, as shown in Figure 5.5.

Formulation

Objective function

$$\min_{\boldsymbol{F},\boldsymbol{x}} \; 0.9979 + 0.00432F_1 + 0.00432F_{13} + 0.01517F_2 + 0.01517F_9$$

Constraints

$$\begin{aligned}
F_1 + F_2 + F_3 + F_4 &= 300 \\
F_5 - F_6 - F_7 &= 0 \\
F_8 - F_9 - F_{10} - F_{11} &= 0 \\
F_{12} - F_{13} - F_{14} - F_{15} &= 0 \\
F_{16} - F_{17} - F_{18} &= 0 \\
F_{13}x_{A,12} - F_5 + 0.333\ F_1 &= 0 \\
F_{13}x_{B,12} - F_8x_{B,8} + 0.333\ F_1 &= 0
\end{aligned}$$

$$\begin{aligned}
-F_8 x_{C,8} + 0.333\ F_1 &= 0 \\
-F_{12} x_{A,12} - 0.333\ F_2 &= 0 \\
F_9 x_{B,8} - F_{12} x_{B,12} + 0.333\ F_2 &= 0 \\
F_9 x_{C,8} - F_{16} + 0.333\ F_2 &= 0 \\
F_{14} x_{A,12} + 0.333\ F_3 + F_6 &= 30 \\
F_{10} x_{B,8} + F_{14} x_{B,12} + 0.333\ F_3 &= 50 \\
F_{10} x_{C,8} + 0.333\ F_3 + F_{17} &= 30 \\
x_{A,8} &= 0 \\
x_{B,8} + x_{C,8} &= 1 \\
x_{A,12} + x_{B,12} &= 1 \\
x_{C,12} &= 0
\end{aligned}$$

Variable bounds

$$\begin{aligned}
0 \le F_i \le 300, &\quad i = 1, \dots, 18 \\
0 \le x_{j,i} \le 1, &\quad j \in \{A, B, C\},\ i \in \{8, 12\}
\end{aligned}$$

Variable definitions
A, B and C denote propane, isobutane and n-butane respectively. F_i denotes the flowrate, in kgmol/h, for stream i as indicated on Figure 5.5. $x_{j,i}$ denotes the mole fraction of component j in stream i.

Problem Statistics

No. of continuous variables	24
No. of linear equalities	9
No. of nonlinear equalities	9
No. of known solutions	1

Global Solution

Several of the streams in Figure 5.5 do not exist at the optimum solution. The corresponding global optimum network (Adjiman et al., 1998b) is therefore shown in Figure 5.6.

- Objective function: 1.8642
- Continuous variables

$F_1 = 60.0601$	$F_5 = 20$	$F_9 = 40$	$F_{13} = 0$	$F_{17} = 0$
$F_2 = 0$	$F_6 = 0$	$F_{10} = 0$	$F_{14} = 20$	$F_{18} = 20$
$F_3 = 90.0901$	$F_7 = 20$	$F_{11} = 0$	$F_{15} = 0$	
$F_4 = 149.8498$	$F_8 = 40$	$F_{12} = 20$	$F_{16} = 20$	
$x_{A,8} = 0$	$x_{B,8} = 0.5$	$x_{C,8} = 0.5$		
$x_{A,12} = 0$	$x_{B,12} = 1$	$x_{B,12} = 0$		

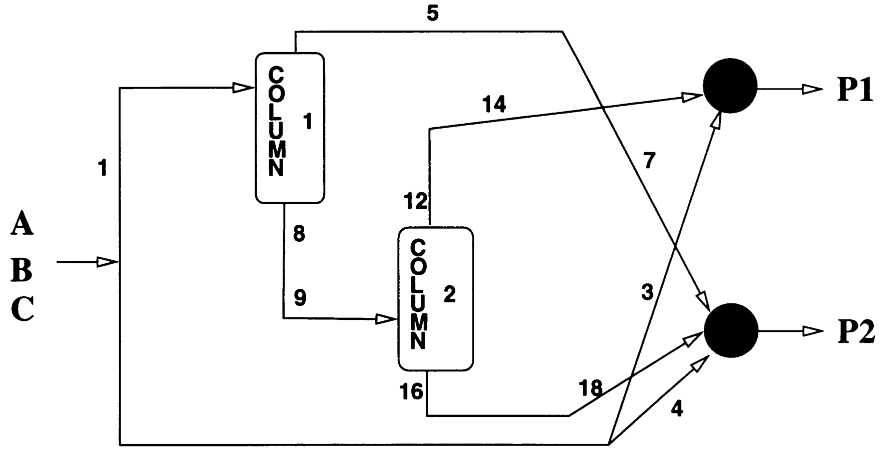


Figure 5.6: Optimal configuration for the separation of a mixture of propane, isobutane and n-butane

5.3.3 Nonsharp separation of propane, isobutane, n-butane and isopentane

In this problem taken from Aggarwal and Floudas (1990) a mixture of propane, isobutane, n-butane and isopentane is considered. It must be separated into two products: $P1$, with a total flow of 315 kgmol/h consisting of 75 kgmol/h of propane, 100 kgmol/h of iso-butane, 40 kgmol/h of n-butane and 100 kgmol/h of isopentane, and $P2$, with a total flow of 285 kgmol/h consisting of 75 kgmol/h of propane, 100 kgmol/h of iso-butane, 60 kgmol/h of n-butane and 50 kgmol/h of isopentane. Three distillation columns and a number of mixers and splitters can be used, as shown in Figure 5.7.

Formulation

Objective function

$$\begin{aligned}\min_{\boldsymbol{F},\boldsymbol{x}} \quad & a_{0,1} + (a_{1,1} + 0.85a_{2,1} + a_{3,1} + b_{A,1}x_{A,6} + b_{B,1}x_{B,6} + b_{C,1}x_{C,6})\,F_6 \\ + \quad & a_{0,2} + (a_{1,2} + 0.85a_{2,2} + 0.85a_{3,2} + b_{A,2}x_{A,15} + b_{B,2}x_{B,15} + b_{C,2}x_{C,15})\,F_{15} \\ + \quad & a_{0,3} + (a_{1,3} + a_{2,3} + 0.85a_{3,3} + b_{A,3}x_{A,24} + b_{B,3}x_{B,24} + b_{C,3}x_{C,24})\,F_{24}\end{aligned}$$

Constraints

$$\begin{aligned} F_1 + F_2 + F_3 + F_4 + F_5 &= 600 \\ F_6 - F_1 - F_{17} - F_{26} &= 0 \\ F_{15} - F_2 - F_{11} - F_{27} &= 0 \\ F_{24} - F_3 - F_{12} - F_{21} &= 0 \end{aligned}$$

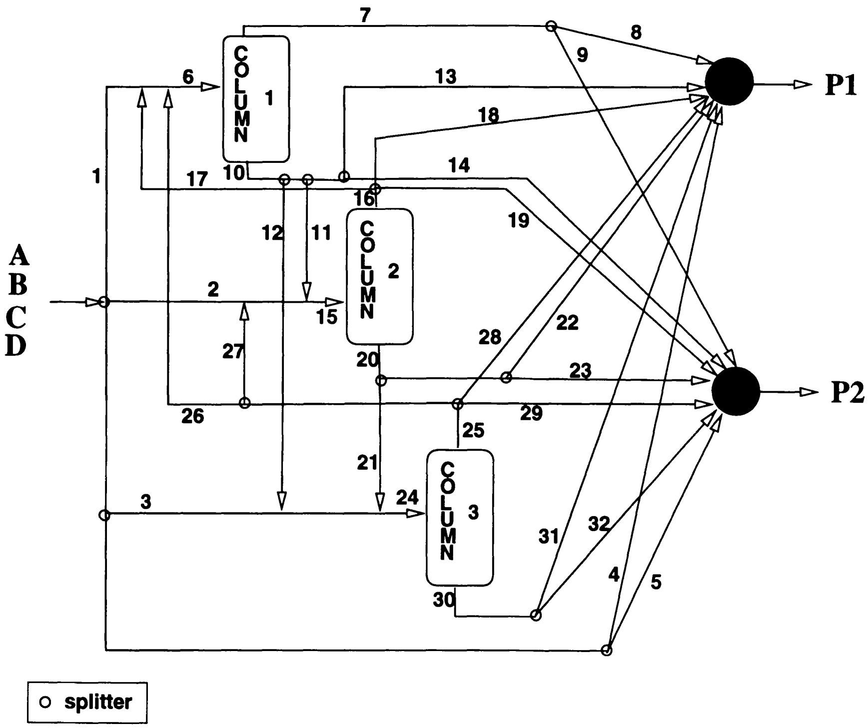


Figure 5.7: Distillation sequence superstructure for the separation of propane, isobutane, n-butane and isopentane

$$
\begin{aligned}
F_7 - F_8 - F_9 &= 0 \\
F_{10} - F_{11} - F_{12} - F_{13} - F_{14} &= 0 \\
F_{16} - F_{17} - F_{18} - F_{19} &= 0 \\
F_{20} - F_{21} - F_{22} - F_{23} &= 0 \\
F_{25} - F_{26} - F_{27} - F_{28} - F_{29} &= 0 \\
F_{30} - F_{31} - F_{32} &= 0 \\
F_7 x_{A,7} - 0.85 F_6 x_{A,6} &= 0 \\
F_{16} x_{B,16} - 0.85 F_{15} x_{B,15} &= 0 \\
F_{25} x_{C,25} - F_{24} x_{C,24} &= 0 \\
F_{10} x_{B,10} - F_6 x_{B,6} &= 0 \\
F_{20} x_{C,20} - 0.85 F_{15} x_{C,15} &= 0 \\
F_{30} x_{D,30} - 0.85 F_{24} x_{D,24} &= 0 \\
F_6 x_{A,6} - F_7 x_{A,7} - F_{10} x_{A,10} &= 0 \\
F_6 x_{B,6} - F_7 x_{B,7} - F_{10} x_{B,10} &= 0
\end{aligned}
$$

$$
\begin{aligned}
F_6 x_{C,6} - F_{10} x_{C,10} &= 0 \\
F_6 x_{D,6} - F_{10} x_{D,10} &= 0 \\
F_{15} x_{A,15} - F_{16} x_{A,16} &= 0 \\
F_{15} x_{B,15} - F_{16} x_{B,16} - F_{20} x_{B,20} &= 0 \\
F_{15} x_{C,15} - F_{16} x_{C,16} - F_{20} x_{C,20} &= 0 \\
F_{15} x_{D,15} - F_{20} x_{D,20} &= 0 \\
F_{24} x_{A,24} - F_{25} x_{A,25} &= 0 \\
F_{24} x_{B,24} - F_{25} x_{B,25} &= 0 \\
F_{24} x_{C,24} - F_{25} x_{C,25} - F_{30} x_{C,30} &= 0 \\
F_{24} x_{D,24} - F_{25} x_{D,25} - F_{30} x_{D,30} &= 0 \\
0.250 F_1 + F_{17} x_{A,16} + F_{26} x_{A,25} - F_6 x_{A,6} &= 0 \\
0.333 F_1 + F_{17} x_{B,16} + F_{26} x_{B,25} - F_6 x_{B,6} &= 0 \\
0.167 F_1 + F_{17} x_{C,16} + F_{26} x_{C,25} - F_6 x_{C,6} &= 0 \\
0.250 F_1 + F_{26} x_{D,25} - F_6 x_{D,6} &= 0 \\
0.250 F_2 + F_{11} x_{A,10} + F_{27} x_{A,25} - F_{15} x_{A,15} &= 0 \\
0.333 F_2 + F_{11} x_{B,10} + F_{27} x_{B,25} - F_{15} x_{B,15} &= 0 \\
0.167 F_2 + F_{11} x_{C,10} + F_{27} x_{C,25} - F_{15} x_{C,15} &= 0 \\
0.250 F_2 + F_{11} x_{D,10} + F_{27} x_{D,25} - F_{15} x_{D,15} &= 0 \\
0.250 F_3 + F_{12} x_{A,10} - F_{24} x_{A,24} &= 0 \\
0.333 F_3 + F_{12} x_{B,10} + F_{21} x_{B,20} - F_{24} x_{B,24} &= 0 \\
0.167 F_3 + F_{12} x_{C,10} + F_{21} x_{C,20} - F_{24} x_{C,24} &= 0 \\
0.250 F_3 + F_{12} x_{D,10} + F_{21} x_{D,20} - F_{24} x_{D,24} &= 0 \\
0.250 F_4 + F_8 x_{A,7} + F_{13} x_{A,10} + F_{18} x_{A,16} + F_{28} x_{A,25} &= 50 \\
0.222 F_4 + F_8 x_{B,7} + F_{13} x_{B,10} + F_{18} x_{B,16} + F_{22} x_{B,20} + F_{28} x_{B,25} &= 100 \\
0.167 F_4 + F_{13} x_{C,10} + F_{18} x_{C,16} + F_{22} x_{C,20} + F_{28} x_{C,25} + F_{31} x_{C,30} &= 40 \\
0.250 F_4 + F_{13} x_{D,10} + F_{22} x_{D,20} + F_{28} x_{D,25} + F_{31} x_{D,30} &= 100 \\
x_{A,6} + x_{B,6} + x_{C,6} + x_{D,6} &= 1 \\
x_{A,7} + x_{B,7} &= 1 \\
x_{A,10} + x_{B,10} + x_{C,10} + x_{D,10} &= 1 \\
x_{A,15} + x_{B,15} + x_{C,15} + x_{D,15} &= 1 \\
x_{A,16} + x_{B,16} + x_{C,16} &= 1 \\
x_{B,20} + x_{C,20} + x_{D,20} &= 1 \\
x_{A,24} + x_{B,24} + x_{C,24} + x_{D,24} &= 1 \\
x_{A,25} + x_{B,25} + x_{C,25} + x_{D,25} &= 1 \\
x_{C,30} + x_{D,30} &= 1
\end{aligned}
$$

Variable bounds

$$\begin{array}{lll} 0 \leq & F_i & \leq 600,\ i = 1, \ldots, 32 \\ 0 \leq & x_{j,i} & \leq 1,\ j \in \{A, B, C, D\},\ i \in \{6, 10, 15, 24, 25\} \\ 0 \leq & x_{j,7} & \leq 1,\ j \in \{A, B\} \\ 0 \leq & x_{j,16} & \leq 1,\ j \in \{A, B, C\} \\ 0 \leq & x_{j,20} & \leq 1,\ j \in \{B, C, D\} \\ 0 \leq & x_{j,30} & \leq 1,\ j \in \{C, D\} \end{array}$$

Variable definitions

A, B, C and D denote propane, iso-butane, n-butane and isopentane respectively. F_i denotes the flowrate, in kgmol/h, for stream i as indicated on Figure 5.7. $x_{j,i}$ denotes the mole fraction of component j in stream i.

Data

$$\boldsymbol{a} = \begin{pmatrix} 0.31569 & 0.96926 & 0.40281 \\ -0.0112812 & -0.0413393 & -0.0119785 \\ 0.0072698 & 0.0228203 & 0.0082055 \\ 0.0064241 & 0.0257035 & 0.009819 \end{pmatrix}$$

$$\boldsymbol{b} = \begin{pmatrix} 0.0016446 & 0.0015625 & -0.001748 \\ 0.0018611 & 0.0091604 & -0.0002583 \\ 0.001262 & 0.0076758 & -0.0004691 \end{pmatrix}$$

Problem Statistics

No. of continuous variables	62
No. of linear equalities	19
No. of nonlinear equalities	34
No. of known solutions	1

Best known solution

Several of the streams in Figure 5.7 do not exist at the optimum solution. The corresponding network is therefore shown in Figure 5.8.

- Objective function: 3.2340
- Continuous variables

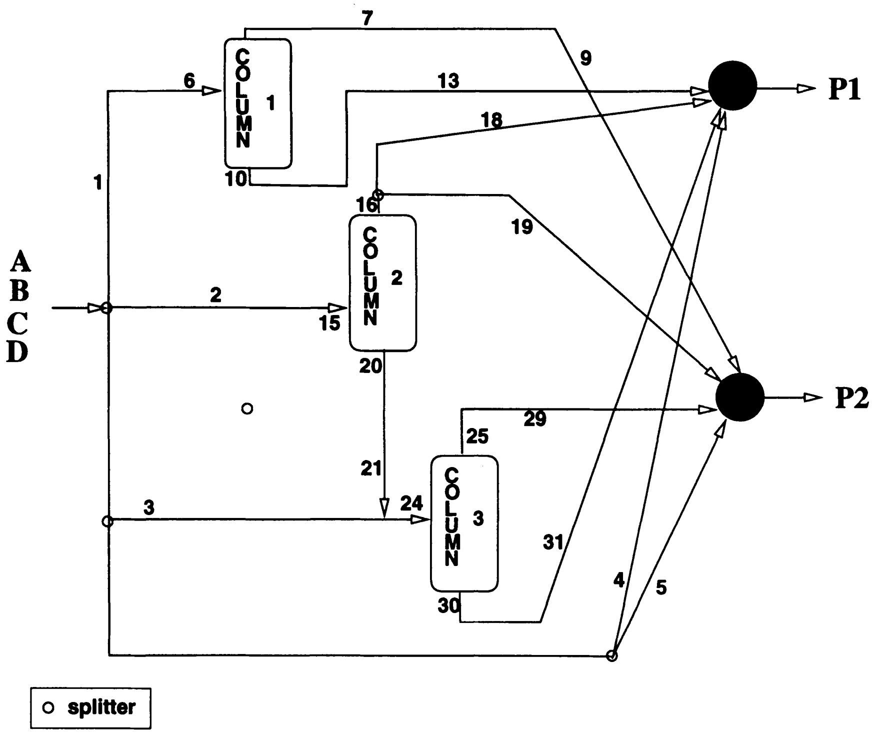


Figure 5.8: Optimal configuration for the separation of a mixture of propane, isobutane, n-butane and isopentane

$F_1 = 161.99$	$F_9 = 34.42$	$F_{17} = 0$	$F_{25} = 100.27$
$F_2 = 115.49$	$F_{10} = 127.57$	$F_{18} = 64.46$	$F_{26} = 0$
$F_3 = 93.68$	$F_{11} = 0$	$F_{19} = 0$	$F_{27} = 0$
$F_4 = 60.20$	$F_{12} = 0$	$F_{20} = 51.04$	$F_{28} = 0$
$F_5 = 168.62$	$F_{13} = 127.57$	$F_{21} = 51.04$	$F_{29} = 100.27$
$F_6 = 161.99$	$F_{14} = 0$	$F_{22} = 0$	$F_{30} = 44.45$
$F_7 = 34.42$	$F_{15} = 115.49$	$F_{23} = 0$	$F_{31} = 44.45$
$F_8 = 0$	$F_{16} = 64.46$	$F_{24} = 144.72$	$F_{32} = 0$
$x_{A,6} = 0.250$	$x_{B,6} = 0.333$	$x_{C,6} = 0.167$	$x_{D,6} = 0.250$
$x_{A,7} = 1.000$	$x_{B,7} = 0.000$		
$x_{A,10} = 0.048$	$x_{B,10} = 0.423$	$x_{C,10} = 0.212$	$x_{D,10} = 0.317$
$x_{A,15} = 0.250$	$x_{B,15} = 0.333$	$x_{C,15} = 0.167$	$x_{D,15} = 0.250$
$x_{A,16} = 0.448$	$x_{B,16} = 0.507$	$x_{C,16} = 0.045$	
	$x_{B,20} = 0.113$	$x_{C,20} = 0.321$	$x_{D,20} = 0.566$
$x_{A,24} = 0.162$	$x_{B,24} = 0.256$	$x_{C,24} = 0.221$	$x_{D,24} = 0.361$
$x_{A,25} = 0.234$	$x_{B,25} = 0.369$	$x_{C,25} = 0.319$	$x_{D,25} = 0.078$
		$x_{C,30} = 0.000$	$x_{D,30} = 1.000$

5.4 Heat Exchanger Network Problems

5.4.1 Introduction

Heat integration brings about significant savings when the right balance between capital investment and operating costs is found. Thus, heat exchanger network problems have attracted attention for many years. Initially, these problems were formulated as bilinear optimization problems.

5.4.2 Test Problem 1

The following problem, from Avriel and Williams (1971), addresses the design of the heat exchanger network shown in Figure 5.9. One cold stream must be heated from 100^oF to 500^oF using three hot streams with different inlet temperatures. The goal is to minimize the overall heat exchange area.

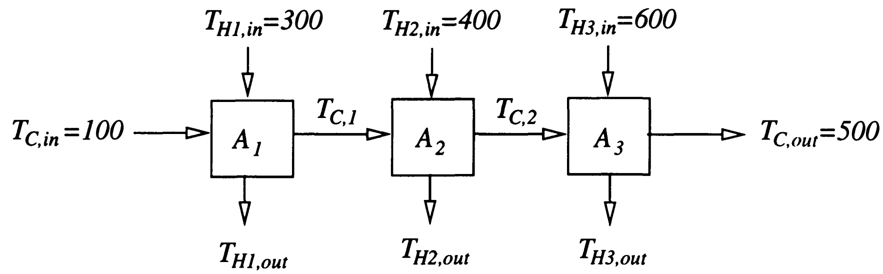


Figure 5.9: Heat exchanger network design problem 1, Avriel and Williams (1971).

Formulation

Objective function

$$\min_{\boldsymbol{A},\boldsymbol{T}_C,\boldsymbol{T}_{H,out}} \quad A_1 + A_2 + A_3$$

Constraints

$$\begin{aligned}
T_{C,1} + T_{H1,out} - T_{C,in} - T_{H1,in} &\leq 0 \\
-T_{C,1} + T_{C,2} + T_{H2,out} - T_{H1,in} &\leq 0 \\
T_{H3,out} - T_{C,2} - T_{H3,in} + T_{C,out} &\leq 0 \\
A_1 - A_1 T_{H1,out} + \frac{FC_p}{U_1} T_{C,1} - \frac{FC_p}{U_1} T_{C,in} &\leq 0 \\
A_2 T_{C,1} - A_2 T_{H2,out} - \frac{FC_p}{U_2} T_{C,1} + \frac{FC_p}{U_2} T_{C,2} &\leq 0 \\
A_3 T_{C,2} - A_3 T_{H3,out} - \frac{FC_p}{U_3} T_{C,2} + \frac{FC_p}{U_3} T_{C,out} &\leq 0
\end{aligned}$$

Variable bounds

$$\begin{array}{rcl} 100 \leq & A_1 & \leq 10000 \\ 1000 \leq & A_2, A_3 & \leq 10000 \\ 10 \leq & T_{C,1} & \leq 1000 \\ 10 \leq & T_{C,2} & \leq 1000 \\ 10 \leq & T_{H1,out} & \leq 1000 \\ 10 \leq & T_{H2,out} & \leq 1000 \\ 10 \leq & T_{H3,out} & \leq 1000 \end{array}$$

Data

$$FC_p = 10^5 \text{ [Btu/(hr } ^o\text{F)]}$$

$$\boldsymbol{U} = (120, 80, 40)^T \text{[Btu/(hr ft}^2 \ ^o\text{F)]}$$

Problem Statistics

No. of continuous variables	8
No. of convex inequalities	3
No. of nonconvex inequalities	3
No. of known solutions	1

Best Known Solution

- Objective function: 7512.23 ft^2
- Continuous variables:

$$\boldsymbol{A} = (102.69, 1000.00, 5485.28)^T$$

$$\boldsymbol{T_C} = (265.06, 280.59)^T$$

$$\boldsymbol{T_{H,out}} = (134.49, 284.47, 380.59)^T$$

5.4.3 Test Problem 2

This problem is taken from Visweswaran and Floudas (1996b). It involves two hot streams and one cold stream. While the objective function is convex, all the nonconvexities in the problem stem from bilinear constraints. The heat exchanger network is shown in Figure 5.10.

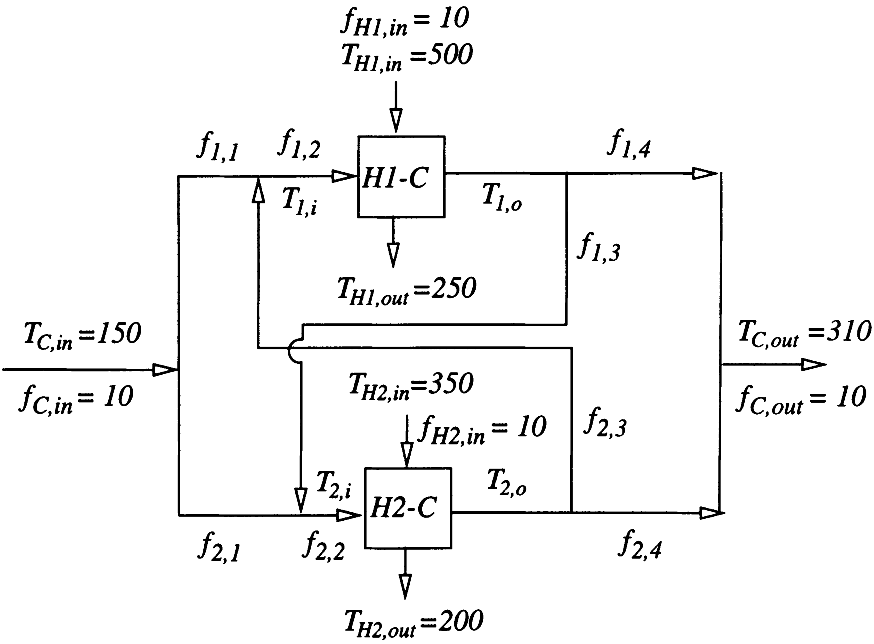


Figure 5.10: Heat exchanger network design problem 2, Visweswaran and Floudas (1996b).

Formulation

Objective function

$$\min_{\Delta T, f, T_i, T_o} \quad 1300\left(\frac{1000}{\frac{1}{30}(\Delta T_{11}\Delta T_{12}) + \frac{1}{6}(\Delta T_{11} + \Delta T_{12})}\right)^{0.6} + 1300\left(\frac{600}{\frac{1}{30}(\Delta T_{21}\Delta T_{22}) + \frac{1}{6}(\Delta T_{21} + \Delta T_{22})}\right)^{0.6}$$

Constraints

$$\begin{aligned}
f_{1,1} + f_{2,1} &= 10 \\
f_{1,1} + f_{2,3} - f_{1,2} &= 0 \\
f_{2,1} + f_{1,3} - f_{2,2} &= 0 \\
f_{1,4} + f_{1,3} - f_{1,2} &= 0 \\
f_{2,4} + f_{2,3} - f_{2,2} &= 0 \\
150 f_{1,1} + T_{2,o} f_{2,3} - T_{1,i} f_{1,2} &= 0 \\
150 f_{2,1} + T_{1,o} f_{1,3} - T_{2,i} f_{2,2} &= 0
\end{aligned}$$

$$\begin{aligned} f_{1,2}(T_{1,o} - T_{1,i}) &= 1000 \\ f_{2,2}(T_{2,o} - T_{2,i}) &= 600 \\ \Delta T_{11} + T_{1,o} &= 500 \\ \Delta T_{12} + T_{1,i} &= 250 \\ \Delta T_{21} + T_{2,o} &= 350 \\ \Delta T_{22} + T_{2,i} &= 200 \end{aligned}$$

Variable bounds

$$\begin{array}{rcl} 10 \leq & \Delta T_{1,1} & \leq 350 \\ 10 \leq & \Delta T_{1,2} & \leq 350 \\ 10 \leq & \Delta T_{2,1} & \leq 200 \\ 10 \leq & \Delta T_{2,2} & \leq 200 \\ 0 \leq & f_{1,j} & \leq 10, \ j = 1, \dots, 4 \\ 0 \leq & f_{2,j} & \leq 10, \ j = 1, \dots, 4 \\ 150 \leq & T_{j,i} & \leq 310, \ j = 1, \dots, 2 \\ 150 \leq & T_{j,o} & \leq 310, \ j = 1, \dots, 2 \end{array}$$

Problem Statistics

No. of continuous variables	16
No. of linear equalities	9
No. of nonlinear equalities	4
No. of known solutions	9

Global Solution

- Objective function: 4845
- Continuous variables:

$$\boldsymbol{\Delta T} = \begin{pmatrix} 190 & 40 \\ 140 & 50 \end{pmatrix}$$

$$\boldsymbol{f} = \begin{pmatrix} 0 & 10 & 0 & 0 \\ 10 & 10 & 10 & 0 \end{pmatrix}$$

$$T_{1,i} = 210 \quad T_{1,o} = 150 \quad T_{2,i} = 310 \quad T_{2,o} = 210$$

5.4.4 Test Problem 3

This problem is taken from Floudas and Ciric (1988). It involves three hot streams and one cold stream. The formulation has a convex objective function and bilinear and linear constraints. The heat exchanger network is shown in Figure 5.11.

Formulation

Objective function

$$
\begin{aligned}
\min_{\Delta T, f, T_i, T_o} \quad & 1300\left(\frac{2000}{\frac{1}{3}(\Delta T_{11}\Delta T_{12})+\frac{1}{6}(\Delta T_{11}+\Delta T_{12})}\right)^{0.6} \\
+ \quad & 1300\left(\frac{1000}{\frac{2}{3}(\Delta T_{21}\Delta T_{22})+\frac{1}{6}(\Delta T_{21}+\Delta T_{22})}\right)^{0.6} \\
+ \quad & 1300\left(\frac{1500}{\frac{4}{3}(\Delta T_{31}\Delta T_{32})+\frac{1}{6}(\Delta T_{31}+\Delta T_{32})}\right)^{0.6}
\end{aligned}
$$

Constraints

$$
\begin{aligned}
f_{1,1}+f_{2,1}+f_{3,1} &= 45 \\
f_{1,1}+f_{2,3}+f_{3,4}-f_{1,2} &= 0 \\
f_{2,1}+f_{1,3}+f_{3,3}-f_{2,2} &= 0 \\
f_{3,1}+f_{1,4}+f_{2,4}-f_{3,2} &= 0 \\
f_{1,5}+f_{1,3}+f_{1,4}-f_{1,2} &= 0 \\
f_{2,5}+f_{2,3}+f_{2,4}-f_{2,2} &= 0 \\
f_{3,5}+f_{3,3}+f_{3,4}-f_{3,2} &= 0 \\
100f_{1,1}+T_{2,o}f_{2,3}+T_{3,o}f_{3,4}-T_{1,i}f_{1,2} &= 0 \\
100f_{2,1}+T_{1,o}f_{1,3}+T_{3,o}f_{3,3}-T_{2,i}f_{2,2} &= 0 \\
100f_{3,1}+T_{1,o}f_{1,4}+T_{2,o}f_{2,4}-T_{3,i}f_{3,2} &= 0 \\
f_{1,2}(T_{1,o}-T_{1,i}) &= 2000 \\
f_{2,2}(T_{2,o}-T_{2,i}) &= 1000 \\
f_{3,2}(T_{3,o}-T_{3,i}) &= 1500 \\
\Delta T_{11}+T_{1,o} &= 210 \\
\Delta T_{12}+T_{1,i} &= 130 \\
\Delta T_{21}+T_{2,o} &= 210 \\
\Delta T_{22}+T_{2,i} &= 160 \\
\Delta T_{31}+T_{3,o} &= 210 \\
\Delta T_{32}+T_{3,i} &= 180
\end{aligned}
$$

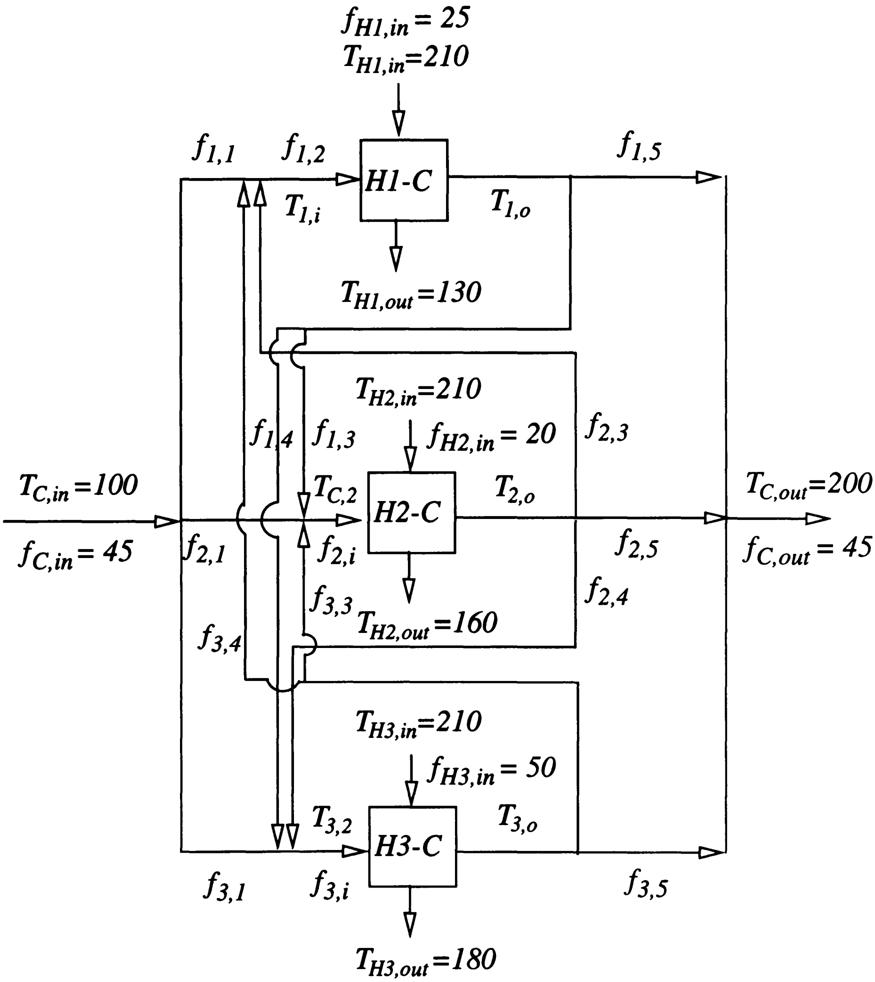


Figure 5.11: Heat exchanger network design problem 3, Floudas and Ciric (1988)

Variable bounds

$$
\begin{array}{rcl}
10 \leq & \Delta T_{1,1} & \leq 110 \\
10 \leq & \Delta T_{1,2} & \leq 110 \\
10 \leq & \Delta T_{2,1} & \leq 110 \\
10 \leq & \Delta T_{2,2} & \leq 110 \\
10 \leq & \Delta T_{3,1} & \leq 110 \\
10 \leq & \Delta T_{3,2} & \leq 110 \\
0 \leq & f_{1,j} & \leq 45, \; j = 1, \ldots, 5 \\
0 \leq & f_{2,j} & \leq 45, \; j = 1, \ldots, 5 \\
0 \leq & f_{3,j} & \leq 45, \; j = 1, \ldots, 5 \\
100 \leq & T_{j,i} & \leq 200, \; j = 1, \ldots, 3 \\
100 \leq & T_{j,o} & \leq 200, \; j = 1, \ldots, 3
\end{array}
$$

Problem Statistics

No. of continuous variables	27
No. of linear equalities	13
No. of nonlinear equalities	6
No. of known solutions	9

Global Solution

- Objective function: 10077.8
- Continuous variables:

$$
\boldsymbol{\Delta T} = \begin{pmatrix} 52.86 & 30.00 \\ 10.00 & 60.00 \\ 10.00 & 22.86 \end{pmatrix}
$$

$$
\boldsymbol{f} = \begin{pmatrix} 35 & 35 & 0 & 35 & 0 \\ 10 & 10 & 0 & 0 & 10 \\ 0 & 35 & 0 & 0 & 35 \end{pmatrix}
$$

$$
\begin{array}{ll}
T_{1,i} = 100 & T_{1,o} = 157.14 \\
T_{2,i} = 100 & T_{2,o} = 200 \\
T_{3,i} = 157.14 & T_{3,o} = 200
\end{array}
$$

Chapter 6

Biconvex and Difference of Convex Functions (D.C.) Problems

6.1 Introduction

Biconvex and Difference of Convex functions (D.C.) problems are subclasses of the general C^2 nonlinear programming problems. However, they possess special structure and therefore are treated separately in this chapter.

Biconvex problems possess the following special characteristic: the variables can be partitioned into two disjoint sets (X,Y) in such a way that when all of the variables in set X are fixed, the problem is convex in the remaining variables Y, and when all of the variables in set Y are fixed, the problem is convex in the set X.

A (D.C.) function $f(\boldsymbol{x})$ is of the form:

$$f(\boldsymbol{x}) = C_1(\boldsymbol{x}) - C_2(\boldsymbol{x})$$

where $C_1(\boldsymbol{x})$ and $C_2(\boldsymbol{x})$ are both convex functions. Therefore the function contains a convex part and a reverse-convex part.

6.2 Phase and Chemical Equilibrium Problems

6.2.1 Introduction

The phase and chemical equilibrium problem is extremely important for predicting fluid phase behavior for most separation process applications. Process simulators must be able to reliably and efficiently predict the correct number and type of phases that exist at equilibrium and the distribution of components within those phases. The Gibbs free energy is the thermodynamic function most often used for equilibrium calculations because it can be applied at

C. A. Floudas et al., *Handbook of Test Problems in Local and Global Optimization*

conditions of constant temperature and pressure. A global minimum of the Gibbs free energy corresponds to the true equilibrium solution. For many systems, the Gibbs free energy surface is nonconvex, therefore local optimization methods can provide no guarantees that the correct equilibrium solution has been located.

White et al. (1958) were among the first to use optimization methods for minimizing the Gibbs free energy with their RAND algorithm, developed for ideal systems. Castillo and Grossmann (1981) proposed a method whereby one problem is solved to determine the maximum number of phases present in the system and then a second problem is solved to minimize the Gibbs free energy. Paules and Floudas (1989) used the Global Optimum Search method of Floudas et al. (1989) to attempt to avoid converging to local extrema of the Gibbs function.

The GLOPEQ algorithm developed by McDonald and Floudas (1997) can provide a theoretical guarantee of convergence to the true equilibrium solution. The GLOPEQ algorithm is a two-step procedure in which the first step is to postulate the number of phases at equilibrium and a solution to the Gibbs free energy minimization problem is obtained. In the second step, the Gibbs tangent plane stability criterion is used to determine whether the candidate solution is the true equilibrium solution. This is done by solving the Gibbs tangent plane distance minimization problem to global optimality. If necessary, the proposed phase configuration is updated and the process is repeated.

A presentation of the thèoretical and algorithmic issues in global optimization approaches for the phase and chemical reaction equilibrium problems can be found in the book by Floudas (2000).

6.2.2 Mathematical Formulation

At constant temperature and pressure, the condition of equilibrium is that the Gibbs free energy function attains its global minimum. The condition is subject only to molar balances in the case of non-reacting systems, or elemental balances for reacting systems. For the following formulations, the Gibbs free energy function is expressed in terms of the activity coefficient for liquid phases, and vapor phases are assumed to be ideal. Depending upon the activity coefficient expression used, this may lead to either a biconvex formulation or a formulation that is the difference of two convex functions.

For nonideal systems, there may be multiple solutions to the Gibbs energy minimization problem. The tangent plane criterion can be used to determine whether or not a candidate solution is the true equilibrium solution. The tangent plane distance function is the difference between the Gibbs energy surface for a potential new phase and the tangent plane to the Gibbs energy surface constructed at the candidate solution point. If the tangent plane distance is non-negative over the whole composition space, then the candidate solution is the true equilibrium solution. The tangent plane distance function may itself be nonconvex, therefore this problem must be solved to global optimality in order to guarantee that the true equilibrium solution has been obtained.

Gibbs Free Energy Minimization

In the Gibbs energy minimization problem we are given a system of C components at a fixed temperature and pressure. P phases are postulated to be present in the equilibrium state. In the case of a reacting system, the components are composed of E elements.

Standard constraints

Elemental Balances - Reacting Systems

$$\sum_{i \in C} \sum_{k \in P} a_{ei} n_i^k = b_e \quad \forall\, e \in E$$

Molar Balances - Non-reacting Systems

$$\sum_{k \in P} n_i^k = n_i^T \quad \forall\, i \in C$$

Variable bounds

$$0 \le n_i^k \le n_i^T$$

Variable definitions

- n_i^k - the number of moles of component i in phase k.

Parameter definitions

- a_{ei} - number of elements e in component i.
- b_i - total number of elements e in mixture.
- n_i^T - total number of moles of component i.

The objective function is the Gibbs free energy function which is given by the equation: $G = \sum_{k \in P} \sum_{i \in C} n_i^k \mu_i^k$. The chemical potential of component i in phase k is denoted as μ_i^k. When the vapor phase is taken as ideal and the set of liquid phases P^L is represented by an activity coefficient equation, the Gibbs free energy minimization problem is formulated as:

$$
\begin{aligned}
\min_{n} \frac{G}{RT} = \quad & \sum_{k \in P} \sum_{i \in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} + \ln \frac{\hat{f}_i^k}{f_i^{k,o}} \right\} \\
& + \sum_{k \in P^L} \sum_{i \in C} n_i^k \left\{ \ln \gamma_i^k \right\} \\
\text{subject to} \quad & \sum_{i \in C} \sum_{k \in P} a_{ei} n_i^k = b_e \quad \forall\, e \in E \\
& 0 \le n_i^k \le n_i^T
\end{aligned}
$$

where $\Delta G_i^{k,f}$ is the Gibbs free energy of formation of component i in phase k at the system temperature. For a liquid phase,

$$\frac{\hat{f}_i^k}{f_i^{k,o}} = \hat{\gamma}_i^k x_i^k$$

and for a vapor phase,

$$\frac{\hat{f}_i^k}{f_i^{k,o}} = \hat{\phi}_i y_i P.$$

The symbol ^ denoted that the property is calculated for a component in a mixture. In the case of an ideal vapor phase, the fugacity coefficient, $\hat{\phi}_i$, is equal to one. If the correct number of phases have been postulated, then the global minimum of the Gibbs free energy will correspond to the true equilibrium state of the system.

In many cases, the formulation shown above can be simplified. In the first case, when reaction does not occur and both vapor and liquid phases are present, the relation $\Delta G_i^{L,f} = \Delta G_i^{V,f} + RT \ln P_i^{sat}$ can be used to remove the need to calculate Gibbs energies of formation. In the second case, when reaction does not occur and only liquid phases are present, the linear term involving the Gibbs energy of formation becomes a constant and can be removed from the objective function. Taking these simplifications into consideration, we define three different formulations of the minimum Gibbs free energy problem.

Objective I - Reacting System

$$\min_{n} \frac{G}{RT} = \sum_{k \in P} \sum_{i \in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} + \ln \frac{\hat{f}_i^k}{f_i^{k,o}} \right\}$$

Objective II - Non-reacting System, both vapor and liquid phases present

$$\min_{n} \frac{G}{RT} = \sum_{k \in P^L} \sum_{i \in C} n_i^k \ln P_i^{sat} + \sum_{k \in P} \sum_{i \in C} n_i^k \ln \frac{\hat{f}_i^k}{f_i^{k,o}}$$

Note that the first summation is only over the liquid phases, P^L.

Objective III - Non-reacting System, only liquid phases present

$$\min_{n} \frac{G}{RT} = \sum_{k \in P} \sum_{i \in C} n_i^k \ln \frac{\hat{f}_i^k}{f_i^{k,o}}$$

Tangent Plane Distance Minimization

In the tangent plane distance minimization problem, we are given a candidate equilibrium solution, $\boldsymbol{z}$, for a system of C components at fixed temperature and pressure. The tangent plane distance minimization problem must be solved to global optimality to determine if the candidate solution is stable or unstable with respect to an incipient phase with composition $\boldsymbol{x}$. If the global minimum is greater than or equal to zero, then the candidate phase is stable, otherwise it is unstable.

Elemental Balances - Reacting Systems

$$\sum_{i \in C} a_{ei} x_i = b_e \quad \forall\, e \in E$$

Molar Balances - Non-reacting Systems

$$\sum_{i \in C} x_i = 1$$

<u>Variable bounds</u>

$$0 \leq x_i \leq 1$$

<u>Variable definitions</u>

- x_i - The mole fraction of component i in the incipient phase.

The tangent plane distance function is the difference between the Gibbs free energy of a phase with composition $\boldsymbol{x}$, given by $\sum_{i \in C} x_i \mu_i(\boldsymbol{x})$, and the tangent plane to the Gibbs free energy surface constructed at the candidate phase composition $\boldsymbol{z}$, given by $\sum_{i \in C} x_i \mu_i(\boldsymbol{z})$. Using these definitions, the tangent plane distance minimization problems is formulated as follows:

$$\begin{aligned}
\min_{\boldsymbol{x}} F = \quad & \sum_{i \in C} x_i \left\{ \Delta G_i^f + \ln x_i + \ln \hat{\gamma}_i - \mu_i(\boldsymbol{z}) \right\} \\
\text{subject to} \quad & \sum_{i \in C} a_{ei} x_i = b_e \quad \forall\, e \in E \\
& \sum_{i \in C} x_i = 1 \\
& 0 \leq x_i \leq 1
\end{aligned}$$

The tangent plane distance formulation shown above can also be simplified, as discussed in the previous section for the Gibbs energy minimization problem.

Objective I - Reacting System

$$\min_{\boldsymbol{x}} F = \sum_{i \in C} x_i \left\{ \Delta G_i^f + \ln x_i + \ln \hat{\gamma}_i - \mu_i(\boldsymbol{z}) \right\}$$

Objective II - Non-reacting System, both vapor and liquid phases present

$$\min_{\boldsymbol{x}} F = \sum_{i \in C} x_i \left\{ RT \ln P_i^{sat} + \ln x_i + \ln \hat{\gamma}_i - \mu_i(\boldsymbol{z}) \right\}$$

Objective III - Non-reacting System, only liquid phases present

$$\min_{\boldsymbol{x}} F = \sum_{i \in C} x_i \left\{ \ln x_i + \ln \hat{\gamma}_i - \mu_i(\boldsymbol{z}) \right\}$$

6.3 Biconvex Problems

6.3.1 NRTL Equation

Renon and Prausnitz (1968) derived the NRTL equation from Scott's two-liquid theory using the assumption of non-randomness. The NRTL equation is capable of representing liquid-liquid immiscibility for multicomponent systems using only binary parameters. The analysis of McDonald and Floudas (1995c) shows that by introducing a substitution variable, Ψ_i^k, the problem can be written in a biconvex form.

Gibbs Free Energy Minimization

Objective function

$$\begin{aligned} \min_{\boldsymbol{n}, \Psi} G = & \sum_{k \in P} \sum_{i \in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} + \ln \frac{n_i^k}{\sum_{j \in C} n_j^k} \right\} \\ & + \sum_{i \in C} \sum_{k \in P_L} n_i^k \left\{ \sum_{j \in C} \mathcal{G}_{ij} \tau_{ij} \Psi_j^k \right\} \end{aligned}$$

where,

$$\mathcal{G}_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

Additional Constraints

Transformation constraint

$$\Psi_i^k \left\{ \sum_{j \in C} \mathcal{G}_{ij} n_j^k \right\} - n_i^k = 0 \quad \forall\, i \in C, k \in P_L$$

Variable definition

- n_i^k - the number of moles of component i in phase k.
- Ψ_i^k - an additional variable created by substitution in order to give the problem a biconvex form.

Parameter definition

- τ_{ij}, $\mathcal{G}_{ij}$ - non-symmetric binary interaction parameters.
- $\Delta G_i^{k,f}$ - Gibbs energy of formation of component i in phase k.
- P_L - denotes the subset of phases that are liquid.

Tangent Plane Distance Minimization

Objective function

$$\begin{aligned} \min_{\boldsymbol{x},\Psi} F = \;& \sum_{i \in C} x_i \left\{ \Delta G_i^f + \ln x_i - \mu_i(\boldsymbol{z}) \right\} \\ & + \sum_{i \in C} x_i \left\{ \sum_{j \in C} \mathcal{G}_{ij} \tau_{ij} \Psi_j \right\} \end{aligned}$$

Additional Constraints

Transformation constraint

$$\Psi_i \left\{ \sum_{j \in C} \mathcal{G}_{ij} x_j \right\} - x_i = 0 \quad \forall\, i \in C$$

Variable definition

- x_i - the mole fraction of component i in the incipient phase.
- Ψ_i - an additional variable created by substitution in order to give the problem a biconvex form.

Parameter definition

- τ_{ij}, $\mathcal{G}_{ij}$ - non-symmetric binary interaction parameters.
- ΔG_i^f - Gibbs energy of formation of component i.
- $\mu_i(z)$ - chemical potential of the candidate solution z.

6.3.2 Test Problem 1

The system of n-Butyl-Acetate and Water is a challenging two component, two phase example. This example was studied by Heidemann and Mandhane (1973) to demonstrate the potential complexities of the NRTL equation. In this example the Gibbs free energy is minimized. The reported global solution is from the work of McDonald and Floudas (1997). Since only liquid phases are present, this problem uses objective III for the Gibbs energy minimization.

Explicit Formulation

$$
\begin{aligned}
\min_{n,\Psi} G = \quad & n_1^1\left[\ln\frac{n_1^1}{n_1^1+n_2^1}\right] + n_2^1\left[\ln\frac{n_2^1}{n_1^1+n_2^1}\right] \\
& + n_1^2\left[\ln\frac{n_1^2}{n_1^2+n_2^2}\right] + n_2^2\left[\ln\frac{n_2^2}{n_1^2+n_2^2}\right] \\
& + n_1^1\left[\mathcal{G}_{11}\tau_{11}\Psi_1^1 + \mathcal{G}_{12}\tau_{12}\Psi_2^1\right] \\
& + n_2^1\left[\mathcal{G}_{21}\tau_{21}\Psi_2^1 + \mathcal{G}_{22}\tau_{22}\Psi_2^1\right] \\
& + n_1^2\left[\mathcal{G}_{11}\tau_{11}\Psi_1^2 + \mathcal{G}_{12}\tau_{12}\Psi_2^2\right] \\
& + n_2^2\left[\mathcal{G}_{21}\tau_{21}\Psi_2^2 + \mathcal{G}_{22}\tau_{22}\Psi_2^2\right]
\end{aligned}
$$

subject to

$$
\begin{aligned}
\mathcal{G}_{11}\Psi_1^1 n_1^1 + \mathcal{G}_{12}\Psi_1^1 n_2^1 - n_1^1 &= 0 \\
\mathcal{G}_{21}\Psi_2^1 n_1^1 + \mathcal{G}_{22}\Psi_2^1 n_2^1 - n_2^1 &= 0 \\
\mathcal{G}_{11}\Psi_1^2 n_1^2 + \mathcal{G}_{12}\Psi_1^2 n_2^2 - n_1^2 &= 0 \\
\mathcal{G}_{21}\Psi_2^2 n_1^2 + \mathcal{G}_{22}\Psi_2^2 n_2^2 - n_2^2 &= 0 \\
n_1^1 + n_1^2 &= n_1^T \\
n_2^1 + n_2^2 &= n_2^T \\
n_1^1, n_2^1, n_1^2, n_2^2 &\geq 0
\end{aligned}
$$

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 298 \text{ K} \\
\boldsymbol{n}^T &= (0.50, 0.50)^T \\
\boldsymbol{\alpha} &= \begin{pmatrix} 0.0 & 0.391965 \\ 0.391965 & 0.0 \end{pmatrix} \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 3.00498 \\ 4.69071 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	8
No. of linear equalities	2
No. of convex inequalities	-
No. of nonlinear equalities	4
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.02020
- Continuous variables

$$
\boldsymbol{n} = \begin{pmatrix} 0.4993 & 0.0007 \\ 0.3441 & 0.1559 \end{pmatrix}
$$

6.3.3 Test Problem 2

This is the same system as Test Problem 1. In this case, the tangent plane distance is minimized for a given candidate solution. The reported global solution is from the work of McDonald and Floudas (1995a). This problem uses objective III for the tangent plane distance minimization.

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 298 \text{ K} \\
\boldsymbol{z} &= (0.50, 0.50)^T \\
\boldsymbol{\mu}_i^0 &= (-0.06391, 0.02875)^T \\
\boldsymbol{\alpha} &= \begin{pmatrix} 0.0 & 0.391965 \\ 0.391965 & 0.0 \end{pmatrix} \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 3.00498 \\ 4.69071 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	2
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.03247
- Continuous variables

  $\boldsymbol{x} = (0.00421, 0.99579)^T$

6.3.4 Test Problem 3

This is a three component system of Toluene - Water - Aniline that was investigated by Castillo and Grossmann (1981). Two liquid phases are postulated and there is no reaction. In this example, the Gibbs free energy is minimized and objective III is used because only liquid phases are present. The reported global solution is from the work of McDonald and Floudas (1995c).

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 298 \text{ K} \\
\boldsymbol{n}^T &= (0.2995, 0.1998, 0.4994)^T \\
\boldsymbol{\alpha} &= \begin{pmatrix} 0.0 & 0.2485 & 0.30 \\ 0.2485 & 0.0 & 0.3412 \\ 0.30 & 0.3412 & 0.0 \end{pmatrix} \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 4.93035 & 1.59806 \\ 7.77063 & 0.0 & 4.18462 \\ 0.03509 & 1.59806 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	12
No. of linear equalities	3
No. of convex inequalities	-
No. of nonlinear equalities	6
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.3574
- Continuous variables

$$n = \begin{pmatrix} 0.29949 & 0.00001 \\ 0.06551 & 0.13429 \\ 0.49873 & 0.00067 \end{pmatrix}$$

6.3.5 Test Problem 4

This is the same three component system as in Test Problem 3, but in this case the tangent plane distance is minimized, using objective III. The reported global solution is from the work of McDonald and Floudas (1995c).

Data

$$\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 298 \text{ K} \\
\boldsymbol{z} &= (0.29989, 0.20006, 0.50005)^T \\
\boldsymbol{\mu}_i^0 &= (-0.28809, 0.29158, -0.59336)^T \\
\boldsymbol{\alpha} &= \begin{pmatrix} 0.0 & 0.2485 & 0.30 \\ 0.2485 & 0.0 & 0.3412 \\ 0.30 & 0.3412 & 0.0 \end{pmatrix} \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 4.93035 & 1.59806 \\ 7.77063 & 0.0 & 4.18462 \\ 0.03509 & 1.27932 & 0.0 \end{pmatrix}
\end{aligned}$$

Problem Statistics

No. of continuous variables	6
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	3
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.29454
- Continuous variables

  $\boldsymbol{x} = (0.00007, 0.99686, 0.00307)^T$

6.4 Difference of Convex Functions (D.C.) Problems

6.4.1 UNIQUAC Equation

The UNIQUAC equation was originally proposed by Abrams and Prausnitz (1975) and postulates that the excess Gibbs energy is composed of a combinatorial contribution due to differences in the sizes of molecules, and a residual contribution due to energetic interactions between molecules. A modified form of the equation proposed by Anderson and Prausnitz (1978a), (1978b) is used for better results with systems containing water and alcohols.

Gibbs Free Energy Minimization

Objective function

$$\min_{n} \hat{G}(n) = \sum_{k \in P} C^k - \sum_{k \in P} \sum_{i \in C} \psi_i n_i^k \ln n_i^k$$

where $C^k(n)$ is convex as is the term, $\sum_{k \in P} \sum_{i \in C} \psi_i n_i^k \ln n_i^k$ and,

$$\begin{aligned}
C^k(n) &= \sum_{i \in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} - z_i^R r_i \ln r_i + \frac{z}{2} q_i \ln q_i \right\} \\
&+ z^A \cdot \sum_{i \in C} r_i n_i^k \ln \left(\sum_{j \in C} r_j n_j^k \right) + \sum_{i \in C} z_i^B r_i n_i^k \ln \left(\frac{n_i^k}{\sum_{j \in C} r_j n_j^k} \right) \\
&+ \frac{z}{2} \sum_{i \in C} q_i n_i^k \ln \left(\frac{q_i n_i^k}{\sum_{j \in C} q_j n_j^k} \right) + q_i' n_i^k \ln \left(\sum_{j \in C} q_j' n_j^k \right) \\
&+ \sum_{i \in C} q_i' n_i^k \ln \left(\frac{n_i^k}{\sum_{j \in C} q_j' \tau_{ji} n_j^k} \right) \\
\psi_i &= q_i' + r_i z^A \quad \forall\, i \in C
\end{aligned}$$

and,

$$\begin{aligned}
z_i^R &= \frac{\frac{z}{2} q_i - 1}{r_i} \\
z^A &= z_M^R + \sum_{i \in C} \left[z_i^R - z_M^R \right] \\
z_i^B &= \sum_{j \neq i} \left[z_j^R - z_M^R \right] \quad \forall\, i \in C \\
z_M^R &= \min_i z_i^R
\end{aligned}$$

Tangent Plane Distance Minimization

Objective function

$$\min_{\boldsymbol{x}} F = \mathcal{C}^U(\boldsymbol{x}) - \sum_{i \in C} \psi_i x_i \ln x_i$$

where $\mathcal{C}^U(\boldsymbol{x})$ is convex as is the term, $\sum_{i \in C} \psi_i x_i \ln x_i$ and,

$$\begin{aligned}
\mathcal{C}^U(\boldsymbol{x}) &= \sum_{i \in C} x_i \left\{ \Delta G_i^f - \mu_i^0(\boldsymbol{z}) - z_i^R r_i \ln r_i \right\} \\
&\quad + z^A \cdot \sum_{i \in C} r_i x_i \ln \left(\sum_{j \in C} r_j x_j \right) + \sum_{i \in C} z_i^B r_i x_i \ln \left(\frac{x_i}{\sum_{j \in C} r_j x_j} \right) \\
&\quad + \tfrac{z}{2} \sum_{i \in C} q_i x_i \ln \left(\frac{q_i x_i}{\sum_{j \in C} q_j x_j} \right) + q_i' x_i \ln \left(\sum_{j \in C} q_j' x_j \right) \\
&\quad + \sum_{i \in C} q_i' x_i \ln \left(\frac{x_i}{\sum_{j \in C} q_j' \tau_{ji} x_j} \right) \\
\psi_i &= q_i' + r_i \left[z_i^R + z_i^B \right] \quad \forall\, i \in C
\end{aligned}$$

6.4.2 Test Problem 5

This ternary example, SBA - DSBE - Water, arises from an azeotropic distillation problem. The data for the problem and the reported global solution are from McDonald and Floudas (1997). Because of the sensitivity of this example to the parameters, it represents a challenging test for a global optimization method. In this example, the Gibbs free energy is minimized for a postulated LLV system, using objective II.

Data

$$\begin{aligned}
P &= 1.16996 \text{ atm} \\
T &= 363.19909 \text{ K} \\
\boldsymbol{n}^T &= (40.30707, 5.14979, 54.54314)^T \\
RT \ln P_i^{sat} &= (-0.3658348, -0.9825555, -0.3663657)^T \\
\boldsymbol{q} &= (3.6640, 5.1680, 1.4000)^T \\
\boldsymbol{q}' &= (4.0643, 5.7409, 1.6741)^T \\
\boldsymbol{r} &= (3.9235, 6.0909, 0.9200)^T \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & -193.141 & 424.025 \\ 415.855 & 0.0 & 315.312 \\ 103.810 & 3922.5 & 0.0 \end{pmatrix}
\end{aligned}$$

Problem Statistics

No. of continuous variables	9
No. of linear equalities	3
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: -70.75208
- Continuous variables

$$\boldsymbol{n} = \begin{pmatrix} 31.459 & 0.902 & 7.946 \\ 3.103 & 0.0 & 2.046 \\ 26.167 & 15.014 & 13.362 \end{pmatrix}$$

6.4.3 Test Problem 6

This is the same system as presented in Test Problem 5, but in this case the tangent plane distance function is minimized for a given candidate solution. Since both vapor and liquid phases are possible, objective II is used. The reported global minimum solution is from McDonald and Floudas (1995a).

Data

$$\begin{aligned}
P &= 1.16996 \text{ atm} \\
T &= 363.19909 \text{ K} \\
\boldsymbol{z} &= (0.51802, 0.05110, 0.43088)^T \\
RT \ln P_i^{sat} &= (-0.3658348, -0.9825555, -0.3663657)^T \\
\mu_i^0 &= (-0.92115, -2.27779, -0.40139)^T \\
\boldsymbol{q} &= (3.6640, 5.1680, 1.4000)^T \\
\boldsymbol{q}' &= (4.0643, 5.7409, 1.6741)^T \\
\boldsymbol{r} &= (3.9235, 6.0909, 0.9200)^T \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & -193.141 & 424.025 \\ 415.855 & 0.0 & 315.312 \\ 103.810 & 3922.5 & 0.0 \end{pmatrix}
\end{aligned}$$

Problem Statistics

No. of continuous variables	3
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: 0.0
- Continuous variables

  $\boldsymbol{x} = (0.51802, 0.05110, 0.43088)^T$

6.4.4 Test Problem 7

The system of Ethylene Glycol - Lauryl Alcohol - Nitromethane presents an interesting and challenging example because it may form three liquid phases. The data for this example and the reported global solution are given in McDonald and Floudas (1997). The Gibbs free energy is minimized for a postulated LLL system, using objective III.

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 295 \text{ K} \\
\boldsymbol{n}^T &= (0.4, 0.1, 0.5)^T \\
\boldsymbol{q} &= (2.2480, 7.3720, 1.8680)^T \\
\boldsymbol{q}' &= (2.2480, 7.3720, 1.8680)^T \\
\boldsymbol{r} &= (2.4088, 8.8495, 2.0086)^T \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 247.2 & 54.701 \\ 69.69 & 0.0 & 305.52 \\ 467.88 & 133.19 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	9
No. of linear equalities	3
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.16085
- Continuous variables

$$n = \begin{pmatrix} 0.00881 & 0.33595 & 0.05525 \\ 0.00065 & 0.00193 & 0.09741 \\ 0.30803 & 0.14703 & 0.04537 \end{pmatrix}$$

6.4.5 Test Problem 8

The system for this example is the same ternary system as Test Problem 7, but in this case the tangent plane distance is minimized using objective III for a given candidate solution. The data for this example and the reported global solution are given in McDonald and Floudas (1995a).

Data

$$\begin{aligned} P &= 1.0 \text{ atm} \\ T &= 295 \text{ K} \\ z &= (0.29672, 0.46950, 0.23378)^T \\ \mu_i^0 &= (-0.20102, -0.56343, -0.02272)^T \\ q &= (2.2480, 7.3720, 1.8680)^T \\ q' &= (2.2480, 7.3720, 1.8680)^T \\ r &= (2.4088, 8.8495, 2.0086)^T \\ \tau &= \begin{pmatrix} 0.0 & 247.2 & 54.701 \\ 69.69 & 0.0 & 305.52 \\ 467.88 & 133.19 & 0.0 \end{pmatrix} \end{aligned}$$

Problem Statistics

No. of continuous variables	3
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.0270
- Continuous variables

  $x = (0.71540, 0.00336, 0.28124)^T$

6.4.6 UNIFAC Equation

The UNIFAC equation was developed by Fredenslund et al. (1975) and is based on the UNIQUAC equation. The UNIFAC equation is a group contribution method and therefore can give estimates of activity coefficients in the absence of reliable experimental data. Many of the same parameters as the UNIQUAC equation are used, and it leads to a formulation that has the same characteristics as the UNIQUAC equation.

Gibbs Free Energy Minimization

Objective function

$$\min_{\boldsymbol{n}} \hat{G}(\boldsymbol{n}) = \sum_{k \in P} \mathcal{C}^k - \sum_{k \in P} \sum_{i \in C} \psi_i n_i^k \ln n_i^k$$

where, $\mathcal{C}^k(\boldsymbol{n})$ is convex as is the term, $\sum_{k \in P} \sum_{i \in C} \psi_i n_i^k \ln n_i^k$ and,

$$\begin{aligned}
\mathcal{C}^k(\boldsymbol{n}) &= \sum_{i \in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} - z_i^R r_i \ln r_i + \frac{z}{2} q_i \ln q_i - v^{(i)} \right\} \\
&\quad + z^A \cdot \sum_{i \in C} r_i n_i^k \ln \left(\sum_{j \in C} r_j n_j^k \right) + \sum_{i \in C} z_i^B r_i n_i^k \ln \left(\frac{n_i^k}{\sum_{j \in C} r_j n_j^k} \right) \\
&\quad + \frac{z}{2} \sum_{i \in C} q_i n_i^k \ln \left(\frac{q_i n_i^k}{\sum_{j \in C} q_j n_j^k} \right) + q_i n_i^k \ln \left(\sum_{j \in C} q_j n_j^k \right) \\
&\quad + \sum_{i \in C} n_i^k \sum_{l \in G} v_{li} Q_l \ln \left(\frac{n_i^k}{\sum_{j \in C} n_j^k \hat{v}_{lj}} \right) \\
\psi_i &= q_i + r_i z^A \quad \forall\, i \in C
\end{aligned}$$

and,

$$
\begin{aligned}
q_i &= \sum_{l \in G} v_{li} Q_l \\
r_i &= \sum_{l \in G} v_{li} R_l \\
\hat{v}_{li} &= \sum_{m \in G} Q_m v_{mi} \Psi_{ml} \\
v^{(i)} &= \sum_{l \in G} v_{li} \Lambda_l^{(i)} \\
\ln \Lambda_l^{(i)} &= Q_l \left\{ 1 - \ln \frac{\hat{v}_{li}}{q_i} - \sum_{m \in G} \frac{v_{mi} Q_m \Psi_{lm}}{\hat{v}_{mi}} \right\} \\
z_i^R &= \frac{\frac{z}{2} q_i - 1}{r_i} \\
z^A &= z_M^R + \sum_{i \in C} \left[z_i^R - z_M^R \right] \\
z_i^B &= \sum_{j \neq i} \left[z_j^R - z_M^R \right] \quad \forall\, i \in C \\
z_M^R &= \min_i z_i^R
\end{aligned}
$$

Tangent Plane Distance Minimization

Objective function

$$
\min_{\boldsymbol{x}} F = \quad \mathcal{C}^U(\boldsymbol{x}) - \sum_{i \in C} \psi_i x_i \ln x_i
$$

where, $\mathcal{C}^U(\boldsymbol{x})$ is convex as is the term, $\sum_{i \in C} \psi_i x_i \ln x_i$ and,

$$
\begin{aligned}
\mathcal{C}^U(\boldsymbol{x}) &= \sum_{i \in C} x_i \left\{ \frac{\Delta G_i^f}{RT} - \mu_i^0(z) - z_i^R r_i \ln r_i + \frac{z}{2} q_i \ln q_i - v^{(i)} \right\} \\
&\quad + z^A \cdot \sum_{i \in C} r_i x_i \ln \left(\sum_{j \in C} r_j x_j \right) + \sum_{i \in C} z_i^B r_i x_i \ln \left(\frac{x_i}{\sum_{j \in C} r_j x_j} \right) \\
&\quad + \frac{z}{2} \sum_{i \in C} q_i x_i \ln \left(\frac{x_i}{\sum_{j \in C} q_j x_j} \right) + q_i x_i \ln \left(\sum_{j \in C} q_j x_j \right) \\
&\quad + \sum_{i \in C} x_i \sum_{l \in G} v_{li} Q_l \ln \left(\frac{x_i}{\sum_{j \in C} x_j \hat{v}_{lj}} \right) \\
\psi_i &= q_i + r_i \left[z_i^R + z_i^B \right] \quad \forall\, i \in C
\end{aligned}
$$

6.4.7 Test Problem 9

The system of n-Butyl-Acetate and Water is a challenging two component, two liquid phase example. This example was studied by Heidemann and Mandhane (1973) to demonstrate the potential complexities of the NRTL equation. In this example the Gibbs free energy is minimized using the UNIFAC equation with objective III. The reported global solution is from the work of McDonald and Floudas (1997).

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 298 \text{ K} \\
\boldsymbol{n}^T &= (0.50, 0.50)^T \\
\boldsymbol{Q} &= (0.540, 0.848, 1.728, 1.400)^T \\
\boldsymbol{R} &= (0.6744, 0.9011, 1.9031, 0.9200)^T \\
\boldsymbol{v}^T &= \begin{pmatrix} 2 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 0.0 & 972.4 & 1300.0 \\ 0.0 & 0.0 & 972.4 & 1300.0 \\ -320.1 & -320.1 & 0.0 & 385.9 \\ 342.4 & 342.4 & -6.32 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	2
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.03407
- Continuous variables

$$
\boldsymbol{n} = \begin{pmatrix} 0.4998 & 0.0002 \\ 0.0451 & 0.4549 \end{pmatrix}
$$

6.4.8 Test Problem 10

The Ethanol - Benzene - Water system has been extensively studied due to the importance of the azeotropic distillation process used to separate ethanol and water using benzene as an entrainer. In this example the Gibbs free energy is minimized using the UNIFAC equation and two liquid phases are postulated, so objective III is used. The binary interaction parameters are obtained from Magnussen et al. (1981). The reported global solution is from the work of McDonald and Floudas (1997).

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 298 \text{ K} \\
\boldsymbol{n}^T &= (0.20, 0.40, 0.40)^T \\
\boldsymbol{Q} &= (1.972, 0.400, 1.400)^T \\
\boldsymbol{R} &= (2.1055, 0.5313, 0.9200)^T \\
\boldsymbol{v} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 6 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 89.60 & 353.5 \\ 636.1 & 0.0 & 903.8 \\ -229.1 & 362.3 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	6
No. of linear equalities	3
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: -3.02954

- Continuous variables

$$
\boldsymbol{n} = \begin{pmatrix} 0.0818 & 0.1181 \\ 0.3910 & 0.0090 \\ 0.0136 & 0.3864 \end{pmatrix}
$$

6.4.9 Test Problem 11

This is the same ternary system as in Test Problem 10, but in this case the tangent plane distance is minimized. The candidate solution is a three phase liquid-liquid-vapor solution, so objective II must be used. The example and the reported global solution appear in McDonald (1995).

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 338 \text{ K} \\
\boldsymbol{z} &= (0.27208, 0.00663, 0.72129)^T \\
RT \ln P_i^{sat} &= (-2.562164, -2.084538, -3.482138)^T \\
\boldsymbol{\mu}_i^0 &= (-1.59634, -0.50349, -1.64535)^T \\
\boldsymbol{Q} &= (1.972, 0.400, 1.400)^T \\
\boldsymbol{R} &= (2.1055, 0.5313, 0.9200)^T \\
\boldsymbol{v} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 6 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 89.60 & 353.5 \\ 636.1 & 0.0 & 903.8 \\ -229.1 & 362.3 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	3
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: 0.0
- Continuous variables

  $\boldsymbol{x} = (0.00565, 0.99054, 0.00381)^T$

6.4.10 ASOG Equation

Like the UNIFAC equation, the ASOG equation is based on group contribution methods. The method is described in the monograph of Kojima and Tochigi (1979). The activity coefficient expression is proposed to be made up of two contributions, one associated with the size of the molecules and a second associated with the groups that make up the molecules. The ASOG equation also leads to a D.C. formulation for the Gibbs energy and tangent plane distance minimization problems.

Gibbs Free Energy Minimization

Objective function

$$\min_{\boldsymbol{n}} \hat{G}(\boldsymbol{n}) = \sum_{k\in P} \mathcal{C}^k - \sum_{k\in P}\sum_{i\in C} \psi_i n_i^k \ln n_i^k$$

where, $\mathcal{C}^k(\boldsymbol{n})$, is convex as is the term, $\sum_{k\in P}\sum_{i\in C} \psi_i n_i^k \ln n_i^k$, and,

$$\begin{aligned}
\mathcal{C}^k(\boldsymbol{n}) &= \sum_{i\in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} + \ln \nu_i - v^{(i)} \right\} \\
&+ \sum_{i\in C} n_i^k \ln \left(\frac{n_i^k}{\sum_{j\in C} \nu_j n_j^k} \right) + \left(\sum_{i\in C} n_i^k v_i^S \right) \ln \left(\sum_{j\in C} n_j^k v_j^S \right) \\
&+ \sum_{i\in C} n_i^k \sum_{l\in G} v_{li} \ln \left(\frac{n_i^k}{\sum_{j\in C} n_j^k \hat{v}_{lj}} \right) \\
\psi_i &= v_i^S \quad \forall\, i \in C
\end{aligned}$$

and,

$$\begin{aligned}
\hat{v}_{li} &= \sum_{m\in G} Q_m v_{mi} a_{lm} \\
v_i^S &= \sum_{l\in G} v_{li} \\
v^{(i)} &= \sum_{l\in G} v_{li} \Lambda_l \\
\ln \Lambda_l &= 1 - \ln \sum_{l\in G} X_m a_{lm} - \sum_{m\in G} \frac{X_m a_{ml}}{\sum_{n\in G} X_n a_{mn}} \\
X_l &= \frac{\sum_{i\in C} x_i v_{li}}{\sum_{i\in C}\sum_{m\in G} x_i v_{mi}} \\
\ln a_{lm} &= m_{lm} + \frac{n_{lm}}{T}
\end{aligned}$$

Tangent Plane Distance Minimization

<u>Objective function</u>

$$\min_{\boldsymbol{x}} F = \mathcal{C}^U(\boldsymbol{x}) - \sum_{i\in C} \psi_i x_i \ln x_i$$

where, $\mathcal{C}^U(\boldsymbol{x})$, is convex as is the term, $\sum_{i\in C} \psi_i x_i \ln x_i$, and,

$$\begin{aligned}
\mathcal{C}^U(\boldsymbol{x}) &= \sum_{i\in C} x_i \left\{ \frac{\Delta G_i^f}{RT} - \mu_i^0(\boldsymbol{z}) + \ln \nu_i - v^{(i)} \right\} \\
&+ \sum_{i\in C} x_i \ln \left(\frac{x_i}{\sum_{j\in C} \nu_j x_j} \right) + \left(\sum_{i\in C} x_i v_i^S \right) \ln \left(\sum_{j\in C} x_j v_j^S \right) \\
&+ \sum_{i\in C} x_i \sum_{l\in G} v_{li} \ln \left(\frac{x_i}{\sum_{j\in C} x_j \hat{v}_{lj}} \right) \\
\psi_i &= v_i^S \quad \forall\, i \in C
\end{aligned}$$

6.4.11 Test Problem 12

The system of n-Butyl-Acetate and Water is a challenging two component, two liquid phase example. This example was studied by Heidemann and Mandhane (1973) to demonstrate the potential complexities of the NRTL equation. In this example the Gibbs free energy is minimized using the ASOG activity coefficient equation and objective III. The reported global solution is from the work of McDonald and Floudas (1997).

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 298 \text{ K} \\
\boldsymbol{n}^T &= (0.50, 0.50)^T \\
\boldsymbol{\nu} &= (8, 1)^T \\
\boldsymbol{v}^T &= \begin{pmatrix} 5 & 3 & 0 \\ 0 & 0 & 1.6 \end{pmatrix} \\
\boldsymbol{m} &= \begin{pmatrix} 0.0 & -15.2623 & -0.2727 \\ -0.3699 & 0.0 & -2.5548 \\ 0.5045 & -2.4686 & 0.0 \end{pmatrix} \\
\boldsymbol{n} &= \begin{pmatrix} 0.0 & 515.0 & -277.3 \\ 162.6 & 0.0 & 659.9 \\ -2382.3 & 565.7 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	2
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: 0.28919
- Continuous variables

$$
\boldsymbol{n} = \begin{pmatrix} 0.4994 & 0.0006 \\ 0.1179 & 0.3821 \end{pmatrix}
$$

6.4.12 Test Problem 13

The ternary system Ethanol - Ethyl Acetate - Water was studied by Walraven and van Rompay (1988) and by McDonald and Floudas (1997), whose global solution is reported. For this problem the Gibbs free energy is minimized using the ASOG activity coefficient equation. Two liquid phases are postulated for the solution, so objective III is used.

Data

$$
\begin{aligned}
P &= 1.0 \text{ atm} \\
T &= 343 \text{ K} \\
\boldsymbol{n}^T &= (0.08, 0.30, 0.62)^T \\
\boldsymbol{\nu} &= (3, 6, 1)^T \\
\boldsymbol{v} &= \begin{pmatrix} 2 & 1 & 0 & 0 \\ 3 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1.6 \end{pmatrix} \\
\boldsymbol{m} &= \begin{pmatrix} 0.0 & -41.2503 & -15.2623 & -0.2727 \\ 4.7125 & 0.0 & 0.0583 & -5.8341 \\ -0.3699 & -0.0296 & 0.0 & -2.5548 \\ 0.5045 & 1.4318 & -2.4686 & 0.0 \end{pmatrix} \\
\boldsymbol{n} &= \begin{pmatrix} 0.0 & 7686.4 & 515.0 & -277.3 \\ -3060.0 & 0.0 & -455.3 & 1582.5 \\ 162.6 & 2.6 & 0.0 & 659.9 \\ -2382.3 & -280.2 & 565.7 & 0.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	6
No. of linear equalities	3
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.25457
- Continuous variables

$$
\boldsymbol{n} = \begin{pmatrix} 0.0480 & 0.0320 \\ 0.0527 & 0.2473 \\ 0.5884 & 0.0316 \end{pmatrix}
$$

6.4.13 Modified Wilson Equation

Wilson (1964) proposed an expression for the excess Gibbs energy that contained a single nonsymmetric binary interaction parameter. The Wilson equation successfully predicts the equilibrium state for a large number of vapor-liquid systems. However, the Gibbs function that is obtained from the Wilson equation is convex, therefore the Wilson equation cannot predict liquid-liquid immiscibility. Tsuboka and Katayama (1975) proposed a modification of the Wilson equation that can overcome this limitation. The T-K-Wilson equation leads to a D.C. formulation for both the Gibbs free energy and tangent plane distance minimization problems.

Gibbs Free Energy Minimization

Objective function

$$\min_{\boldsymbol{n}} \hat{G}(\boldsymbol{n}) = \sum_{k\in P} \mathcal{C}^k - \sum_{k\in P}\sum_{i\in C} \psi_i n_i^k \ln n_i^k$$

where, $\mathcal{C}^k(\boldsymbol{n})$, is convex as is the term, $\sum_{k\in P}\sum_{i\in C} \psi_i n_i^k \ln n_i^k$, and,

$$\begin{aligned}
\mathcal{C}^k(\boldsymbol{n}) &= \sum_{i\in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} + \ln \frac{n_i^k}{\sum_{j\in C} n_j^k} + \ln \frac{n_i^k}{\sum_{j\in C} n_j^k \Lambda_{ji}} \right\} \\
&\quad + \sum_{i\in C} \left\{ \sum_{j\in C} \rho_{ji} n_j^k \right\} \ln \left\{ \sum_{j\in C} \rho_{ji} n_j^k \right\} + \sum_{i\in C}\sum_{j\neq i} \rho_{ji} n_j^k \ln \frac{n_j^k}{\sum_{l\in C} \rho_{li} n_l^k} \\
\psi_i &= 1 + \sum_{j\neq i} \rho_{ji} \quad \forall\, i \in C
\end{aligned}$$

Tangent Plane Distance Minimization

Objective function

$$\min_{\boldsymbol{x}} F = \mathcal{C}^U(\boldsymbol{x}) - \sum_{i\in C} \psi_i x_i \ln x_i$$

where, $\mathcal{C}^U(\boldsymbol{x})$, is convex as is the term, $\sum_{i\in C} \psi_i x_i \ln x_i$, and,

$$\begin{aligned}
\mathcal{C}^U(\boldsymbol{x}) &= \sum_{i\in C} x_i \left\{ \frac{\Delta G_i^f}{RT} - \mu_i^0(\boldsymbol{z}) + \ln \frac{x_i}{\sum_{j\in C} \Lambda_{ji} x_j} \right\} \\
&\quad + \sum_{i\in C} \left\{ \sum_{j\in C} \rho_{ji} x_j \right\} \ln \left\{ \sum_{j\in C} \rho_{ji} x_j \right\} + \sum_{i\in C}\sum_{j\neq i} \rho_{ji} x_j \ln \frac{x_j}{\sum_{l\in C} \rho_{li} x_l} \\
\psi_i &= \sum_{j\neq i} \rho_{ji} \quad \forall\, i \in C
\end{aligned}$$

6.4.14 Test Problem 14

The binary system Methanol - Cyclohexane is considered for the modified Wilson equation. The system was studied by Tsuboka and Katayama (1975) and McDonald and Floudas (1995b). The Gibbs free energy is minimized with two liquid phases postulated using objective III.

Data

$$\begin{aligned} P &= 1.0 \text{ atm} \\ T &= 298 \text{ K} \\ \boldsymbol{n}^T &= (0.50, 0.50)^T \\ \boldsymbol{\Lambda} &= \begin{pmatrix} 1.0 & 0.30384 \\ 0.095173 & 1.0 \end{pmatrix} \\ \boldsymbol{\rho} &= \begin{pmatrix} 1.0 & 0.374 \\ 2.6738 & 1.0 \end{pmatrix} \end{aligned}$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	2
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-

Global Solution

- Objective function: -0.07439
- Continuous variables

$$\boldsymbol{n} = \begin{pmatrix} 0.0583 & 0.4417 \\ 0.4080 & 0.0920 \end{pmatrix}$$

Chapter 7

Generalized Geometric Programming Problems

In this chapter, we will discuss test problems that arise from generalized geometric programming applications. For a thorough theoretical and algorithmic exposition of global optimization approaches for generalized geometric programming problems, the reader is directed to the article of Maranas and Floudas (1997), and the book by Floudas (2000).

7.1 Introduction

Generalized geometric or signomial programming *(GGP)* is the class of optimization problems where the objective function and constraints are the difference of two *posynomials*. A posynomial $G(\boldsymbol{x})$ is simply the sum of a number of *posynomial terms* or *monomials* $g_k(\boldsymbol{x}),\ k = 1, \dots, K$ multiplied by some positive real constants $c_k,\ k = 1, \dots, K$.

$$G(\boldsymbol{x}) \;=\; c_1 g_1(\boldsymbol{x}) + c_2 g_2(\boldsymbol{x}) + \cdots + c_K g_K(\boldsymbol{x})$$

Note that $c_k \in \Re^+,\ k = 1, \dots, K$. Each monomial $g_k(\boldsymbol{x})$ is in turn the product of a number of positive variables raised to some real power,

$$g_k(\boldsymbol{x}) \;=\; x_1^{d_{1,k}} x_2^{d_{2,k}} \cdots x_n^{d_{N,k}}, \;\; k = 1, \dots, K$$

where $d_{1,k}, d_{2,k}, \dots, d_{N,k} \in \Re$ and are not necessarily integer. The term geometric programming was adopted because of the key role that the well known arithmetic–geometric inequality played in the initial developments.

By grouping together monomials with identical sign, the generalized geometric *(GGP)* problem can be formulated as the following nonlinear optimization problem:

$$
\begin{array}{rrcl}
\min\limits_{t} & G_0(t) & = & G_0^+(t) \ - \ G_0^-(t) \\
\text{subject to} & G_j(t) & = & G_j^+(t) \ - \ G_j^-(t) \ \leq \ 0, \quad j = 1, \dots, M \\
& t_i \ \geq \ 0, & & i = 1, \dots, N \\
\text{where} & G_j^+(t) & = & \sum\limits_{k \in K_j^+} c_{jk} \prod\limits_{i=1}^{N} t_i^{\alpha_{ijk}}, \quad j = 0, \dots, M \\
& G_j^-(t) & = & \sum\limits_{k \in K_j^-} c_{jk} \prod\limits_{i=1}^{N} t_i^{\alpha_{ijk}}, \quad j = 0, \dots, M
\end{array}
$$

where $\boldsymbol{t} = (t_1, \dots, t_N)$ is the positive variable vector; G_j^+, G_j^-, $j = 0, \dots, M$ are positive posynomial functions in $\boldsymbol{t}$; α_{ijk} are arbitrary real constant exponents; whereas c_{jk} are given *positive* coefficients. Finally, sets K_j^+, K_j^- count how many positively/negatively signed monomials form posynomials G_j^+, G_j^- respectively. In general, formulation *(GGP)* corresponds to a highly nonlinear optimization problem with nonconvex objective function and/or constraint set and possibly disjoint feasible region.

A review of the previous work for posynomials and signomials along with global optimization methods for generalized geometric programming problem can be found in the book by Floudas (2000).

7.2 Literature Problems

In this section, chemical engineering example problems that are modelled as generalized geometric programming problems will be presented. The following examples correspond to an alkylation process design, a CSTR sequence design, a heat exchanger design, an optimal reactor design, and several problems taken from the literature. The reported global solutions are from the work of Maranas and Floudas (1997) and Adjiman et al. (1998b).

7.2.1 Test Problem 1 : Alkylation process design

This example involves the design of an alkylation unit as modeled by Dembo (1976). The objective is to improve the octane number of some olefin feed by reacting it with isobutane in the presence of acid.

Objective Function

$$\min \ c_1 x_1 + c_2 x_1 x_6 + c_3 x_3 + c_4 x_2 + c_5 - c_6 x_3 x_5$$

Constraints

$$
\begin{aligned}
c_7x_6^2 + c_8x_1^{-1}x_3 - c_9x_6 &\leq 1\\
c_{10}x_1x_3^{-1} + c_{11}x_1x_3^{-1}x_6 - c_{12}x_1x_3^{-1}x_6^2 &\leq 1\\
c_{13}x_6^2 + c_{14}x_5 - c_{15}x_4 - c_{16}x_6 &\leq 1\\
c_{17}x_5^{-1} + c_{18}x_5^{-1}x_6 + c_{19}x_4x_5^{-1} - c_{20}x_5^{-1}x_6^2 &\leq 1\\
c_{21}x_7 + c_{22}x_2x_3^{-1}x_4^{-1} - c_{23}x_2x_3^{-1} &\leq 1\\
c_{24}x_7^{-1} + c_{25}x_2x_3^{-1}x_7^{-1} - c_{26}x_2x_3^{-1}x_4^{-1}x_7^{-1} &\leq 1\\
c_{27}x_5^{-1} + c_{28}x_5^{-1}x_7 &\leq 1\\
c_{29}x_5 - c_{30}x_7 &\leq 1\\
c_{31}x_3 - c_{32}x_1 &\leq 1\\
c_{33}x_1x_3^{-1} + c_{34}x_3^{-1} &\leq 1\\
c_{35}x_2x_3^{-1}x_4^{-1} - c_{36}x_2x_3^{-1} &\leq 1\\
c_{37}x_4 + c_{38}x_2^{-1}x_3x_4 &\leq 1\\
c_{39}x_1x_6 + c_{40}x_1 - c_{41}x_3 &\leq 1\\
c_{42}x_1^{-1}x_3 + c_{43}x_1^{-1} - c_{44}x_6 &\leq 1
\end{aligned}
$$

Variable Bounds

$$
\begin{aligned}
1500 \leq\ & x_1 \leq 2000\\
1 \leq\ & x_2 \leq 120\\
3000 \leq\ & x_3 \leq 3500\\
85 \leq\ & x_4 \leq 93\\
90 \leq\ & x_5 \leq 95\\
3 \leq\ & x_6 \leq 12\\
145 \leq\ & x_7 \leq 162
\end{aligned}
$$

Data

The parameters c_i, $i = 1, \ldots, 44$ are shown in Table 7.1.

Problem Statistics

No. of continuous variables	7
No. of linear inequalities	2
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	12

Global Solution

- Objective Function : 1227.23

i	c_i	i	c_i	i	c_i
1	1.715	16	0.19120592 E-1	31	0.00061000
2	0.035	17	0.56850750 E+2	32	0.0005
3	4.0565	18	1.08702000	33	0.81967200
4	10.000	19	0.32175000	34	0.81967200
5	3000.0	20	0.03762000	35	24500.0
6	0.063	21	0.00619800	36	250.0
7	0.59553571 E-2	22	0.24623121 E+4	37	0.10204082 E-1
8	0.88392857	23	0.25125634 E+2	38	0.12244898 E-4
9	0.11756250	24	0.16118996 E+3	39	0.00006250
10	1.10880000	25	5000.0	40	0.00006250
11	0.13035330	26	0.48951000 E+6	41	0.00007625
12	0.00660330	27	0.44333333 E+2	42	1.22
13	0.66173269 E-3	28	0.33000000	43	1.0
14	0.17239878 E-1	29	0.02255600	44	1.0
15	0.56595559 E-2	30	0.00759500		

Table 7.1: Coefficients for alkylation example

- Continuous Variables

$$
\begin{aligned}
x_1^* &= 1698.18 \\
x_2^* &= 53.66 \\
x_3^* &= 3031.30 \\
x_4^* &= 90.11 \\
x_5^* &= 95 \\
x_6^* &= 10.50 \\
x_7^* &= 153.53
\end{aligned}
$$

7.2.2 Test Problem 2 : CSTR Sequence Design

This example was originally posed by Manousiouthakis and Sourlas (1992) and has been studied by Maranas and Floudas (1997), Ryoo and Sahinidis (1995) and Adjiman et al. (1998b). It involves the design of a sequence of two CSTR reactors where the consecutive reaction $A \rightarrow B \rightarrow C$ takes place. This problem is known to have caused difficulties for other global optimization methods.

Objective Function

$$\min -x_4$$

Constraints

$$
\begin{aligned}
x_1 + k_1 x_1 x_5 &= 1 \\
x_2 - x_1 + k_2 x_2 x_6 &= 0 \\
x_3 + x_1 + k_3 x_3 x_5 &= 1 \\
x_4 - x_3 + x_2 - x_1 + k_4 x_4 x_6 &= 0 \\
x_5^{0.5} + x_6^{0.5} &\leq 4 \\
k_1 &= 0.09755988 \\
k_2 &= 0.99 k_1 \\
k_3 &= 0.0391908 \\
k_4 &= 0.9
\end{aligned}
$$

Variable Bounds

$$(0, 0, 0, 10^{-5}, 10^{-5}) \leq (x_1, x_2, x_3, x_4, x_5) \leq (1, 1, 1, 1, 16, 16)$$

Problem Statistics

No. of continuous variables	6
No. of linear inequalities	–
No. of convex inequalities	–
No. of nonlinear equalities	4
No. of nonconvex inequalities	1

Global Solution

A number of close local minima exist, as shown below.

	obj	x_1	x_2	x_3	x_4	x_5	x_6
Global	-0.38881	0.772	0.517	0.204	0.388	3.036	5.097
Local 1	-0.38808	1.0	0.393	0.0	0.388	10^{-5}	15.975
Local 2	-0.37461	0.391	0.391	0.375	0.375	15.975	10^{-5}

7.2.3 Test Problem 3 : Heat exchanger design

This standard heat exchanger design problem was first formulated as a generalized geometric problem by Avriel and Williams (1971), as an alternative to the formulation of Test Problem 1 of Section 5.4. It can be written as follows:

Objective Function

$$\min \quad x_1 + x_2 + x_3$$

Constraints

$$\begin{aligned}
833.33252x_1^{-1}x_4x_6^{-1} + 100.0x_6^{-1} - 83333.333x_1^{-1}x_6^{-1} &\leq 1 \\
1250.0x_2^{-1}x_5x_7^{-1} + 1.0x_4x_7^{-1} - 1250.0x_2^{-1}x_4x_7^{-1} &\leq 1 \\
1250000.0x_3^{-1}x_8^{-1} + 1.0x_5x_8^{-1} - 2500.0x_3^{-1}x_5x_8^{-1} &\leq 1 \\
0.0025x_4 + 0.0025x_6 &\leq 1 \\
-0.0025x_4 + 0.0025x_5 + 0.0025x_7 &\leq 1 \\
0.01x_8 - 0.01x_5 &\leq 1
\end{aligned}$$

Variable Bounds

$$\begin{array}{rcccl}
100 & \leq & x_1 & \leq & 10000 \\
1000 & \leq & x_2 & \leq & 10000 \\
1000 & \leq & x_3 & \leq & 10000 \\
10 & \leq & x_4 & \leq & 1000 \\
10 & \leq & x_5 & \leq & 1000 \\
10 & \leq & x_6 & \leq & 1000 \\
10 & \leq & x_7 & \leq & 1000 \\
10 & \leq & x_8 & \leq & 1000
\end{array}$$

Problem Statistics

No. of continuous variables	8
No. of linear inequalities	3
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	3

Global Solution

- Objective Function : 7049.25
- Continuous Variable

$$
\begin{aligned}
x_1^* &= 579.31 \\
x_2^* &= 1359.97 \\
x_3^* &= 5109.97 \\
x_4^* &= 182.01 \\
x_5^* &= 295.60 \\
x_6^* &= 217.98 \\
x_7^* &= 286.42 \\
x_8^* &= 395.60
\end{aligned}
$$

7.2.4 Test Problem 4 : Optimal Reactor Design

This problem has been proposed by Dembo (1976) and it addresses the optimal design of a reactor.

Objective Function

$$
\min \quad 0.4x_1^{0.67}x_7^{-0.67} + 0.4x_2^{0.67}x_8^{-0.67} + 10.0 - x_1 - x_2
$$

Constraints

$$
\begin{aligned}
0.0588x_5x_7 + 0.1x_1 &\leq 1 \\
0.0588x_6x_8 + 0.1x_1 + 0.1x_2 &\leq 1 \\
4x_3x_5^{-1} + 2x_3^{-0.71}x_5^{-1} + 0.0588x_3^{-1.3}x_7 &\leq 1 \\
4x_4x_6^{-1} + 2x_4^{-0.71}x_6^{-1} + 0.0588x_4^{-1.3}x_8 &\leq 1
\end{aligned}
$$

Variable Bounds

$$
0.1 \leq x_i \leq 10, \quad i = 1, \ldots, 8
$$

Problem Statistics

No. of continuous variables	8
No. of linear inequalities	–
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	4

Global Solution

- Objective Function : 3.9511

- Continuous Variables

$$\begin{aligned} x_1^* &= 6.4747 \\ x_2^* &= 2.2340 \\ x_3^* &= 0.6671 \\ x_4^* &= 0.5957 \\ x_5^* &= 5.9310 \\ x_6^* &= 5.5271 \\ x_7^* &= 1.0108 \\ x_8^* &= 0.4004 \end{aligned}$$

7.2.5 Test Problem 5 : Colville's Test Problem

This problem is taken from the compilation of test problems by Rijckaert and Martens (1978b) and it appears to have troubled the local solvers on it was tested.

Objective Function

$$\min \; 5.3578t_3^2 + 0.8357t_1t_5 + 37.2392t_1$$

Constraints

$$\begin{aligned} 0.00002584t_3t_5 - 0.00006663t_2t_5 - 0.0000734t_1t_4 &\leq 1 \\ 0.000853007t_2t_5 + 0.00009395t_1t_4 - 0.00033085t_3t_5 &\leq 1 \\ 1330.3294t_2^{-1}t_5^{-1} - 0.42t_1t_5^{-1} - 0.30586t_2^{-1}t_3^2t_5^{-1} &\leq 1 \\ 0.00024186t_2t_5 + 0.00010159t_1t_2 + 0.00007379t_3^2 &\leq 1 \\ 2275.1327t_3^{-1}t_5^{-1} - 0.2668t_1t_5^{-1} - 0.40584t_4t_5^{-1} &\leq 1 \\ 0.00029955t_3t_5 + 0.00007992t_1t_3 + 0.00012157t_3t_4 &\leq 1 \end{aligned}$$

Variable Bounds

$$\begin{aligned} 78 \leq\; & t_1 \leq 102 \\ 33 \leq\; & t_2 \leq 45 \\ 27 \leq\; & t_3 \leq 45 \\ 27 \leq\; & t_4 \leq 45 \\ 27 \leq\; & t_5 \leq 45 \end{aligned}$$

Problem Statistics

No. of continuous variables	5
No. of linear inequalities	–
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	6

Global Solution

- Objective Function : 1.1436
- Continuous Variables

$$\begin{aligned} t_1^* &= 78 \\ t_2^* &= 33 \\ t_3^* &= 29.998 \\ t_4^* &= 45 \\ t_5^* &= 36.7673 \end{aligned}$$

7.2.6 Test Problem 6

This is problem 10 of Rijckaert and Martens (1978b).

Objective Function

$$\min \ 0.5t_1t_2^{-1} - t_1 - 5t_2^{-1}$$

Constraints

$$0.01t_2t_3^{-1} + 0.01t_1 + 0.0005t_1t_3 \leq 1$$

Variable Bounds

$$1 \leq t_1, t_2, t_3 \leq 100$$

Problem Statistics

No. of continuous variables	3
No. of linear inequalities	–
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	1

Global Solution

- Objective Function : -83.254
- Continuous Variables

$$\begin{aligned} t_1^* &= 88.2890 \\ t_2^* &= 7.7737 \\ t_3^* &= 1.3120 \end{aligned}$$

7.2.7 Test Problem 7

This is problem 11 from Rijckaert and Martens (1978b).

Objective Function

$$\min \quad -t_1 + 0.4t_1^{0.67}t_3^{-0.67}$$

Constraints

$$\begin{aligned} 0.05882t_3t_4 + 0.1t_1 &\leq 1 \\ 4t_2t_4^{-1} + 2t_2^{-0.71}t_4^{-1} + 0.05882t_2^{-1.3}t_3 &\leq 1 \end{aligned}$$

Variable Bounds

$$0.1 \leq t_1, t_2, t_3, t_4 \leq 10$$

Problem Statistics

No. of continuous variables	4
No. of linear inequalities	–
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	2

Global Solution

- Objective Function : -5.7398
- Continuous Variables

$$\begin{aligned} t_1^* &= 8.1267 \\ t_2^* &= 0.6154 \\ t_3^* &= 0.5650 \\ t_4^* &= 5.6368 \end{aligned}$$

7.2.8 Test Problem 8

This is Problem 12 from Rijckaert and Martens (1978b).

Objective Function

$$\min \quad -t_1 - t_5 + 0.4t_1^{0.67}t_3^{-0.67} + 0.4t_5^{0.67}t_7^{-0.67}$$

Constraints

$$\begin{aligned} 0.05882t_3t_4 + 0.1t_1 &\leq 1 \\ 0.05882t_7t_8 + 0.1t_1 + 0.1t_5 &\leq 1 \\ 4t_2t_4^{-1} + 2t_2^{-0.71}t_4^{-1} + 0.05882t_2^{-1.3}t_3 &\leq 1 \\ 4t_6t_8^{-1} + 2t_6^{-0.71}t_8^{-1} + 0.05882t_6^{-1.3}t_7 &\leq 1 \end{aligned}$$

Variable Bounds

$$0.01 \leq t_i \leq 10, \quad i = 1, \ldots, 8$$

Problem Statistics

No. of continuous variables	8
No. of linear inequalities	–
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	4

Global Solution

- Objective Function : -6.0482
- Continuous Variables

$$\begin{aligned} t_1^* &= 6.4225 \\ t_2^* &= 0.6686 \\ t_3^* &= 1.0239 \\ t_4^* &= 5.9399 \\ t_5^* &= 2.2673 \\ t_6^* &= 0.5960 \\ t_7^* &= 0.4029 \\ t_8^* &= 5.5288 \end{aligned}$$

7.2.9 Test Problem 9

This is Problem 14 from Rijckaert and Martens (1978b).

Objective Function

$$\min \; t_6 + 0.4t_4^{0.67} + 0.4t_9^{0.67}$$

Constraints

$$\begin{aligned} t_1^{-1}t_2^{-1.5}t_3t_4^{-1}t_5^{-1} + 5t_1^{-1}t_2^{-1}t_3t_5^{1.2} &\leq 1 \\ 0.05t_3 + 0.05t_2 &\leq 1 \\ 10t_3^{-1} - t_1t_3^{-1} &\leq 1 \\ t_6^{-1}t_7^{-1.5}t_8t_9^{-1}t_{10}^{-1} + 5t_6^{-1}t_7^{-1}t_8t_{10}^{1.2} &\leq 1 \\ t_2^{-1}t_7 + t_2^{-1}t_8 &\leq 1 \\ t_1t_8^{-1} - t_6t_8^{-1} &\leq 1 \\ t_{10} &\leq 0.1 \end{aligned}$$

Variable Bounds

$$0.01 \leq t_i \leq 15, \quad i = 1, \ldots, 10$$

Problem Statistics

No. of continuous variables	10
No. of linear inequalities	1
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	6

Best Known Solution

- Objective Function : 1.1436
- Continuous Variables

$$
\begin{array}{rclrcl}
t_1^* & = & 2.0953 & t_6^* & = & 0.4548 \\
t_2^* & = & 12.0953 & t_7^* & = & 10.4548 \\
t_3^* & = & 7.9047 & t_8^* & = & 1.6405 \\
t_4^* & = & 0.4594 & t_9^* & = & 1.1975 \\
t_5^* & = & 0.3579 & t_{10}^* & = & 0.1000
\end{array}
$$

7.2.10 Test Problem 10

This is Problem 17 from Rijckaert and Martens (1978b).

Objective Function

$$\min \; t_3^{-1}$$

Constraints

$$
\begin{array}{rcl}
0.1t_{10} + t_7 t_{10} & \leq & 1 \\
10t_1 t_4 + 10t_1 t_4 t_7^2 & \leq & 1 \\
t_4^{-1} - 100t_7 t_{10} & \leq & 1 \\
t_{10} t_{11}^{-1} - 10t_8 & \leq & 1 \\
t_1^{-1} t_2 t_5 + t_1^{-1} t_2 t_5 t_8^2 & \leq & 1 \\
t_5^{-1} - 10t_1^{-1} t_8 t_{11} & \leq & 1 \\
10t_{11} - 10t_9 & \leq & 1 \\
t_2^{-1} t_3 t_6 + t_2^{-1} t_3 t_6 t_9^2 & \leq & 1 \\
t_6^{-1} - t_2^{-1} t_9 & \leq & 1
\end{array}
$$

Variable Bounds

$$0.01 \leq t_i \leq 10, \; i = 1, \ldots, 11$$

Problem Statistics

No. of continuous variables	11
No. of linear inequalities	–
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	9

Best Known Solution

- Objective Function : 1.1406
- Continuous Variables

$$\begin{array}{rcl} t_1^* & = & 7.004 \\ t_2^* & = & 7.646 \\ t_3^* & = & 7.112 \\ t_4^* & = & 0.0125 \\ t_5^* & = & 0.8120 \\ t_6^* & = & 0.9558 \end{array} \qquad \begin{array}{rcl} t_7^* & = & 0.3820 \\ t_8^* & = & 0.3580 \\ t_9^* & = & 0.3530 \\ t_{10}^* & = & 2.0770 \\ t_{11}^* & = & 0.4530 \end{array}$$

7.3 Robust Stability Analysis

Robust stability analysis of linear systems involves the identification of the largest possible region in the uncertain model parameter space for which the controller manages to stabilize any disturbances in the system. The stability of a feedback structure is determined by the roots of the closed loop characteristic equation:

$$\det\left(I + P(s, \boldsymbol{q})C(s, \boldsymbol{q})\right) = 0$$

where $\boldsymbol{q}$ is the vector of the uncertain model parameters, and $P(s), C(s)$ are the transfer functions of the plant and controller respectively. After expanding the determinant we have:

$$P(s, \boldsymbol{q}) = a_n(\boldsymbol{q})s^n + a_{n-1}(\boldsymbol{q})s^{n-1} + \cdots + a_1(\boldsymbol{q})s + a_0(\boldsymbol{q}) = 0$$

where the coefficients $a_i(\boldsymbol{q}),\ i = 0, \ldots, n$ are typically multivariable polynomial functions.

A stability margin k_m can then be defined as follows:

$$k_m(j\omega) = \inf\{k \ : \ P(j\omega,\ \boldsymbol{q}(k)) = 0,\ \forall\, \boldsymbol{q} \in \mathcal{Q}\}$$

Robust stability for this model is then guaranteed if and only if:

$$k_m \geq 1$$

Note that, real parameter uncertainty is typically expressed as positive and negative deviations of the real parameters from some nominal values. Checking the stability of a particular system with characteristic equation $P(j\omega, \boldsymbol{q})$ involves the solution of the following nonconvex optimization problem.

$$\min_{q_i, k \geq 0, \omega \geq 0} \quad k \tag{S}$$

$$\begin{aligned} \text{subject to} \quad Re\,[P(j\omega, \boldsymbol{q})] &= 0 \\ Im\,[P(j\omega, \boldsymbol{q})] &= 0 \\ q_i^N - \Delta q_i^- \, k \leq q_i &\leq q_i^N + \Delta q_i^+ \, k, \quad i = 1, \ldots, n \end{aligned}$$

where $\boldsymbol{q}^N$ is a stable nominal point for the uncertain parameters and $\Delta \boldsymbol{q}^+, \Delta \boldsymbol{q}^-$ are the estimated bounds. Note that it is important to be able to always locate the global minimum of *(S)*, otherwise the stability margin might be overestimated. This overestimation can sometimes lead to the erroneous conclusion that a system is stable when it is not.

The reported global solutions are from the work of Maranas and Floudas (1997) and Adjiman et al. (1998b).

7.3.1 Test Problem 11

This example was first proposed by de Gaston and Safonov (1988). The stability margin formulation is:

Objective Function

$$\min \ k$$

Constraints

$$\begin{aligned} &10q_2^2q_3^3 + 10q_2^3q_3^2 + 200q_2^2q_3^2 + 100q_2^3q_3 \\ &+100q_2q_3^3 + q_1q_2q_3^2 + q_1q_2^2q_3 + 1000q_2q_3^2 \\ &+8q_1q_3^2 + 1000q_2^2q_3 + 8q_1q_2^2 + 6q_1q_2q_3 \\ &+60q_1q_3 + 60q_1q_2 - q_1^2 - 200q_1 \ \leq \ 0 \end{aligned}$$

$$\begin{aligned} 800 - 800k \ &\leq q_1 \leq \ 800 + 800k \\ 4 - 2k \ &\leq q_2 \leq \ 4 + 2k \\ 6 - 3k \ &\leq q_3 \leq \ 6 + 3k \end{aligned}$$

Problem Statistics

No. of continuous variables	4
No. of linear inequalities	6
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	1

Global Solution

- Objective Function : 0.3417
- Continuous Variables

$$\begin{aligned} q_1^* &= 1073.4 \\ q_2^* &= 3.318 \\ q_3^* &= 4.975 \end{aligned}$$

7.3.2 Test Problem 12

This example examines the l_∞ stability margin for the closed–loop system described in Sideris and Sànchez (1988).

Objective Function

$$\min \ k$$

Constraints

$$q_1^4 q_2^4 - q_1^4 - q_2^4 q_3 = 0$$

$$\begin{aligned} 1.4 - 0.25k &\leq q_1 \leq 1.4 + 0.25k \\ 1.5 - 0.20k &\leq q_2 \leq 1.5 + 0.20k \\ 0.8 - 0.20k &\leq q_3 \leq 0.8 + 0.20k \end{aligned}$$

Problem Statistics

No. of continuous variables	4
No. of linear inequalities	6
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	1

Global Solution

- Objective Function : 1.089

- Continuous Variables

$$\begin{aligned} q_1^* &= 1.1275 \\ q_2^* &= 1.2820 \\ q_3^* &= 1.0179 \end{aligned}$$

7.3.3 Test Problem 13

This example involves affine coefficient functions and it was first proposed by Ackermann et al. (1991).

Objective Function

$$\min \; k$$

Constraints

$$\begin{aligned} q_3 + 9.625q_1\omega + 16q_2\omega + 16\omega^2 + 12 - 4q_1 - q_2 - 78\omega &= 0 \\ 16q_1\omega + 44 - 19q_1 - 8q_2 - q_3 - 24\omega &= 0 \end{aligned}$$

$$\begin{aligned} 2.25 - 0.25k \;\leq\; &q_1 \;\leq\; 2.25 + 0.25k \\ 1.5 - 0.50k \;\leq\; &q_2 \;\leq\; 1.5 + 0.50k \\ 1.5 - 1.50k \;\leq\; &q_3 \;\leq\; 1.5 + 1.50k \end{aligned}$$

Problem Statistics

No. of continuous variables	5
No. of linear inequalities	6
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	2

Global Solution

This solution is valid for $0 \leq \omega \leq 10$.

- Objective Function : 0.8175

- Continuous Variables

$$\begin{aligned} q_1^* &= 2.4544 \\ q_2^* &= 1.9088 \\ q_3^* &= 2.7263 \\ \omega^* &= 1.3510 \end{aligned}$$

7.3.4 Test Problem 14

This example studies the stability of the mechanical system introduced by Vicino et al. (1990).

Objective Function

$$\min \ k$$

Constraints

$$\begin{aligned} a_4(\boldsymbol{q})\omega^4 - a_2(\boldsymbol{q})\omega^2 + a_0(\boldsymbol{q}) &= 0 \\ a_3(\boldsymbol{q})\omega^2 - a_1(\boldsymbol{q}) &= 0 \end{aligned}$$

$$\begin{array}{rcl} 10.0 - 1.0k \le & q_1 & \le 10.0 + 1.0k \\ 1.0 - 0.1k \le & q_2 & \le 1.0 + 0.1k \\ 1.0 - 0.1k \le & q_3 & \le 1.0 + 0.1k \\ 0.2 - 0.01k \le & q_4 & \le 0.2 + 0.01k \\ 0.05 - 0.005k \le & q_5 & \le 0.05 + 0.005k \end{array}$$

$$\begin{aligned} \text{where } a_4(\boldsymbol{q}) &= q_3^2 q_2 (4q_2 + 7q_1) \\ a_3(\boldsymbol{q}) &= 7q_4 q_3^2 q_2 - 64.918 q_3^2 q_2 + 380.067 q_3 q_2 + 3q_5 q_2 + 3q_5 q_1 \\ a_2(\boldsymbol{q}) &= 3\left(-9.81 q_3 q_2^2 - 9.81 q_3 q_1 q_2 - 4.312 q_3^2 q_2 + 264.896 q_3 q_2\right) \\ &+ 3(q_4 q_5 - 9.274 q_5) \\ a_1(\boldsymbol{q}) &= \frac{1}{5}(-147.15 q_4 q_3 q_2 + 1364.67 q_3 q_2 - 27.72 q_5) \\ a_0(\boldsymbol{q}) &= 54.387 q_3 q_2 \end{aligned}$$

Problem Statistics

No. of continuous variables	7
No. of linear inequalities	10
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	2

Global Solution

This solution is valid for $0 \le \omega \le 10$.

- Objective Function : 6.2746

- Continuous Variables

$$
\begin{aligned}
q_1^* &= 16.2746 \\
q_2^* &= 1.6275 \\
q_3^* &= 1.6275 \\
q_4^* &= 0.1373 \\
q_5^* &= 0.0186 \\
\omega^* &= 0.9864
\end{aligned}
$$

7.3.5 Test Problem 15

This example addresses the stability of a wire guided Daimler Benz 0305 bus and was studied by Ackermann et al. (1991).

Objective Function

$$\min \ k$$

Constraints

$$
\begin{aligned}
a_8(\boldsymbol{q})\omega^8 - a_6(\boldsymbol{q})\omega^6 + a_4(\boldsymbol{q})\omega^4 - a_2(\boldsymbol{q})\omega^2 + a_0(\boldsymbol{q}) &= 0 \\
a_7(\boldsymbol{q})\omega^6 - a_5(\boldsymbol{q})\omega^4 + a_3(\boldsymbol{q})\omega^2 - a_1(\boldsymbol{q}) &= 0 \\
17.5 - 14.5k \ \leq \ q_1 \ \leq \ 17.5 + 14.5k & \\
20.0 - 15.0k \ \leq \ q_2 \ \leq \ 20.0 + 15.0k &
\end{aligned}
$$

$$
\begin{aligned}
\text{where } a_0(q_1, q_2) &= 453\,10^6 q_1^2 \\
a_1(q_1, q_2) &= 528\,10^6 q_1^2 + 3640\,10^6 q_1 \\
a_2(q_1, q_2) &= 5.72\,10^6 q_1^2 q_2 + 113\,10^6 q_1^2 + 4250\,10^6 q_1 \\
a_3(q_1, q_2) &= 6.93\,10^6 q_1^2 q_2 + 911\,10^6 q_1 + 4220\,10^6 \\
a_4(q_1, q_2) &= 1.45\,10^6 q_1^2 q_2 + 16.8\,10^6 q_1 q_2 + 338\,10^6 \\
a_5(q_1, q_2) &= 15.6\,10^3 q_1^2 q_2^2 + 840 q_1^2 q_2 + 1.35\,10^6 q_1 q_2 + 13.5\,10^6 \\
a_6(q_1, q_2) &= 1.25\,10^3 q_1^2 q_2^2 + 16.8 q_1^2 q_2 + 53.9\,10^3 q_1 q_2 + 270\,10^3 \\
a_7(q_1, q_2) &= 50 q_1^2 q_2^2 + 1080 q_1 q_2 \\
a_8(q_1, q_2) &= q_1^2 q_2^2
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear inequalities	4
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	2

Global Solution

The system was found to be stable, $k_m > 1.0$, for the given range of uncertain parameters and $0 \leq \omega leq 10$.

7.3.6 Test Problem 16

In this example, an analysis of the stability margin of the spark ignition engine Fiat Dedra (Barmish (1994), Abate et al. (1994)) is carried out for a continuous range of operating conditions involving seven uncertain parameters.

Objective Function

$$\min \; k$$

Constraints

$$\begin{aligned} -a_6(\boldsymbol{q})\omega^6 + a_4(\boldsymbol{q})\omega^4 + -a_2(\boldsymbol{q})\omega^2 + a_0(\boldsymbol{q}) &= 0 \\ a_7(\boldsymbol{q})\omega^6 - a_5(\boldsymbol{q})\omega^4 + a_3(\boldsymbol{q})\omega^2 - a_1(\boldsymbol{q}) &= 0 \end{aligned}$$

$$\begin{array}{rcccl} 3.4329 - 1.2721k & \leq & q_1 & \leq & 3.4329 \\ 0.1627 - 0.06k & \leq & q_2 & \leq & 0.1627 \\ 0.1139 - 0.0782k & \leq & q_3 & \leq & 0.1139 \\ 0.2539 & \leq & q_4 & \leq & 0.2539 + 0.3068k \\ 0.0208 - 0.0108k & \leq & q_5 & \leq & 0.0208 \\ 2.0247 & \leq & q_6 & \leq & 2.0247 + 2.4715k \\ 1.0000 & \leq & q_7 & \leq & 1.0000 + 9.0000k \end{array}$$

$$a_7(\boldsymbol{q}) = q_7^2$$

$$a_6(\boldsymbol{q}) = 0.1586 q_1 q_7^2 + 2 q_2 q_7^2 + 2 q_5 q_7 + 0.1826 q_6 q_7 + 0.0552 q_7^2$$

$$\begin{aligned} a_5(\boldsymbol{q}) = \; & 0.0189477 q_1 q_7^2 + 0.11104 q_2 q_7^2 + 0.1826 q_5 q_6 + 0.1104 q_5 q_7 \\ & + 0.0237398 q_6 q_7 + q_2^2 q_7^2 + 0.1586 q_1 q_2 q_7^2 + 0.0872 q_1 q_4 q_7 \\ & + 0.0215658 q_1 q_6 q_7 + 0.3652 q_2 q_6 q_7 + 2 q_3 q_4 q_7 - 0.0848 q_3 q_6 q_7 \\ & + q_5^2 + 7.61760\ 10^{-4} q_7^2 + 0.3172 q_1 q_5 q_7 + 4 q_2 q_5 q_7 \end{aligned}$$

$$\begin{aligned} a_4(\boldsymbol{q}) = \; & 0.1586 q_1 q_5^2 + 4.02141\ 10^{-4} q_1 q_7^2 + 2 q_2 q_5^2 + 0.00152352 q_2 q_7^2 \\ & + 0.0237398 q_5 q_6 + 0.00152352 q_5 q_7 + 5.16120\ 10^{-4} q_6 q_7 \\ & + 0.0552 q_2^2 q_7^2 + 0.01898477 q_1 q_2 q_7^2 + 0.0872 q_1 q_4 q_5 \\ & + 0.034862 q_1 q_4 q_7 + 0.0215658 q_1 q_5 q_6 + 0.00287416 q_1 q_6 q_7 \\ & + 0.0474795 q_2 q_6 q_7 + 2 q_3 q_4 q_5 + 0.1826 q_3 q_4 q_6 + 0.1104 q_3 q_4 q_7 \\ & - 0.0848 q_3 q_5 q_6 - 0.00234048 q_3 q_6 q_7 + 2 q_2^2 q_5 q_7 + 0.1826 q_2^2 q_6 q_7 \\ + \; & 0.0872 q_1 q_2 q_4 q_7 + 0.3172 q_1 q_2 q_5 q_7 + 0.0215658 q_1 q_2 q_6 q_7 + 0.1586 q_1 q_3 q_4 q_7 \\ + \; & 2 q_2 q_3 q_4 q_7 - 0.0848 q_2 q_3 q_6 q_7 + 0.0552 q_5^2 \\ & + 0.3652 q_2 q_5 q_6 + 0.0378954 q_1 q_5 q_7 + 0.2208 q_2 q_5 q_7 \end{aligned}$$

$$
\begin{aligned}
a_3(\boldsymbol{q}) &= 0.0189477q_1q_5^2 + 0.1104q_2q_5^2 + 5.16120\ 10^{-4}q_5q_6 + q_2^2q_5^2 \\
& \quad +7.61760\ 10^{-4}q_2^2q_7^2 + q_3^2q_4^2 + 0.1586q_1q_2q_5^2 + 4.02141\ 10^{-4}q_1q_2q_7^2 \\
& \quad +0.0872q_1q_3q_4^2 + 0.034862q_1q_4q_5 + 0.00336706q_1q_4q_7 \\
&+ \quad 0.00287416q_1q_5q_6 + 6.28987\ 10^{-5}q_1q_6q_7 + 0.00103224q_2q_6q_7 \\
&+ \quad 0.1104q_3q_4q_5 + 0.0237398q_3q_4q_6 + 0.00152352q_3q_4q_7 \\
&- \quad 0.00234048q_3q_5q_6 + 0.1826q_2^2q_5q_6 + 0.1104q_2^2q_5q_7 \\
& \quad +0.0237398q_2^2q_6q_7 - 0.0848q_3^2q_4q_6 + 0.0872q_1q_2q_4q_5 \\
&+ \quad 0.034862q_1q_2q_4q_7 + 0.0215658q_1q_2q_5q_6 + 0.0378954q_1q_2q_5q_7 \\
&+ \quad 0.00287416q_1q_2q_6q_7 + 0.1586q_1q_3q_4q_5 + 0.0215658q_1q_3q_4q_6 \\
&+ \quad 0.0189477q_1q_3q_4q_7 + 2q_2q_3q_4q_5 + 0.1826q_2q_3q_4q_6 + 0.1104q_2q_3q_4q_7 \\
&- \quad 0.0848q_2q_3q_5q_6 - 0.00234048q_2q_3q_6q_7 + 7.61760\ 10^{-4}q_5^2 \\
&+ \quad 0.0474795q_2q_5q_6 + 8.04282\ 10^{-4}q_1q_5q_7 + 0.00304704q_2q_5q_7
\end{aligned}
$$

$$
\begin{aligned}
a_2(\boldsymbol{q}) &= 4.02141\ 10^{-4}q_1q_5^2 + 0.00152352q_2q_5^2 + 0.0552q_2^2q_5^2 + 0.0552q_3^2q_4^2 \\
& \quad +0.0189477q_1q_2q_5^2 + 0.034862q_1q_3q_4^2 + 0.00336706q_1q_4q_5 \\
& \quad +6.82079\ 10^{-5}q_1q_4q_7 + 6.28987\ 10^{-5}q_1q_5q_6 + 0.00152352q_3q_4q_5 \\
& \quad +5.16120\ 10^{-4}q_3q_4q_6 - 0.00234048q_3^2q_4q_6 + 0.034862q_1q_2q_4q_5 \\
& \quad +0.0237398q_2^2q_5q_6 + 0.00152352q_2^2q_5q_7 + 5.16120\ 10^{-4}q_2^2q_6q_7 \\
& \quad +0.00336706q_1q_2q_4q_7 + 0.00287416q_1q_2q_5q_6 + 8.04282\ 10^{-4}q_1q_2q_5q_7 \\
& \quad +6.28987\ 10^{-5}q_1q_2q_6q_7 + 0.0189477q_1q_3q_4q_5 + 0.00287416q_1q_3q_4q_6 \\
& \quad +4.02141\ 10^{-4}q_1q_3q_4q_7 + 0.1104q_2q_3q_4q_5 + 0.0237398q_2q_3q_4q_6 \\
& \quad +0.00152352q_2q_3q_4q_7 - 0.00234048q_2q_3q_5q_6 + 0.00103224q_2q_5q_6
\end{aligned}
$$

$$
\begin{aligned}
a_1(\boldsymbol{q}) &= 7.61760\ 10^{-4}q_2^2q_5^2 + 7.61760\ 10^{-4}q_3^2q_4^2 + 4.02141\ 10^{-4}q_1q_2q_5^2 \\
& \quad +0.00336706q_1q_3q_4^2 + 6.82079\ 10^{-5}q_1q_4q_5 + 5.16120\ 10^{-4}q_2^2q_5q_6 \\
& \quad +0.00336706q_1q_2q_4q_5 + 6.82079\ 10^{-5}q_1q_2q_4q_7 + 6.28987\ 10^{-5}q_1q_2q_5q_6 \\
& \quad +4.02141\ 10^{-4}q_1q_3q_4q_5 + 6.28987\ 10^{-5}q_1q_3q_4q_6 + 0.00152352q_2q_3q_4q_5 \\
& \quad +5.16120\ 10^{-4}q_2q_3q_4q_6
\end{aligned}
$$

$$
a_0(\boldsymbol{q}) = 6.82079\ 10^{-5}q_1q_3q_4^2 + 6.82079\ 10^{-5}q_1q_2q_4q_5
$$

Problem Statistics

No. of continuous variables	9
No. of linear inequalities	14
No. of convex inequalities	–
No. of nonlinear equalities	–
No. of nonconvex inequalities	2

Global Solution

The system was found to be stable $k_m > 1.0$, for the given range of uncertain parameters and $0 \leq \omega leq 10$.

Chapter 8

Twice Continuously Differentiable NLP Problems

8.1 Introduction

Twice continuously differentiable NLPs represent a very broad class of problems with diverse applications in the fields of engineering, science, finance and economics. Specific problems include phase equilibrium characterization, minimum potential energy conformation of clusters and molecules, distillation sequencing, reactor network design, batch process design, VLSI chip design, protein folding, and portfolio optimization.

The general form of the optimization problems to be solved is

$$\begin{array}{rr} \min\limits_{\boldsymbol{x}} & f(\boldsymbol{x}) \\ s.t. & \boldsymbol{g}(\boldsymbol{x}) \leq 0 \\ & \boldsymbol{h}(\boldsymbol{x}) = 0 \\ & \boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U] \end{array}$$

where $\boldsymbol{x}$ is a vector of n continuous variables, $f(\boldsymbol{x})$ is the objective function, $\boldsymbol{g}(\boldsymbol{x})$ is a vector of inequality constraints, and $\boldsymbol{h}(\boldsymbol{x})$ is a vector of equality constraints. $\boldsymbol{x}^L$ and $\boldsymbol{x}^U$ denote the lower and upper bounds on $\boldsymbol{x}$ respectively. All the functions are twice continuously differentiable.

Many local optimization techniques are available to solve this type of problem. The most popular are reduced gradient techniques and successive quadratic programming. Commercial implementations of algorithms based on these approaches have been available for many years. When the objective function and the inequality constraints are convex and the equality constraints are linear, there is a unique solution which can be identified with a local solver.

In many applications, NLPs have several local solutions because of the nonconvexity of the objective function and/or feasible region. The global optimization of these problems has attracted growing attention in the last two decades, either through stochastic or deterministic methods. The stochastic algorithms fit within the following classes: genetic algorithms (Goldberg,

C. A. Floudas et al., *Handbook of Test Problems in Local and Global Optimization*

1989), taboo search (Glover *et al.*, 1993; Cvijović and Klinowski, 1995), and simulated annealing (Kirkpatrick et al., 1983). The deterministic approaches include primal-dual methods (Stephanopoulos and Westerberg, 1975; Floudas and Visweswaran, 1990, 1993, 1996a, 1996b), interval methods (Neumaier, 1990; Hansen, 1992; Vaidyanathan and El-Halwagi, 1994) and branch-and-bound methods (Horst and Tuy, 1993; Ryoo and Sahinidis, 1995; Smith and Pantelides, 1996; Adjiman et al., 1998a,b). The difficulty of these problems arises from the wide variety of functional forms that can be encountered. As a result, the techniques developed must be applicable to and effective for very broad classes of problems.

The reader is referred to Floudas and Grossmann (1995), Horst and Pardalos (1995), Floudas and Pardalos (1996), Grossmann (1996), and Floudas (1997) for thorough descriptions of these methods and their applications to process synthesis and design, process control and computational chemistry. The forthcoming book of Floudas (2000) discusses the theoretical, algorithmic and application-oriented issues of deterministic global optimization approaches applicable to twice continuously differentiable NLPs.

This chapter presents a variety of test problems that demonstrate the breadth of global optimization applications of twice continuously differentiable NLPs. Section 8.2 discusses literature test problems. Section 8.3 presents applications from the area of batch design under uncertainty. Section 8.4 introduces test problems from the area of chemical reactor network synthesis. Section 8.5 discusses applications that arise in parameter estimation and data reconcilliation. Section 8.6 describes test problems from the area of phase and chemical reaction equilibrium using equations of state. Finally, section 8.7 discusses test problems that arise in atomic and molecular clusters.

8.2 Literature Problems

8.2.1 Test Problem 1

This unconstrained problem and the reported global solution are taken from Adjiman et al. (1998a).

Formulation

Objective function

$$\min_{x_1,x_2} \quad \cos x_1 \sin x_2 - \frac{x_1}{x_2^2+1}$$

Variable bounds

$$\begin{aligned} -1 \leq \ & x_1 \ \leq 2 \\ -1 \leq \ & x_2 \ \leq 1 \end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of known solutions	3

Global Solution

- Objective function: -2.02181.
- Continuous variables

$$x_1 = 2 \qquad x_2 = 0.10578$$

8.2.2 Test Problem 2: Pseudoethane

The goal of this example is to determine the molecular conformation of pseudoethane, an ethane molecule in which all the hydrogen atoms have been replaced by C, N or O atoms. It is taken from Maranas and Floudas (1994), where the global minimum potential energy conformation of small molecules is studied. The Lennard-Jones potential is expressed in terms of a single dihedral angle. The contribution from 1–2 and 1–3 atom interactions have not been included in the formulation since they are constant. This problem has three very close minima.

Formulation

Objective function

$$\begin{aligned}\min_t \quad & \frac{588600}{\left(3\,r_0^2 - 4\,\cos\theta r_0^2 - 2\,\left(\sin^2\theta\cos(t-\frac{2\pi}{3}) - \cos^2\theta\right) r_0^2\right)^6} \\ & - \frac{1079.1}{\left(3\,r_0^2 - 4\,\cos\theta r_0^2 - 2\,\left(\sin^2\theta\cos(t-\frac{2\pi}{3}) - \cos^2\theta\right) r_0^2\right)^3} \\ & + \frac{600800}{\left(3\,r_0^2 - 4\,\cos\theta r_0^2 - 2\,\left(\sin^2\theta\cos(t) - \cos^2\theta\right) r_0^2\right)^6} \\ & - \frac{1071.5}{\left(3\,r_0^2 - 4\,\cos\theta r_0^2 - 2\,\left(\sin^2\theta\cos(t) - \cos^2\theta\right) r_0^2\right)^3} \\ & + \frac{481300}{\left(3\,r_0^2 - 4\,\cos\theta r_0^2 - 2\,\left(\sin^2\theta\cos(t+\frac{2\pi}{3}) - \cos^2\theta\right) r_0^2\right)^6} \\ & - \frac{1064.6}{\left(3\,r_0^2 - 4\,\cos\theta r_0^2 - 2\,\left(\sin^2\theta\cos(t+\frac{2\pi}{3}) - \cos^2\theta\right) r_0^2\right)^3}\end{aligned}$$

Variable bounds

$$0 \le t \le 2\pi$$

Variable definitions

r_0 is the covalent bond length (1.54 Å), θ is the covalent bond angle (109.5^o), and t is the dihedral angle.

Problem Statistics

No. of continuous variables	1
No. of known solutions	3

Global Solution

- Objective function: -1.0711 kcal/mol.
- Continuous variable: $t = 183.45^o$.

8.2.3 Test Problem 3: Goldstein and Price function

This problem is taken from Goldstein and Price (1971).

Formulation

Objective function

$$\begin{aligned}\min_{x,y} \quad & \left[1 + (x + y + 1)^2 \left(19 - 14x + 3x^2 - 14y + 6xy + 3y^2\right)\right] \\ \times \quad & \left[30 + (2x - 3y)^2 \left(18 - 32x + 12x^2 + 48y - 36xy + 27y^2\right)\right]\end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of known solutions	4

Global Solution

- Objective function: 3
- Continuous variables: $x = 0$, $y = -1$.

8.2.4 Test problem 4: Three-hump camelback function

This problem is taken from Dixon and Szegö (1975).

Formulation

Objective function

$$\min_{x,y} \; 12x^2 - 6.3x^4 + x^6 - 6xy + 6y^2$$

Problem Statistics

No. of continuous variables	2
No. of known solutions	3

Global Solution

- Objective function: 0
- Continuous variables: $x = 0$, $y = 0$.

8.2.5 Test Problem 5: Six-hump Camelback Function

This problem is taken from Dixon and Szegö (1975).

Formulation

Objective function

$$\min_{x,y} \; 4x^2 - 2.1x^4 + \frac{1}{3}x^6 + xy - 4y^2 + 4y^4$$

Problem Statistics

No. of continuous variables	2
No. of known solutions	6

Global Solution

The six solutions represent only three objective function values. For each pair with the same objective function, the variable values are opposite in sign.

- Objective function: -1.03163
- Continuous variables: $x = 0.08984$, $y = -0.71266$.

8.2.6 Test Problem 6: Shekel Function

This problem is taken from Dixon and Szegö (1975).

Formulation

Objective function

$$\min_{x,y} \; -\frac{1}{(x-4)^2+(y-4)^2+0.1} - \frac{1}{(x-1)^2+(y-1)^2+0.2} - \frac{1}{(x-8)^2+(y-8)^2+0.2}$$

Problem Statistics

No. of continuous variables	2
No. of known solutions	3

Global Solution

- Objective function: -10.0860
- Continuous variables: $x = 4$, $y = 4$.

8.2.7 Test Problem 7

This is a small nonconvex problem from Murtagh and Saunders (1993). The reported global solution is from the work of Adjiman et al. (1998b).

Formulation

Objective function

$$\min_{\boldsymbol{x}} \ (x_1 - 1)^2 + (x_1 - x_2)^2 + (x_2 - x_3)^3 + (x_3 - x_4)^4 + (x_4 - x_5)^4$$

Constraints

$$\begin{aligned} x_1 + x_2^2 + x_3^3 &= 3\sqrt{2} + 2 \\ x_2 - x_3^2 + x_4 &= 2\sqrt{2} - 2 \\ x_1 x_5 &= 2 \end{aligned}$$

Variable bounds

$$\boldsymbol{x} \in [-5, 5]^5$$

Problem Statistics

No. of continuous variables	5
No. of linear equalities	–
No. of convex inequalities	–
No. of nonlinear equalities	3
No. of nonconvex inequalities	–
No. of known solutions	5

Global Solution

- Objective function: 0.0293
- Continuous variables

$$\boldsymbol{x} = (1.1166, 1.2204, 1.5378, 1.9728, 1.7911)^T$$

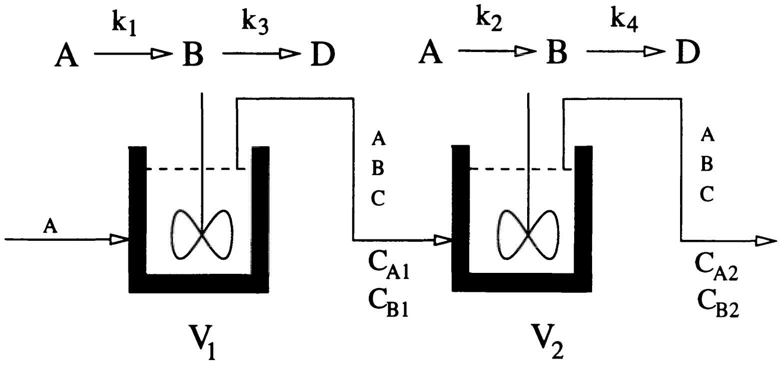


Figure 8.1: Test problem 8.

8.2.8 Test Problem 8

The following example, taken from Ryoo and Sahinidis (1995), is a reactor network design problem, describing the system shown in Figure 8.1. The goal is to maximize the concentration of product B in the exit stream, C_{B2}. The reported global solution is from the work of Adjiman et al. (1998b). This problem has three solutions with very close objective function values. However, these solutions correspond to markedly different network configurations.

Formulation

Objective function

$$\min -C_{B2}$$

Constraints

$$\begin{aligned}
C_{A1} + k_1 C_{A1} V_1 &= 1 \\
C_{A2} - C_{A1} + k_2 C_{A2} V_2 &= 0 \\
C_{B1} + C_{A1} + k_3 C_{B1} V_1 &= 1 \\
C_{B2} - C_{B1} + C_{A2} - C_{A1} + k_4 C_{B2} V_2 &= 0 \\
V_1^{0.5} + V_2^{0.5} &\leq 4
\end{aligned}$$

Variable bounds

$$(0,0,0,0,10^{-5},10^{-5}) \leq (C_{A1}, C_{A2}, C_{B1}, C_{B2}, V_1, V_2) \leq (1,1,1,1,16,16)$$

Data

$k_1 = 0.09755988\ s^{-1}$	$k_2 = 0.09658428\ s^{-1}$
$k_3 = 0.0391908\ s^{-1}$	$k_4 = 0.9\ s^{-1}$

Problem Statistics

No. of continuous variables	6
No. of linear equalities	–
No. of convex inequalities	–
No. of nonlinear equalities	4
No. of nonconvex inequalities	1
No. of known solutions	3

Global Solution

- Objective function: -0.38881.
- Continuous variables

$C_{A1} = 0.772$	$C_{A2} = 0.517$	$C_{B1} = 0.204$	$C_{B2} = 0.388$
$V_1 = 3.036$	$V_2 = 5.097$		

8.3 Batch Plant Design Under Uncertainty

8.3.1 Introduction

The design of batch processes has received much attention in the literature over the past two decades. Batch processing is a popular method for manufacturing products in low volume or which require several complicated steps in the synthesis procedure. Batch plant designs are generally grouped into two categories: (1) multiproduct batch plants, where all products follow the same sequence of processing steps, and (2) multipurpose batch plants, where equipment can be used for more than one task and products may have different routes through the plant. In addition, batch plants can be operated according to different scheduling policies. In a single-product campaign (SPC), all batches of one product are manufactured in order, followed by all batches of another product. Mixed-product campaigns do not have this restriction, and therefore allow for more efficient operation of the plant.

The final design of the batch plant is dependent upon the values of several parameters. These include the demand for the products and the processing times for each product in every stage. A batch plant design based on fixed values for these parameters can lead to poor performance if the parameters change (i.e., the demand for the products increases). Batch design under uncertainty models the range of possible parameter values and determines the best trade-off between efficiency and flexibility. Among the first to address the problem of batch design under uncertainty were Marketos (1975) and Johns et al. (1978). Reinhart and Rippin (1986), (1987) formulated the multiproduct batch plant design problem with uncertainties in the demand for the products and in the processing times and size factors for each product in each stage.

Subrahmanyam et al. (1994) addressed the problem by using a discrete probability distribution for the demands. They formulated the problem using scenarios for different demand realizations. Ierapetritou and Pistikopoulos (1995), (1996) used a continuous probability distribution for the demands and used a stochastic programming formulation. In addition, they allowed for uncertainty in the size factors and processing times by using scenarios. Their formulation results in a single large-scale nonconvex optimization problem. Harding and Floudas (1997) studied the mathematical structure via eigenvalue analysis and identified exact lower bounds. Based on these properties, they proposed a global optimization approach based on the αBB method (Androulakis et al. (1995); Adjiman and Floudas (1996)) to solve this problem for large examples in reasonable CPU time. They also extended the formulation to apply to multipurpose batch plant design under uncertainty. For a detailed exposition to the global optimization approach for the design of batch processes under uncertainty, the reader is directed to the book by Floudas (2000) and the article of Harding and Floudas (1997).

8.3.2 Single-Product Campaign Formulation

In the design of multiproduct batch plants, a scheduling policy is given (e.g., single product campaign or mixed product campaign), and the task is to determine the optimal equipment sizes in each processing step, and the optimal batch sizes for each product. When uncertainty is introduced in the processing times, t_{ij}, and size parameters, S_{ij}, the design must be feasible over the whole range of possible parameter values. The range of parameter values are represented using a number of scenarios, $\mathcal{P}$. When uncertainty is introduced in the product demands, then the amount of each product to be produced becomes a variable to be optimized. The joint probability distribution for the product demands is discretized using Gaussian quadrature with a total of $\mathcal{Q}$ quadrature points. The objective of batch plant design under uncertainty is to minimize equipment costs minus the expected revenues from the sale of the products. The chosen scheduling policy must be enforced, and production must be completed by some time, H, for all scenarios, $\mathcal{P}$. Finally, the batch sizes for all of the products must not be too large for the equipment, for all scenarios, $\mathcal{P}$.

<u>Objective function</u>

The objective is to minimize the equipment cost less the expected revenues plus a penalty term that reflects the cost of unfilled orders.

$$\begin{aligned}\min_{b_i, v_j, Q_i^{qp}} \quad & \delta \sum_{j=1}^{\mathcal{M}} \alpha_j N_j \exp(\beta_j v_j) \\ & - \sum_{p=1}^{\mathcal{P}} \frac{1}{w^p} \sum_{q=1}^{\mathcal{Q}} \omega^q J^q \sum_{i=1}^{\mathcal{N}} p_i Q_i^{qp} \\ & + \gamma \sum_{p=1}^{\mathcal{P}} \frac{1}{w^p} \sum_{q=1}^{\mathcal{Q}} \omega^q J^q \left\{ \sum_{i=1}^{\mathcal{N}} p_i \theta_i^q - \sum_{i=1}^{\mathcal{N}} p_i Q_i^{qp} \right\}\end{aligned}$$

<u>Constraints</u>

Batch Size Constraints

The batch size for each product must be small enough to fit in the equipment in each stage.

$$v_j - b_i \geq \ln(S_{ij}^p) \qquad \forall\, i \in \mathcal{N} \quad \forall\, j \in \mathcal{M} \quad \forall\, p \in \mathcal{P}$$

Planning Horizon Constraint

All products must be manufactured in H hours or less.

$$\sum_{i=1}^{\mathcal{N}} Q_i^{qp} \cdot \exp(t_{Li}^p - b_i) \leq H \quad \forall\, q \in \mathcal{Q} \quad \forall\, p \in \mathcal{P}$$

where the limiting time step is defined as,

$$t_{Li}^p = \max_j \left\{ \ln \frac{t_{ij}^p}{N_j} \right\}$$

<u>Variable bounds</u>

$$\begin{array}{ll} \theta_i^L \leq Q_i^{qp} \leq \theta_i^q & \forall\, i \in \mathcal{N} \quad \forall\, q \in \mathcal{Q} \quad \forall\, p \in \mathcal{P} \\ \ln(V_j^L) \leq v_j \leq \ln(V_j^U) & \forall\, j \in \mathcal{M} \\ \min_{j,p} \ln(\frac{V_j^L}{S_{ij}^p}) \leq b_i \leq \min_{j,p} \ln(\frac{V_j^U}{S_{ij}^p}) & \forall\, i \in \mathcal{N} \end{array}$$

<u>Variable definition</u>

- Q_i^{qp} - the amount of product i made given process parameter scenario p and market demand corresponding to Gaussian quadrature grid point q.
- v_j - Natural logarithm of the equipment volume in stage j.

- b_i - Natural logarithm of the batch size of product i.

Parameter definition

- S_{ij} - size factor for product i in stage j for scenario p.
- t_{ij}^p - processing time for product i in stage j for scenario p.
- N_j - number of parallel units in stage j.
- H - planning horizon time.
- θ_i^q - the demand realization for product i at quadrature point q.

$$\begin{aligned}
\theta_i^q &= \frac{\theta_i^U(1+v_i^q)+\theta_i^L(1-v_i^q)}{2} \\
\theta_i^U &= \theta_i^\mu + 4\theta_i^\sigma \\
\theta_i^L &= \theta_i^\mu - 4\theta_i^\sigma
\end{aligned}$$

- $\theta_i^\mu, \theta_i^\sigma$ - the mean and standard deviation of the probability distribution of the demand for product i.
- $\omega^q J^q$ - the weighted probability density function for the demands.

$$J^q = \frac{\exp\left(-\frac{\sum\limits_{i\in\mathcal{N}}\left(\frac{\theta_i^q-\theta_i^\mu}{\theta_i^\sigma}\right)^2}{2}\right)}{\prod\limits_{i\in\mathcal{N}}\sqrt{2\pi}\theta_i^\sigma}$$

- v_i^q, ω^q - Gaussian quadrature parameters that depend on the number of quadrature points used. These can be obtained from handbooks of mathematical tables. The values for a five-point quadrature, which is used in all of the test problems in this handbook, are provided in the table below.

Quadrature Point	v^q	ω^q
1	-0.9061798459	0.23692885
2	-0.5384693101	0.4786286705
3	0.0	0.56888889
4	0.5384693101	0.4786286705
5	0.9061798459	0.23692885

- w^p - the weight for scenario p.
- p_i - the price of product i.
- γ - penalty parameter.
- δ,α_j,β_j - cost function parameters.

8.3.3 Test Problem 1

The first example originally appeared in Grossmann and Sargent (1979). Harding and Floudas (1997) proposed a global optimization approach for the formulation given above. This example is for a batch plant with ($\mathcal{N} = 2$) products in ($\mathcal{M} = 3$) stages with only ($\mathcal{P} = 1$) scenario for the processing parameters. For each product, five quadrature points are used to approximate the demand distribution, giving a total of ($\mathcal{Q} = 25$) quadrature points for the problem. The reported global solution is from the work of Harding and Floudas (1997).

Explicit Formulation

Objective function

$$\begin{aligned}
\min \quad & \delta\left[\alpha_1 N_1 \exp(\beta_1 v_1) + \alpha_2 N_2 \exp(\beta_2 v_2) + \alpha_3 N_3 \exp(\beta_3 v_3) + \alpha_4 N_4 \exp(\beta_4 v_4)\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(1,1)} J^{(1,1)} \left[(1-\gamma)p_1 Q_1^{(1,1),1} + (1-\gamma)p_2 Q_2^{(1,1),1} + \gamma p_1 \theta_1^{(1,1)} + \gamma p_2 \theta_2^{(1,1)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(1,2)} J^{(1,2)} \left[(1-\gamma)p_1 Q_1^{(1,2),1} + (1-\gamma)p_2 Q_2^{(1,2),1} + \gamma p_1 \theta_1^{(1,2)} + \gamma p_2 \theta_2^{(1,2)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(1,3)} J^{(1,3)} \left[(1-\gamma)p_1 Q_1^{(1,3),1} + (1-\gamma)p_2 Q_2^{(1,3),1} + \gamma p_1 \theta_1^{(1,3)} + \gamma p_2 \theta_2^{(1,3)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(1,4)} J^{(1,4)} \left[(1-\gamma)p_1 Q_1^{(1,4),1} + (1-\gamma)p_2 Q_2^{(1,4),1} + \gamma p_1 \theta_1^{(1,4)} + \gamma p_2 \theta_2^{(1,4)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(1,5)} J^{(1,5)} \left[(1-\gamma)p_1 Q_1^{(1,5),1} + (1-\gamma)p_2 Q_2^{(1,5),1} + \gamma p_1 \theta_1^{(1,5)} + \gamma p_2 \theta_2^{(1,5)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(2,1)} J^{(2,1)} \left[(1-\gamma)p_1 Q_1^{(2,1),1} + (1-\gamma)p_2 Q_2^{(2,1),1} + \gamma p_1 \theta_1^{(2,1)} + \gamma p_2 \theta_2^{(2,1)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(2,2)} J^{(2,2)} \left[(1-\gamma)p_1 Q_1^{(2,2),1} + (1-\gamma)p_2 Q_2^{(2,2),1} + \gamma p_1 \theta_1^{(2,2)} + \gamma p_2 \theta_2^{(2,2)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(2,3)} J^{(2,3)} \left[(1-\gamma)p_1 Q_1^{(2,3),1} + (1-\gamma)p_2 Q_2^{(2,3),1} + \gamma p_1 \theta_1^{(2,3)} + \gamma p_2 \theta_2^{(2,3)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(2,4)} J^{(2,4)} \left[(1-\gamma)p_1 Q_1^{(2,4),1} + (1-\gamma)p_2 Q_2^{(2,4),1} + \gamma p_1 \theta_1^{(2,4)} + \gamma p_2 \theta_2^{(2,4)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(2,5)} J^{(2,5)} \left[(1-\gamma)p_1 Q_1^{(2,5),1} + (1-\gamma)p_2 Q_2^{(2,5),1} + \gamma p_1 \theta_1^{(2,5)} + \gamma p_2 \theta_2^{(2,5)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(3,1)} J^{(3,1)} \left[(1-\gamma)p_1 Q_1^{(3,1),1} + (1-\gamma)p_2 Q_2^{(3,1),1} + \gamma p_1 \theta_1^{(3,1)} + \gamma p_2 \theta_2^{(3,1)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(3,2)} J^{(3,2)} \left[(1-\gamma)p_1 Q_1^{(3,2),1} + (1-\gamma)p_2 Q_2^{(3,2),1} + \gamma p_1 \theta_1^{(3,2)} + \gamma p_2 \theta_2^{(3,2)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(3,3)} J^{(3,3)} \left[(1-\gamma)p_1 Q_1^{(3,3),1} + (1-\gamma)p_2 Q_2^{(3,3),1} + \gamma p_1 \theta_1^{(3,3)} + \gamma p_2 \theta_2^{(3,3)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(3,4)} J^{(3,4)} \left[(1-\gamma)p_1 Q_1^{(3,4),1} + (1-\gamma)p_2 Q_2^{(3,4),1} + \gamma p_1 \theta_1^{(3,4)} + \gamma p_2 \theta_2^{(3,4)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(3,5)} J^{(3,5)} \left[(1-\gamma)p_1 Q_1^{(3,5),1} + (1-\gamma)p_2 Q_2^{(3,5),1} + \gamma p_1 \theta_1^{(3,5)} + \gamma p_2 \theta_2^{(3,5)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(4,1)} J^{(4,1)} \left[(1-\gamma)p_1 Q_1^{(4,1),1} + (1-\gamma)p_2 Q_2^{(4,1),1} + \gamma p_1 \theta_1^{(4,1)} + \gamma p_2 \theta_2^{(4,1)}\right] \\
& + \tfrac{1}{w^{\mathrm{I}}} \omega^{(4,2)} J^{(4,2)} \left[(1-\gamma)p_1 Q_1^{(4,2),1} + (1-\gamma)p_2 Q_2^{(4,2),1} + \gamma p_1 \theta_1^{(4,2)} + \gamma p_2 \theta_2^{(4,2)}\right]
\end{aligned}$$

$$
\begin{aligned}
&+\tfrac{1}{w^{\mathrm{T}}}\omega^{(4,3)}J^{(4,3)}\left[(1-\gamma)p_1Q_1^{(4,3),1}+(1-\gamma)p_2Q_2^{(4,3),1}+\gamma p_1\theta_1^{(4,3)}+\gamma p_2\theta_2^{(4,3)}\right]\\
&+\tfrac{1}{w^{\mathrm{T}}}\omega^{(4,4)}J^{(4,4)}\left[(1-\gamma)p_1Q_1^{(4,4),1}+(1-\gamma)p_2Q_2^{(4,4),1}+\gamma p_1\theta_1^{(4,4)}+\gamma p_2\theta_2^{(4,4)}\right]\\
&+\tfrac{1}{w^{\mathrm{T}}}\omega^{(4,5)}J^{(4,5)}\left[(1-\gamma)p_1Q_1^{(4,5),1}+(1-\gamma)p_2Q_2^{(4,5),1}+\gamma p_1\theta_1^{(4,5)}+\gamma p_2\theta_2^{(4,5)}\right]\\
&+\tfrac{1}{w^{\mathrm{T}}}\omega^{(5,1)}J^{(5,1)}\left[(1-\gamma)p_1Q_1^{(5,1),1}+(1-\gamma)p_2Q_2^{(5,1),1}+\gamma p_1\theta_1^{(5,1)}+\gamma p_2\theta_2^{(5,1)}\right]\\
&+\tfrac{1}{w^{\mathrm{T}}}\omega^{(5,2)}J^{(5,2)}\left[(1-\gamma)p_1Q_1^{(5,2),1}+(1-\gamma)p_2Q_2^{(5,2),1}+\gamma p_1\theta_1^{(5,2)}+\gamma p_2\theta_2^{(5,2)}\right]\\
&+\tfrac{1}{w^{\mathrm{T}}}\omega^{(5,3)}J^{(5,3)}\left[(1-\gamma)p_1Q_1^{(5,3),1}+(1-\gamma)p_2Q_2^{(5,3),1}+\gamma p_1\theta_1^{(5,3)}+\gamma p_2\theta_2^{(5,3)}\right]\\
&+\tfrac{1}{w^{\mathrm{T}}}\omega^{(5,4)}J^{(5,4)}\left[(1-\gamma)p_1Q_1^{(5,4),1}+(1-\gamma)p_2Q_2^{(5,4),1}+\gamma p_1\theta_1^{(5,4)}+\gamma p_2\theta_2^{(5,4)}\right]\\
&+\tfrac{1}{w^{\mathrm{T}}}\omega^{(5,5)}J^{(5,5)}\left[(1-\gamma)p_1Q_1^{(5,5),1}+(1-\gamma)p_2Q_2^{(5,5),1}+\gamma p_1\theta_1^{(5,5)}+\gamma p_2\theta_2^{(5,5)}\right]
\end{aligned}
$$

Constraints

$$
\begin{aligned}
v_1-b_1 &\geq \ln S_{11}^1\\
v_2-b_1 &\geq \ln S_{12}^1\\
v_3-b_1 &\geq \ln S_{13}^1\\
v_1-b_2 &\geq \ln S_{21}^1\\
v_2-b_2 &\geq \ln S_{22}^1\\
v_3-b_2 &\geq \ln S_{23}^1\\
Q_1^{(1,1),1}\exp(t_{L1}^1-b_1)+Q_2^{(1,1),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(1,2),1}\exp(t_{L1}^1-b_1)+Q_2^{(1,2),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(1,3),1}\exp(t_{L1}^1-b_1)+Q_2^{(1,3),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(1,4),1}\exp(t_{L1}^1-b_1)+Q_2^{(1,4),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(1,5),1}\exp(t_{L1}^1-b_1)+Q_2^{(1,5),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(2,1),1}\exp(t_{L1}^1-b_1)+Q_2^{(2,1),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(2,2),1}\exp(t_{L1}^1-b_1)+Q_2^{(2,2),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(2,3),1}\exp(t_{L1}^1-b_1)+Q_2^{(2,3),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(2,4),1}\exp(t_{L1}^1-b_1)+Q_2^{(2,4),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(2,5),1}\exp(t_{L1}^1-b_1)+Q_2^{(2,5),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(3,1),1}\exp(t_{L1}^1-b_1)+Q_2^{(3,1),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(3,2),1}\exp(t_{L1}^1-b_1)+Q_2^{(3,2),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(3,3),1}\exp(t_{L1}^1-b_1)+Q_2^{(3,3),1}\exp(t_{L2}^1-b_2) &\leq H\\
Q_1^{(3,4),1}\exp(t_{L1}^1-b_1)+Q_2^{(3,4),1}\exp(t_{L2}^1-b_2) &\leq H
\end{aligned}
$$

$$
\begin{aligned}
Q_1^{(3,5),1}\exp(t_{L1}^1 - b_1) + Q_2^{(3,5),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(4,1),1}\exp(t_{L1}^1 - b_1) + Q_2^{(4,1),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(4,2),1}\exp(t_{L1}^1 - b_1) + Q_2^{(4,2),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(4,3),1}\exp(t_{L1}^1 - b_1) + Q_2^{(4,3),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(4,4),1}\exp(t_{L1}^1 - b_1) + Q_2^{(4,4),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(4,5),1}\exp(t_{L1}^1 - b_1) + Q_2^{(4,5),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(5,1),1}\exp(t_{L1}^1 - b_1) + Q_2^{(5,1),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(5,2),1}\exp(t_{L1}^1 - b_1) + Q_2^{(5,2),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(5,3),1}\exp(t_{L1}^1 - b_1) + Q_2^{(5,3),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(5,4),1}\exp(t_{L1}^1 - b_1) + Q_2^{(5,4),1}\exp(t_{L2}^1 - b_2) &\leq H \\
Q_1^{(5,5),1}\exp(t_{L1}^1 - b_1) + Q_2^{(5,5),1}\exp(t_{L2}^1 - b_2) &\leq H
\end{aligned}
$$

Data

$\theta_1(\mu = 200, \sigma = 10) \quad \theta_2(\mu = 100, \sigma = 10)$

$$
\begin{aligned}
\boldsymbol{S} &= \begin{pmatrix} 2.0 & 3.0 & 4.0 \\ 4.0 & 6.0 & 3.0 \end{pmatrix} \\
\boldsymbol{T} &= \exp(\boldsymbol{t}) = \begin{pmatrix} 8.0 & 20.0 & 8.0 \\ 16.0 & 4.0 & 4.0 \end{pmatrix} \\
\boldsymbol{\alpha} &= (10.0, 10.0, 10.0)^T \\
\boldsymbol{\beta} &= (0.6, 0.6, 0.6)^T \\
\boldsymbol{N} &= (1, 1, 1)^T \\
\boldsymbol{p} &= (5.5, 7.0)^T \\
\gamma &= 0.0 \\
\delta &= 0.3 \\
H &= 8.0 \\
w &= 1.0 \\
\boldsymbol{V}^L &= (500, 500, 500)^T \\
\boldsymbol{V}^U &= (4500, 4500, 4500)^T
\end{aligned}
$$

Problem Statistics

No. of continuous variables	55
No. of linear equalities	6
No. of nonconvex inequalities	25

Global Solution

- Objective function: -979.186

- Continuous variables

$$
\begin{aligned}
\boldsymbol{V} &= \exp(v) = (1800, 2700, 3600)^T \\
\boldsymbol{B} &= \exp(b) = (900, 450)^T \\
\boldsymbol{Q}_1 &= \begin{pmatrix} 163.753, & 163.753, & 163.753, & 163.753, & 163.753 \\ 178.461, & 178.461, & 178.461, & 178.461, & 178.461 \\ 200.000, & 200.000, & 200.000, & 200.000, & 200.000 \\ 221.539, & 221.539, & 221.539, & 221.539, & 221.539 \\ 236.247, & 236.247, & 236.247, & 236.247, & 236.247 \end{pmatrix} \\
\boldsymbol{Q}_2 &= \begin{pmatrix} 63.753, & 78.461, & 100.000, & 121.539, & 122.654 \\ 63.753, & 78.461, & 100.000, & 113.461, & 113.461 \\ 63.753, & 78.461, & 100.000, & 100.000, & 100.000 \\ 63.753, & 78.461, & 86.539, & 86.539, & 86.539 \\ 63.753, & 77.346, & 77.346, & 77.346, & 77.346 \end{pmatrix}
\end{aligned}
$$

8.3.4 Test Problem 2

This example is for a batch plant with ($\mathcal{N} = 4$) products in ($\mathcal{M} = 6$) stages with ($\mathcal{P} = 3$) scenarios for the processing parameters. For each product, five quadrature points are used to approximate the demand distribution, giving a total of ($\mathcal{Q} = 625$) quadrature points for the problem. Due to its size in terms of variables (7510) and number of nonconvex inequality constraints (1875), this is a challenging problem. This example and the reported global solution are taken from Harding and Floudas (1997).

Data

$\theta_1(\mu = 150, \sigma = 10)$ $\quad \theta_2(\mu = 150, \sigma = 8)$
$\theta_3(\mu = 180, \sigma = 9)$ $\quad \theta_4(\mu = 160, \sigma = 10)$

$$
\begin{aligned}
\boldsymbol{S}^1 &= \begin{pmatrix} 8.0 & 2.0 & 5.2 & 4.9 & 6.1 & 4.2 \\ 0.7 & 0.8 & 0.9 & 3.8 & 2.1 & 2.5 \\ 0.7 & 2.6 & 1.6 & 3.4 & 3.2 & 2.9 \\ 4.7 & 2.3 & 1.6 & 2.7 & 1.2 & 2.5 \end{pmatrix} \\
\boldsymbol{S}^2 &= \begin{pmatrix} 8.5 & 2.5 & 5.7 & 5.4 & 6.6 & 4.7 \\ 1.2 & 1.3 & 1.4 & 4.3 & 2.6 & 3.0 \\ 1.2 & 3.1 & 2.1 & 3.9 & 3.7 & 3.4 \\ 5.2 & 2.8 & 2.1 & 3.2 & 1.7 & 3.0 \end{pmatrix} \\
\boldsymbol{S}^3 &= \begin{pmatrix} 7.5 & 1.5 & 4.7 & 4.4 & 5.6 & 3.7 \\ 0.2 & 0.3 & 0.4 & 3.3 & 1.6 & 2.0 \\ 0.2 & 2.1 & 1.1 & 2.9 & 2.7 & 2.4 \\ 4.2 & 1.8 & 1.1 & 2.2 & 0.7 & 2.0 \end{pmatrix} \\
\boldsymbol{T}^1 &= \begin{pmatrix} 7.0 & 8.3 & 6.0 & 7.0 & 6.5 & 8.0 \\ 6.8 & 5.0 & 6.0 & 4.8 & 5.5 & 5.8 \\ 4.0 & 5.9 & 5.0 & 6.0 & 5.5 & 4.5 \\ 2.4 & 3.0 & 3.5 & 2.5 & 3.0 & 2.8 \end{pmatrix} \\
\boldsymbol{T}^2 &= \begin{pmatrix} 6.0 & 7.3 & 5.0 & 6.0 & 5.5 & 7.0 \\ 5.8 & 4.0 & 5.0 & 3.8 & 4.5 & 4.8 \\ 3.0 & 4.9 & 4.0 & 5.0 & 4.5 & 3.5 \\ 1.4 & 2.0 & 2.5 & 1.5 & 2.0 & 1.8 \end{pmatrix} \\
\boldsymbol{T}^3 &= \begin{pmatrix} 8.0 & 9.3 & 7.0 & 8.0 & 7.5 & 9.0 \\ 7.8 & 6.0 & 7.0 & 5.8 & 6.5 & 6.8 \\ 5.0 & 6.9 & 6.0 & 7.0 & 6.5 & 5.5 \\ 3.4 & 4.0 & 4.5 & 3.5 & 4.0 & 3.8 \end{pmatrix} \\
\boldsymbol{\alpha} &= (10.0, 10.0, 10.0, 10.0, 10.0, 10.0)^T \\
\boldsymbol{\beta} &= (0.6, 0.6, 0.6, 0.6, 0.6, 0.6)^T \\
\boldsymbol{N} &= (1, 1, 1, 1, 1, 1)^T \\
\boldsymbol{p} &= (3.5, 4.0, 3.0, 2.0)^T \\
\boldsymbol{w} &= (3.0, 3.0, 3.0)^T \\
\gamma &= 0.0 \\
\delta &= 0.3 \\
H &= 8.0 \\
\boldsymbol{V}^L &= (500, 500, 500, 500, 500, 500)^T \\
\boldsymbol{V}^U &= (4500, 4500, 4500, 4500, 4500, 4500)^T
\end{aligned}
$$

Problem Statistics

No. of continuous variables	7510
No. of linear equalities	72
No. of nonconvex inequalities	1875

Global Solution

- Objective function: -552.665

- Continuous variables

$$\begin{aligned} \boldsymbol{V} &= \exp(v) = (3036, 1726, 2036, 2714, 2357, 1894)^T \\ \boldsymbol{B} &= \exp(b) = (357, 631, 557, 584)^T \end{aligned}$$

8.3.5 Test Problem 3

This example is for a batch plant with ($\mathcal{N} = 5$) products in ($\mathcal{M} = 6$) stages with ($\mathcal{P} = 1$) scenario for the processing parameters. For each product, five quadrature points are used to approximate the demand distribution, giving a total of ($\mathcal{Q} = 3125$) quadrature points for the problem. Due to its size in terms of variables (15636) and number of nonconvex inequality constraints (3125), this is a challenging problem. This example and the reported global solution are taken from Harding and Floudas (1997).

Data

$$\begin{array}{ll} \theta_1 & (\mu = 250, \sigma = 10) \\ \theta_2 & (\mu = 150, \sigma = 8) \\ \theta_3 & (\mu = 180, \sigma = 9) \\ \theta_4 & (\mu = 160, \sigma = 6) \\ \theta_5 & (\mu = 120, \sigma = 3) \end{array}$$

$$\begin{aligned}
\boldsymbol{S} &= \begin{pmatrix} 7.9 & 2.0 & 5.2 & 4.9 & 6.1 & 4.2 \\ 0.7 & 0.8 & 0.9 & 3.4 & 2.1 & 2.5 \\ 0.7 & 2.6 & 1.6 & 3.6 & 3.2 & 2.9 \\ 4.7 & 2.3 & 1.6 & 2.7 & 1.2 & 2.5 \\ 1.2 & 3.6 & 2.4 & 4.5 & 1.6 & 2.1 \end{pmatrix} \\
\boldsymbol{T} &= \begin{pmatrix} 6.4 & 4.7 & 8.3 & 3.9 & 2.1 & 1.2 \\ 6.8 & 6.4 & 6.5 & 4.4 & 2.3 & 3.2 \\ 1.0 & 6.3 & 5.4 & 11.9 & 5.7 & 6.2 \\ 3.2 & 3.0 & 3.5 & 3.3 & 2.8 & 3.4 \\ 2.1 & 2.5 & 4.2 & 3.6 & 3.7 & 2.2 \end{pmatrix} \\
\boldsymbol{\alpha} &= (0.25, 0.25, 0.25, 0.25, 0.25, 0.25)^T \\
\boldsymbol{\beta} &= (0.6, 0.6, 0.6, 0.6, 0.6, 0.6)^T \\
\boldsymbol{N} &= (3, 2, 3, 2, 1, 2)^T \\
\boldsymbol{p} &= (3.5, 4.0, 3.0, 2.0, 4.5)^T \\
\gamma &= 0.0 \\
\delta &= 0.3 \\
H &= 6.0 \\
w &= 1.0 \\
\boldsymbol{V}^L &= (500, 500, 500, 500, 500, 500)^T \\
\boldsymbol{V}^U &= (4500, 4500, 4500, 4500, 4500, 4500)^T
\end{aligned}$$

Problem Statistics

No. of continuous variables	15636
No. of linear equalities	30
No. of nonconvex inequalities	3125

Global Solution

- Objective function: -3731.079
- Continuous variables

$$\begin{aligned}
\boldsymbol{V} &= \exp(v) = (2789, 1901, 1836, 2460, 2187, 1982)^T \\
\boldsymbol{B} &= \exp(b) = (353, 724, 683, 593, 528)^T
\end{aligned}$$

8.3.6 Unlimited Intermediate Storage Formulation

The single-product campaign formulation uses the maximum processing time for each product, $t_{Li} = \max\limits_{j=1,\dots,M} \left\{ \frac{t_{ij}}{N_j} \right\}$. Therefore, it overestimates the time required to process each product. This can result in an overdesign of the equipment sizes. A mixed-product campaign allows for products to be processed in any order that is desired. In general, mixed-product campaigns require less time to process the required amount of products.

In order to allow mixed-product campaigns, the horizon constraint must be replaced by an expression that takes into account the processing times in each stage, rather than the maximum processing time. This can be done according to the analysis of Birewar and Grossmann. The new horizon constraint has the form:

$$\sum_{i=1}^{\mathcal{N}} Q_i^{qp} \cdot \exp(t_{ij}^p - b_i) \leq H \quad \forall\, q \in \mathcal{Q} \quad \forall\, p \in \mathcal{P}$$

Using this analysis, the unlimited intermediate storage problem is formulated as follows.

Objective function

The objective is to minimize the equipment cost less the expected revenues plus a penalty term that reflects the cost of unfilled orders.

$$\begin{aligned} \min_{b_i, v_j, Q_i^{qp}} \quad & \delta \sum_{j=1}^{\mathcal{M}} \alpha_j N_j \exp(\beta_j v_j) \\ & - \sum_{p=1}^{\mathcal{P}} \frac{1}{w^p} \sum_{q=1}^{\mathcal{Q}} \omega^q J^q \sum_{i=1}^{\mathcal{N}} p_i Q_i^{qp} \\ & + \gamma \sum_{p=1}^{\mathcal{P}} \frac{1}{w^p} \sum_{q=1}^{\mathcal{Q}} \omega^q J^q \left\{ \sum_{i=1}^{\mathcal{N}} p_i \theta_i^q \; - \; \sum_{i=1}^{\mathcal{N}} p_i Q_i^{qp} \right\} \end{aligned}$$

Constraints

Batch Size Constraints

$$v_j \geq \ln(S_{ij}^p) + b_i \qquad \forall\, i \in \mathcal{N} \quad \forall\, j \in \mathcal{M} \quad \forall\, p \in \mathcal{P}$$

Planning Horizon Constraint

$$\sum_{i=1}^{\mathcal{N}} Q_i^{qp} \cdot \exp(t_{ij}^p - b_i) \leq H \quad \forall\, q \in \mathcal{Q} \quad \forall\, p \in \mathcal{P}$$

Variable bounds

$$
\begin{array}{llll}
\theta_i^L \;\leq\; Q_i^{qp} \;\leq\; \theta_i^q & \forall\, i \in \mathcal{N} \quad \forall\, q \in \mathcal{Q} \quad \forall\, p \in \mathcal{P} \\
\ln(V_j^L) \;\leq\; v_j \;\leq\; \ln(V_j^U) & \forall\, j \in \mathcal{M} \\
\min\limits_{j,p} \ln(\frac{V_j^L}{S_{ij}^p}) \;\leq\; b_i \;\leq\; \min\limits_{j,p} \ln(\frac{V_j^U}{S_{ij}^p}) & \forall\, i \in \mathcal{N}
\end{array}
$$

Variable and Parameter definitions - For a description of the variables and parameters that are used in this formulation, refer to section 8.3.2.

8.3.7 Test Problem 4

This example is for a batch plant with ($\mathcal{N} = 2$) products in ($\mathcal{M} = 3$) stages with ($\mathcal{P} = 1$) scenario for the processing parameters. For each product, five quadrature points are used to approximate the demand distribution, giving a total of ($\mathcal{Q} = 25$) quadrature points for the problem. This example and the reported global solution are taken from Harding and Floudas (1997).

Data

$\theta_1(\mu = 200, \sigma = 10) \quad \theta_2(\mu = 100, \sigma = 10)$

$$
\begin{aligned}
\boldsymbol{S} &= \begin{pmatrix} 2.0 & 3.0 & 4.0 \\ 4.0 & 6.0 & 3.0 \end{pmatrix} \\
\boldsymbol{T} &= \begin{pmatrix} 8.0 & 20.0 & 8.0 \\ 16.0 & 4.0 & 4.0 \end{pmatrix} \\
\boldsymbol{\alpha} &= (10.0, 10.0, 10.0)^T \\
\boldsymbol{\beta} &= (0.6, 0.6, 0.6)^T \\
\boldsymbol{N} &= (1, 1, 1)^T \\
\boldsymbol{p} &= (5.5, 7.0)^T \\
\gamma &= 0.0 \\
\delta &= 0.3 \\
H &= 8.0 \\
w &= 1.0 \\
\boldsymbol{V}^L &= (500, 500, 500)^T \\
\boldsymbol{V}^U &= (4500, 4500, 4500)^T
\end{aligned}
$$

Problem Statistics

No. of continuous variables	55
No. of linear equalities	6
No. of nonconvex inequalities	75

Global Solution

- Objective function: -1197.132
- Continuous variables

$$
\begin{aligned}
\boldsymbol{V} = \exp(v) &= (1200, 1800, 2400)^T \\
\boldsymbol{B} = \exp(b) &= (600, 300)^T
\end{aligned}
$$

8.3.8 Test Problem 5

This example is for a batch plant with ($\mathcal{N} = 4$) products in ($\mathcal{M} = 6$) stages with ($\mathcal{P} = 1$) scenario for the processing parameters. For each product, five quadrature points are used to approximate the demand distribution, giving a total of ($\mathcal{Q} = 625$) quadrature points for the problem. Due to its size in terms of variables (2510) and number of nonconvex inequality constraints (3750), this is a challenging problem.

Data

$\theta_1(\mu = 150, \sigma = 10) \quad \theta_2(\mu = 150, \sigma = 8) \quad \theta_3(\mu = 180, \sigma = 9) \quad \theta_4(\mu = 160, \sigma = 10)$

$$
\begin{aligned}
\boldsymbol{S}^1 &= \begin{pmatrix} 8.0 & 2.0 & 5.2 & 4.9 & 6.1 & 4.2 \\ 0.7 & 0.8 & 0.9 & 3.8 & 2.1 & 2.5 \\ 0.7 & 2.6 & 1.6 & 3.4 & 3.2 & 2.9 \\ 4.7 & 2.3 & 1.6 & 2.7 & 1.2 & 2.5 \end{pmatrix} \\
\boldsymbol{T}^1 &= \begin{pmatrix} 7.0 & 8.3 & 6.0 & 7.0 & 6.5 & 8.0 \\ 6.8 & 5.0 & 6.0 & 4.8 & 5.5 & 5.8 \\ 4.0 & 5.9 & 5.0 & 6.0 & 5.5 & 4.5 \\ 2.4 & 3.0 & 3.5 & 2.5 & 3.0 & 2.8 \end{pmatrix} \\
\boldsymbol{\alpha} &= (10.0, 10.0, 10.0, 10.0, 10.0, 10.0)^T \\
\boldsymbol{\beta} &= (0.6, 0.6, 0.6, 0.6, 0.6, 0.6)^T \\
\boldsymbol{N} &= (1, 1, 1, 1, 1, 1)^T \\
\boldsymbol{p} &= (3.5, 4.0, 3.0, 2.0)^T \\
\gamma &= 0.0 \\
\delta &= 0.3 \\
H &= 8.0 \\
w &= 1.0 \\
\boldsymbol{V}^L &= (500, 500, 500, 500, 500, 500)^T \\
\boldsymbol{V}^U &= (4500, 4500, 4500, 4500, 4500, 4500)^T
\end{aligned}
$$

Problem Statistics

No. of continuous variables	2510
No. of linear equalities	24
No. of nonconvex inequalities	3750

Global Solution

- Objective function: -830.338
- Continuous variables

$$\begin{aligned} \boldsymbol{V} &= \exp(v) = (2703, 1323, 1757, 2045, 2061, 1475)^T \\ \boldsymbol{B} &= \exp(b) = (338, 538, 509, 575)^T \end{aligned}$$

8.4 Chemical Reactor Network Problems

8.4.1 Introduction

Reactor network synthesis has been a widely studied problem in the area of process synthesis. It deals with determining the types, sizes, and interconnections of reactors which optimize a desired performance objective.

Previous work in the area of reactor network synthesis can be categorized as either superstructure-based approaches or targeting approaches. The superstructure-based approaches propose a network of reactors which contain all the possible design alternatives of interest. The solution strategy then determines the optimal structure of the flowsheet. The early developments of this approach was done by Horn and Tsai (1967) and Jackson (1968). The approach was further developed by Achenie and Biegler (1986), Kokossis and Floudas (1990), Kokossis and Floudas (1994), and Schweiger and Floudas (1998b).

The targeting approaches determine a target or bound on the performance index of the reactor network regardless of the reactor types and configuration. These approaches utilize the idea of the attainable region, which was first defined by Horn (1964), as the set of all possible conditions that can be achieved through reaction and mixing. Further work in this area has been done by Glasser et al. (1987), Hildebrandt et al. (1990), Hildebrandt and Glasser (1990), Achenie and Biegler (1988), Balakrishna and Biegler (1992a), Balakrishna and Biegler (1992b), and Feinberg and Hildebrandt (1997). The work of Lakshmanan and Biegler (1996) combined the ideas of the targeting approaches with the superstructure approaches.

Problem Statement

In reactor network synthesis, the goal is to determine the reactor network that transforms the given raw materials into the desired products. The following information is assumed to be given in the problem definition:

- the reaction mechanism and stoichiometry
- the chemical kinetic data
- the rate laws
- the energetic data
- the inlet stream(s) conditions
- the performance objective (output).

The synthesis problem is to determine:

- the type, size, and interconnection of reactor units
- the stream flowrates, compositions, and temperatures
- the composition and temperatures within the reactors
- the heating and cooling requirements
- the optimal performance objective

There are many different reactor types that can be considered for the reactor network. Two extreme reactor types are often considered: the Continuous Stirred Tank Reactor (CSTR) and the Plug Flow Reactor (PFR). The CSTR is assumed to be perfectly mixed such that there are no spatial variations in concentration, temperature, and reaction rate within the reactor. The PFR is a tubular reactor where there are no radial variations in concentration, temperature, and reaction rate. Since the mathematical modeling of the PFR results in differential equations and leads to a dynamic model, they will be omitted from the present model. The network that will be considered here consists only of CSTRs. Models and test problems which include the dynamic models are discussed in Chapter 15, Section 15.2.

The reactor network consists of mixers, splitters, and CSTRs. Splitters are used to split the feed and the outlet of each reactor. Mixers are situated at the inlet to each reactor to mix the streams which come from the feed splitter and the splitters after each reactor. A final mixer is used to mix the streams which go from the splitter after each reactor unit to the product stream. A flowsheet which has two CSTRs is shown in Figure 8.2

8.4.2 General Formulation

In the general formulation, two assumptions will be made. First, constant density is assumed which implies that volume is conserved. The second assumption is that for nonisothermal systems, the heat capacity is assumed to be constant in temperature and the same for all the components.

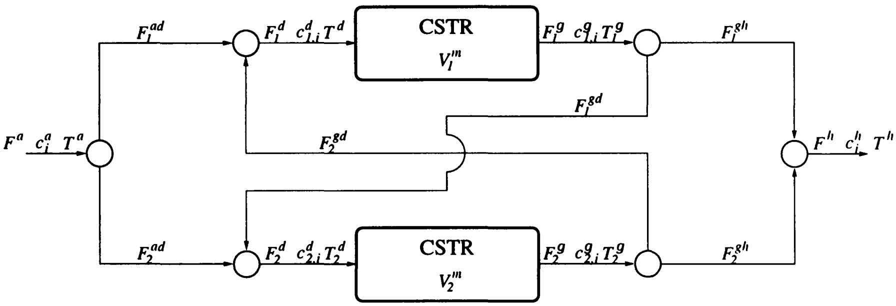


Figure 8.2: Reactor network consisting of two CSTRs

The general formulation described below has been taken from Schweiger and Floudas (1998b). It has been derived for any number of CSTR reactor units, any number of reaction components, any number of reaction paths, any number of feed streams, and any number of product streams.

In the general formulation, the following sets will be used:

Set	Description
I	Components
J	Reactions
L	CSTR units
R	Feeds
P	Products

Constraints

Feed splitter

$$F_r^a = \sum_{l \in L} F_{r,l}^{ad} \quad \forall r \in R$$

CSTR inlet mixer total balance

$$F_l^d = \sum_{r \in R} F_{r,l}^{ad} + \sum_{l' \in L} F_{l',l}^{gd} \quad \forall l \in L$$

CSTR inlet mixer component balance

$$c_{l,i}^d F_l^d = \sum_{r \in R} c_{r,i}^a F_{r,l}^{ad} + \sum_{l' \in L} c_{l',i}^g F_{l',l}^{gb} \quad \forall i \in I \quad \forall l \in L$$

CSTR total balance

$$F_l^g = F_l^d \quad \forall l \in L$$

CSTR component balance

$$c_{l,i}^g F_l^g = c_{l,i}^d F_l^d + V_l^m \sum_{j \in J} \nu_{i,j} r_{l,j}^m \quad \forall i \in I \quad \forall l \in L$$

CSTR reaction rates

$$r_{l,j}^{m} = f_j^r(c_{l,i}^{m}, T_l^{m}) \quad \forall j \in J \quad \forall l \in L$$

CSTR outlet splitter

$$F_l^g = \sum_{l' \in L} F_{l,l'}^{gd} + \sum_{p \in P} F_{l,p}^{gh} \quad \forall l \in L$$

Product mixer total balance

$$F_p^h = \sum_{l \in L} F_{l,p}^{gh} \quad \forall p \in P$$

Product mixer component balance

$$c_{p,i}^h F_p^h = \sum_{l \in L} c_{l,i}^g F_{l,p}^{gh} \quad \forall i \in I \quad \forall p \in P$$

Objective Function

The objective function varies from problem to problem. In many cases it is the maximization of the yield of the desired product. It may be based upon economic criteria reflecting the value of the products, cost of reactants, cost of the utilities, and the cost of the reactors.

Variables

			Flowrates
$F^{ad}_{r,l}$	$\forall r \in R$	$\forall l \in L$	Volumetric flowrates from feed splitters to CSTR mixers
F^{d}_{l}	$\forall l \in L$		Volumetric flowrates into CSTRs
F^{g}_{l}	$\forall l \in L$		Volumetric flowrates out of CSTRs
$F^{gd}_{l,l'}$	$\forall l \in L$	$\forall l' \in L$	Volumetric flowrates from CSTR outlets to CSTR inlets
$F^{gh}_{l,p}$	$\forall l \in L$	$\forall p \in P$	Volumetric flowrates from CSTR outlets to product mixer
F^{h}_{p}	$\forall p \in P$		Volumetric flowrates of the product streams
			Concentrations
$c^{d}_{l,i}$	$\forall l \in L$	$\forall i \in I$	Concentrations of species in the CSTR inlet streams
$c^{g}_{l,i}$	$\forall l \in L$	$\forall i \in I$	Concentrations of species in the CSTR outlet streams
$c^{h}_{p,i}$	$\forall p \in P$	$\forall i \in I$	Concentrations of species in the product streams
			Temperatures
T^{m}_{l}	$\forall l \in L$		Temperatures in the CSTRs
			Reactor Volumes
V^{m}_{l}	$\forall l \in L$		Volume of the CSTRs
			Reaction Rates
$r^{m}_{l,j}$	$\forall l \in L$	$\forall j \in J$	Rate of reaction j in reactor l

<u>Variable Bounds</u>

The variable bounds vary from one problem to the next. The flowrates, concentrations, temperatures, volumes and reaction rates have a lower bound of zero due to physical restrictions. The upper bounds on the flow rates are set arbitrarily to help the solution algorithm. The upper bounds on the concentrations are set to maximum possible concentration that any species could achieve. The temperature ranges for the nonisothermal problems are usually specified for each problem. The upper bounds on the reactor volumes and reaction rates are set arbitrarily to help the solution algorithm.

Since the recycle around a CSTR unit is not necessary, the upper and lower bounds for these flowrates are set to zero.

8.4.3 Specific Information

Specific information is provided for each problem. This information includes the reaction mechanism, the reaction parameters, the rate expressions, and any additional information required for the problem.

Reaction Mechanism
For each problem, a reaction mechanism indicating the species and reaction steps involved is provided.

Parameters
The parameters for the problems are the stoichiometric coefficient matrix, the kinetic constants, and the feed conditions. The stoichiometric coefficient matrix, $\nu_{i,j}$ indicates the relative number of moles of products and reactants that participate in a given reaction.

			Reaction constants
$\nu_{i,j}$	$\forall i \in I$	$\forall j \in J$	Stoichiometric coefficient matrix
k_j	$\forall j \in J$		Kinetic rate constant
$\hat{k}_j$	$\forall j \in J$		Pre-exponential factor
E_j	$\forall j \in J$		Activation Energy
ΔH_j	$\forall j \in J$		Heat of reaction
			Feed conditions
F_r^a	$\forall r \in R$		Flowrate of feed streams
$c_{r,i}^a$	$\forall r \in R$	$\forall i \in I$	Concentrations of species in feed streams

Rate Expressions
The rate expressions ($f_j^r(c_i, T)$) are specified for each problem. These expressions often involve the products of the concentrations of the species. The rate expressions have the form

$$f_j^r(c_i, T) = k_j(T) \prod_{i \in I} c_i^{\nu_{i,j}^f}$$

where $\nu_{i,j}^f$ correspond to the positive coefficients in the stoichiometric matrix representing the forward reactions. (For equilibrium reactions, both the forward and reverse reactions must appear separately and the rate constants for both must be provided.)

For isothermal reactions, the values of k_j are fixed. For most nonisothermal problems, Arrhenius temperature dependence will be assumed:

$$k_j(T) = \hat{k}_j \exp\left(\frac{-E_j}{RT}\right)$$

Additional Information
Some problems have additional restrictions on the sizes of the reactors and the amount of conversion.

8.4.4 Problem Characteristics

This problem has bilinearities which result from the mass balances of the mixers. The rate expressions usually involve the products of the concentrations and thus lead to squared or bilinear terms for first order kinetics, trilinear terms for second order kinetics, and so on. For nonisothermal problems, the temperature dependence is an exponential which is multiplied by the product of the concentrations. Because of these terms in the formulation, the problem is nonconvex.

For each problem, the number of CSTRs in the network must be given. Existence of the CSTRs in the network could be handled with binary variables, however, this would lead to an MINLP.

8.4.5 Test Problems

For all of the example problems, 5 CSTRs are included in the reactor network. The test problems described here have been used as examples in many of the references listed above. These problems have been formulated in both the MINOPT and GAMS modeling languages and the solutions provided have been obtained using MINOPT (Schweiger and Floudas, 1998c, 1997). These problems have multiple local optima which have been found by using MINOPT to solve the problem with random starting points.

8.4.6 Test Problem 1 : Nonisothermal Van de Vusse Reaction Case I

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$

$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:
Maximize the yield of **B**

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	5.4 $\times 10^9$ h^{-1}	15.84 kcal/mol	84 K L/mol
2	1.6 $\times 10^{12}$ L/(mol h)	23.76 kcal/mol	108 K L/mol
3	3.6 $\times 10^5$ h^{-1}	7.92 kcal/mol	60 K L/mol
Feed Conditions			
F_r^a	100 L/s		
$c_{r,i}^a$	1.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**		

Rate Expressions

$$
\begin{aligned}
f_1^r &= \hat{k}_1 e^{\frac{-E_1}{RT}} c_A \\
f_2^r &= \hat{k}_2 e^{\frac{-E_2}{RT}} c_B \\
f_3^r &= \hat{k}_3 e^{\frac{-E_3}{RT}} c_A^2
\end{aligned}
$$

Additional Information
The temperatures in the reactors are bounded between 300 K and 810 K.

Explicit Formulation

$$
\begin{aligned}
\max &= -c_{1,B}^h \\
F_1^a &= F_{1,1}^{ad} + F_{1,2}^{ad} + F_{1,3}^{ad} + F_{1,4}^{ad} + F_{1,5}^{ad} \\
F_1^d &= F_{1,1}^{ad} + F_{1,1}^{gd} + F_{2,1}^{gd} + F_{3,1}^{gd} + F_{4,1}^{gd} + F_{5,1}^{gd} \\
F_2^d &= F_{1,2}^{ad} + F_{1,2}^{gd} + F_{2,2}^{gd} + F_{3,2}^{gd} + F_{4,2}^{gd} + F_{5,2}^{gd} \\
F_3^d &= F_{1,3}^{ad} + F_{1,3}^{gd} + F_{2,3}^{gd} + F_{3,3}^{gd} + F_{4,3}^{gd} + F_{5,3}^{gd} \\
F_4^d &= F_{1,4}^{ad} + F_{1,4}^{gd} + F_{2,4}^{gd} + F_{3,4}^{gd} + F_{4,4}^{gd} + F_{5,4}^{gd} \\
F_5^d &= F_{1,5}^{ad} + F_{1,5}^{gd} + F_{2,5}^{gd} + F_{3,5}^{gd} + F_{4,5}^{gd} + F_{5,5}^{gd} \\
c_{1,A}^d F_1^d &= c_{1,A}^a F_{1,1}^{ad} + c_{1,A}^g F_{1,1}^{gb} + c_{2,A}^g F_{2,1}^{gb} + c_{3,A}^g F_{3,1}^{gb} + c_{4,A}^g F_{4,1}^{gb} + c_{5,A}^g F_{5,1}^{gb} \\
c_{1,B}^d F_1^d &= c_{1,B}^a F_{1,1}^{ad} + c_{1,B}^g F_{1,1}^{gb} + c_{2,B}^g F_{2,1}^{gb} + c_{3,B}^g F_{3,1}^{gb} + c_{4,B}^g F_{4,1}^{gb} + c_{5,B}^g F_{5,1}^{gb} \\
c_{1,C}^d F_1^d &= c_{1,C}^a F_{1,1}^{ad} + c_{1,C}^g F_{1,1}^{gb} + c_{2,C}^g F_{2,1}^{gb} + c_{3,C}^g F_{3,1}^{gb} + c_{4,C}^g F_{4,1}^{gb} + c_{5,C}^g F_{5,1}^{gb} \\
c_{1,D}^d F_1^d &= c_{1,D}^a F_{1,1}^{ad} + c_{1,D}^g F_{1,1}^{gb} + c_{2,D}^g F_{2,1}^{gb} + c_{3,D}^g F_{3,1}^{gb} + c_{4,D}^g F_{4,1}^{gb} + c_{5,D}^g F_{5,1}^{gb} \\
c_{2,A}^d F_2^d &= c_{2,A}^a F_{1,2}^{ad} + c_{1,A}^g F_{1,2}^{gb} + c_{2,A}^g F_{2,2}^{gb} + c_{3,A}^g F_{3,2}^{gb} + c_{4,A}^g F_{4,2}^{gb} + c_{5,A}^g F_{5,2}^{gb} \\
c_{2,B}^d F_2^d &= c_{2,B}^a F_{1,2}^{ad} + c_{1,B}^g F_{1,2}^{gb} + c_{2,B}^g F_{2,2}^{gb} + c_{3,B}^g F_{3,2}^{gb} + c_{4,B}^g F_{4,2}^{gb} + c_{5,B}^g F_{5,2}^{gb} \\
c_{2,C}^d F_2^d &= c_{2,C}^a F_{1,2}^{ad} + c_{1,C}^g F_{1,2}^{gb} + c_{2,C}^g F_{2,2}^{gb} + c_{3,C}^g F_{3,2}^{gb} + c_{4,C}^g F_{4,2}^{gb} + c_{5,C}^g F_{5,2}^{gb} \\
c_{2,D}^d F_2^d &= c_{2,D}^a F_{1,2}^{ad} + c_{1,D}^g F_{1,2}^{gb} + c_{2,D}^g F_{2,2}^{gb} + c_{3,D}^g F_{3,2}^{gb} + c_{4,D}^g F_{4,2}^{gb} + c_{5,D}^g F_{5,2}^{gb}
\end{aligned}
$$

$$
\begin{aligned}
c^d_{3,A}F^d_3 &= c^a_{3,A}F^{ad}_{1,3} + c^g_{1,A}F^{gb}_{1,3} + c^g_{2,A}F^{gb}_{2,3} + c^g_{3,A}F^{gb}_{3,3} + c^g_{4,A}F^{gb}_{4,3} + c^g_{5,A}F^{gb}_{5,3} \\
c^d_{3,B}F^d_3 &= c^a_{3,B}F^{ad}_{1,3} + c^g_{1,B}F^{gb}_{1,3} + c^g_{2,B}F^{gb}_{2,3} + c^g_{3,B}F^{gb}_{3,3} + c^g_{4,B}F^{gb}_{4,3} + c^g_{5,B}F^{gb}_{5,3} \\
c^d_{3,C}F^d_3 &= c^a_{3,C}F^{ad}_{1,3} + c^g_{1,C}F^{gb}_{1,3} + c^g_{2,C}F^{gb}_{2,3} + c^g_{3,C}F^{gb}_{3,3} + c^g_{4,C}F^{gb}_{4,3} + c^g_{5,C}F^{gb}_{5,3} \\
c^d_{3,D}F^d_3 &= c^a_{3,D}F^{ad}_{1,3} + c^g_{1,D}F^{gb}_{1,3} + c^g_{2,D}F^{gb}_{2,3} + c^g_{3,D}F^{gb}_{3,3} + c^g_{4,D}F^{gb}_{4,3} + c^g_{5,D}F^{gb}_{5,3} \\
c^d_{4,A}F^d_4 &= c^a_{4,A}F^{ad}_{1,4} + c^g_{1,A}F^{gb}_{1,4} + c^g_{2,A}F^{gb}_{2,4} + c^g_{3,A}F^{gb}_{3,4} + c^g_{4,A}F^{gb}_{4,4} + c^g_{5,A}F^{gb}_{5,4} \\
c^d_{4,B}F^d_4 &= c^a_{4,B}F^{ad}_{1,4} + c^g_{1,B}F^{gb}_{1,4} + c^g_{2,B}F^{gb}_{2,4} + c^g_{3,B}F^{gb}_{3,4} + c^g_{4,B}F^{gb}_{4,4} + c^g_{5,B}F^{gb}_{5,4} \\
c^d_{4,C}F^d_4 &= c^a_{4,C}F^{ad}_{1,4} + c^g_{1,C}F^{gb}_{1,4} + c^g_{2,C}F^{gb}_{2,4} + c^g_{3,C}F^{gb}_{3,4} + c^g_{4,C}F^{gb}_{4,4} + c^g_{5,C}F^{gb}_{5,4} \\
c^d_{4,D}F^d_4 &= c^a_{4,D}F^{ad}_{1,4} + c^g_{1,D}F^{gb}_{1,4} + c^g_{2,D}F^{gb}_{2,4} + c^g_{3,D}F^{gb}_{3,4} + c^g_{4,D}F^{gb}_{4,4} + c^g_{5,D}F^{gb}_{5,4} \\
c^d_{5,A}F^d_5 &= c^a_{5,A}F^{ad}_{1,5} + c^g_{1,A}F^{gb}_{1,5} + c^g_{2,A}F^{gb}_{2,5} + c^g_{3,A}F^{gb}_{3,5} + c^g_{4,A}F^{gb}_{4,5} + c^g_{5,A}F^{gb}_{5,5} \\
c^d_{5,B}F^d_5 &= c^a_{5,B}F^{ad}_{1,5} + c^g_{1,B}F^{gb}_{1,5} + c^g_{2,B}F^{gb}_{2,5} + c^g_{3,B}F^{gb}_{3,5} + c^g_{4,B}F^{gb}_{4,5} + c^g_{5,B}F^{gb}_{5,5} \\
c^d_{5,C}F^d_5 &= c^a_{5,C}F^{ad}_{1,5} + c^g_{1,C}F^{gb}_{1,5} + c^g_{2,C}F^{gb}_{2,5} + c^g_{3,C}F^{gb}_{3,5} + c^g_{4,C}F^{gb}_{4,5} + c^g_{5,C}F^{gb}_{5,5} \\
c^d_{5,D}F^d_5 &= c^a_{5,D}F^{ad}_{1,5} + c^g_{1,D}F^{gb}_{1,5} + c^g_{2,D}F^{gb}_{2,5} + c^g_{3,D}F^{gb}_{3,5} + c^g_{4,D}F^{gb}_{4,5} + c^g_{5,D}F^{gb}_{5,5}
\end{aligned}
$$

$$
\begin{aligned}
F^g_1 &= F^d_1 \\
F^g_2 &= F^d_2 \\
F^g_3 &= F^d_3 \\
F^g_4 &= F^d_4 \\
F^g_5 &= F^d_5 \\
c^g_{1,A}F^g_1 &= c^d_{1,A}F^d_1 + V^m_1(\nu_{A,1}r^m_{1,1} + \nu_{A,2}r^m_{1,2} + \nu_{A,3}r^m_{1,3}) \\
c^g_{1,B}F^g_1 &= c^d_{1,B}F^d_1 + V^m_1(\nu_{B,1}r^m_{1,1} + \nu_{B,2}r^m_{1,2} + \nu_{B,3}r^m_{1,3}) \\
c^g_{1,C}F^g_1 &= c^d_{1,C}F^d_1 + V^m_1(\nu_{C,1}r^m_{1,1} + \nu_{C,2}r^m_{1,2} + \nu_{C,3}r^m_{1,3}) \\
c^g_{1,D}F^g_1 &= c^d_{1,D}F^d_1 + V^m_1(\nu_{D,1}r^m_{1,1} + \nu_{D,2}r^m_{1,2} + \nu_{D,3}r^m_{1,3}) \\
c^g_{2,A}F^g_2 &= c^d_{2,A}F^d_2 + V^m_2(\nu_{A,1}r^m_{2,1} + \nu_{A,2}r^m_{2,2} + \nu_{A,3}r^m_{2,3}) \\
c^g_{2,B}F^g_2 &= c^d_{2,B}F^d_2 + V^m_2(\nu_{B,1}r^m_{2,1} + \nu_{B,2}r^m_{2,2} + \nu_{B,3}r^m_{2,3}) \\
c^g_{2,C}F^g_2 &= c^d_{2,C}F^d_2 + V^m_2(\nu_{C,1}r^m_{2,1} + \nu_{C,2}r^m_{2,2} + \nu_{C,3}r^m_{2,3}) \\
c^g_{2,D}F^g_2 &= c^d_{2,D}F^d_2 + V^m_2(\nu_{D,1}r^m_{2,1} + \nu_{D,2}r^m_{2,2} + \nu_{D,3}r^m_{2,3}) \\
c^g_{3,A}F^g_2 &= c^d_{3,A}F^d_3 + V^m_3(\nu_{A,1}r^m_{3,1} + \nu_{A,2}r^m_{3,2} + \nu_{A,3}r^m_{3,3}) \\
c^g_{3,B}F^g_3 &= c^d_{3,B}F^d_3 + V^m_3(\nu_{B,1}r^m_{3,1} + \nu_{B,2}r^m_{3,2} + \nu_{B,3}r^m_{3,3}) \\
c^g_{3,C}F^g_3 &= c^d_{3,C}F^d_3 + V^m_3(\nu_{C,1}r^m_{3,1} + \nu_{C,2}r^m_{3,2} + \nu_{C,3}r^m_{3,3}) \\
c^g_{3,D}F^g_3 &= c^d_{3,D}F^d_3 + V^m_3(\nu_{D,1}r^m_{3,1} + \nu_{D,2}r^m_{3,2} + \nu_{D,3}r^m_{3,3}) \\
c^g_{4,A}F^g_4 &= c^d_{4,A}F^d_4 + V^m_4(\nu_{A,1}r^m_{4,1} + \nu_{A,2}r^m_{4,2} + \nu_{A,3}r^m_{4,3}) \\
c^g_{4,B}F^g_4 &= c^d_{4,B}F^d_4 + V^m_4(\nu_{B,1}r^m_{4,1} + \nu_{B,2}r^m_{4,2} + \nu_{B,3}r^m_{4,3}) \\
c^g_{4,C}F^g_4 &= c^d_{4,C}F^d_4 + V^m_4(\nu_{C,1}r^m_{4,1} + \nu_{C,2}r^m_{4,2} + \nu_{C,3}r^m_{4,3}) \\
c^g_{4,D}F^g_4 &= c^d_{4,D}F^d_4 + V^m_4(\nu_{D,1}r^m_{4,1} + \nu_{D,2}r^m_{4,2} + \nu_{D,3}r^m_{4,3}) \\
c^g_{5,A}F^g_5 &= c^d_{5,A}F^d_5 + V^m_5(\nu_{A,1}r^m_{5,1} + \nu_{A,2}r^m_{5,2} + \nu_{A,3}r^m_{5,3}) \\
c^g_{5,B}F^g_5 &= c^d_{5,B}F^d_5 + V^m_5(\nu_{B,1}r^m_{5,1} + \nu_{B,2}r^m_{5,2} + \nu_{B,3}r^m_{5,3}) \\
c^g_{5,C}F^g_5 &= c^d_{5,C}F^d_5 + V^m_5(\nu_{C,1}r^m_{5,1} + \nu_{C,2}r^m_{5,2} + \nu_{C,3}r^m_{5,3}) \\
c^g_{5,D}F^g_5 &= c^d_{5,D}F^d_5 + V^m_5(\nu_{D,1}r^m_{5,1} + \nu_{D,2}r^m_{5,2} + \nu_{D,3}r^m_{5,3})
\end{aligned}
$$

$$
\begin{aligned}
r_{1,1}^m &= 5.4 \times 10^9 e^{-7971.82/T_1^m} c_{1,A}^g \\
r_{1,2}^m &= 1.6 \times 10^{12} e^{-11957.7/T_1^m} c_{1,B}^g \\
r_{1,3}^m &= 3.6 \times 10^5 e^{-3985.91/T_1^m} c_{1,A}^g c_{1,A}^g \\
r_{2,1}^m &= 5.4 \times 10^9 e^{-7971.82/T_2^m} c_{2,A}^g \\
r_{2,2}^m &= 1.6 \times 10^{12} e^{-11957.7/T_2^m} c_{2,B}^g \\
r_{2,3}^m &= 3.6 \times 10^5 e^{-3985.91/T_2^m} c_{2,A}^g c_{2,A}^g \\
r_{3,1}^m &= 5.4 \times 10^9 e^{-7971.82/T_3^m} c_{3,A}^g \\
r_{3,2}^m &= 1.6 \times 10^{12} e^{-11957.7/T_3^m} c_{3,B}^g \\
r_{3,3}^m &= 3.6 \times 10^5 e^{-3985.91/T_3^m} c_{3,A}^g c_{3,A}^g \\
r_{4,1}^m &= 5.4 \times 10^9 e^{-7971.82/T_4^m} c_{4,A}^g \\
r_{4,2}^m &= 1.6 \times 10^{12} e^{-11957.7/T_4^m} c_{4,B}^g \\
r_{4,3}^m &= 3.6 \times 10^5 e^{-3985.91/T_4^m} c_{4,A}^g c_{4,A}^g \\
r_{5,1}^m &= 5.4 \times 10^9 e^{-7971.82/T_5^m} c_{5,A}^g \\
r_{5,2}^m &= 1.6 \times 10^{12} e^{-11957.7/T_5^m} c_{5,B}^g \\
r_{5,3}^m &= 3.6 \times 10^5 e^{-3985.91/T_5^m} c_{5,A}^g c_{5,A}^g \\
F_1^g &= F_{1,1}^{gd} + F_{1,1}^{gd} + F_{1,1}^{gd} + F_{1,1}^{gd} + F_{1,1}^{gd} + F_{1,1}^{gh} \\
F_2^g &= F_{2,1}^{gd} + F_{2,1}^{gd} + F_{2,1}^{gd} + F_{2,1}^{gd} + F_{2,1}^{gd} + F_{2,1}^{gh} \\
F_3^g &= F_{3,1}^{gd} + F_{3,1}^{gd} + F_{3,1}^{gd} + F_{3,1}^{gd} + F_{3,1}^{gd} + F_{3,1}^{gh} \\
F_4^g &= F_{4,1}^{gd} + F_{4,1}^{gd} + F_{4,1}^{gd} + F_{4,1}^{gd} + F_{4,1}^{gd} + F_{4,1}^{gh} \\
F_5^g &= F_{5,1}^{gd} + F_{5,1}^{gd} + F_{5,1}^{gd} + F_{5,1}^{gd} + F_{5,1}^{gd} + F_{5,1}^{gh} \\
F_1^h &= F_{1,1}^{gh} + F_{2,1}^{gh} + F_{3,1}^{gh} + F_{4,1}^{gh} + F_{5,1}^{gh} \\
c_{1,A}^h F_1^h &= c_{1,A}^g F_{1,1}^{gh} + c_{2,A}^g F_{2,1}^{gh} + c_{3,A}^g F_{3,1}^{gh} + c_{4,A}^g F_{4,1}^{gh} + c_{5,A}^g F_{5,1}^{gh} \\
c_{1,B}^h F_1^h &= c_{1,B}^g F_{1,1}^{gh} + c_{2,B}^g F_{2,1}^{gh} + c_{3,B}^g F_{3,1}^{gh} + c_{4,B}^g F_{4,1}^{gh} + c_{5,B}^g F_{5,1}^{gh} \\
c_{1,C}^h F_1^h &= c_{1,C}^g F_{1,1}^{gh} + c_{2,C}^g F_{2,1}^{gh} + c_{3,C}^g F_{3,1}^{gh} + c_{4,C}^g F_{4,1}^{gh} + c_{5,C}^g F_{5,1}^{gh} \\
c_{1,D}^h F_1^h &= c_{1,D}^g F_{1,1}^{gh} + c_{2,D}^g F_{2,1}^{gh} + c_{3,D}^g F_{3,1}^{gh} + c_{4,D}^g F_{4,1}^{gh} + c_{5,D}^g F_{5,1}^{gh}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	115
No. of linear equalities	17
No. of nonlinear equalities	59

Best Known Solution

The best known solution is a network of the 5 CSTRs connected in series.

- Objective function: 0.8189924 mol/L
- Variables

$$F_{r,l}^{ad} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_l^d = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_l^g = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_{l,l'}^{gd} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F_{l,p}^{gh} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F_p^h = 100.00$$

$$c_{l,i}^d = \begin{pmatrix} 1.000000 & 0.000000 & 0.0000000 & 0.0000000 \\ 0.831745 & 0.150840 & 0.0086813 & 0.0043669 \\ 0.589306 & 0.355891 & 0.0257788 & 0.0145124 \\ 0.309826 & 0.581538 & 0.0495779 & 0.0295292 \\ 0.022384 & 0.805048 & 0.0779508 & 0.0473088 \end{pmatrix}$$

$$c_{l,i}^g = \begin{pmatrix} 0.831745 & 0.150840 & 0.0086813 & 0.0043669 \\ 0.589306 & 0.355891 & 0.0257788 & 0.0145124 \\ 0.309826 & 0.581538 & 0.0495779 & 0.0295292 \\ 0.022384 & 0.805048 & 0.0779508 & 0.0473088 \\ 0.003923 & 0.818992 & 0.0809024 & 0.0480911 \end{pmatrix}$$

$$c_{p,i}^h = (0.003923, 0.818992, 0.0809024, 0.0480911)^T$$

$$V_l^m = (0.00346267, 0.0377339, 0.506607, 1865.11, 10000.00)^T$$

$$T_l^m = (578.081, 514.215, 459.703, 347.888, 311.952)^T$$

$$r_{l,j}^m = \begin{pmatrix} 4606.885 & 250.7101 & 252.2287 \\ 588.7233 & 45.31080 & 53.77399 \\ 49.23861 & 4.697744 & 5.928367 \\ 0.0135050 & 0.00152125 & 0.00190655 \\ 0.000168959 & 2.95161 \times 10^{-5} & 1.56466 \times 10^{-5} \end{pmatrix}$$

8.4.7 Test Problem 2 : Isothermal Van de Vusse Reaction Case I

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_2} \mathbf{C}$$
$$2\mathbf{A} \xrightarrow{k_3} \mathbf{D}$$

Objective:
Maximize the yield of **B**:

$$\max c_{1,B}^{h}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	10 s^{-1} (first order)
k_2	1 s^{-1} (first order)
k_3	0.5 L/(mol s) (second order)
	Feed Conditions
F_r^a	100 L/s
$c_{r,i}^a$	0.58 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f_1^r = k_1 c_A$$
$$f_2^r = k_2 c_B$$
$$f_3^r = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	110
No. of linear equalities	27
No. of nonlinear equalities	49

Best Known Solution

The best known solution is a network of the 5 CSTRs connected in series.

- Objective function: 0.41233 mol/L
- Variables

$$F^{ad}_{r,l} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F^d_l = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F^g_l = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F^{gd}_{l,l'} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F^{gh}_{l,p} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F^h_p = 100.00$$

$$c^d_{l,i} = \begin{pmatrix} 0.580000 & 0.000000 & 0.0000000 & 0.00000000 \\ 0.355250 & 0.204543 & 0.0124966 & 0.00385517 \\ 0.227037 & 0.312646 & 0.0297604 & 0.00527831 \\ 0.147296 & 0.371414 & 0.0495755 & 0.00585706 \\ 0.096150 & 0.400948 & 0.0707007 & 0.00610060 \end{pmatrix}$$

$$c^g_{l,i} = \begin{pmatrix} 0.355250 & 0.204543 & 0.0124966 & 0.00385517 \\ 0.227037 & 0.312646 & 0.0297604 & 0.00527831 \\ 0.147296 & 0.371414 & 0.0495755 & 0.00585706 \\ 0.096150 & 0.400948 & 0.0707007 & 0.00610060 \\ 0.062929 & 0.412330 & 0.0923321 & 0.00620448 \end{pmatrix}$$

$$c^h_{p,i} = (0.062929, 0.412330, 0.0923321, 0.00620448)^T$$

$$V^m_l = (6.10951, 5.52155, 5.33504, 5.26882, 5.24612)^T$$

$$r^m_{l,j} = \begin{pmatrix} 3.55250 & 0.204543 & 0.0631012 \\ 2.27037 & 0.312646 & 0.0257729 \\ 1.47296 & 0.371414 & 0.0108481 \\ 0.96150 & 0.400948 & 0.0046224 \\ 0.62929 & 0.412330 & 0.0019800 \end{pmatrix}$$

8.4.8 Test Problem 3 : Isothermal Van de Vusse Reaction Case II

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_2} \mathbf{C}$$
$$\mathbf{2A} \xrightarrow{k_3} \mathbf{D}$$

Objective:
Maximize the yield of **B**:

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -1 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	10 s^{-1} (first order)
k_2	1 s^{-1} (first order)
k_3	0.5 L/(mol s) (second order)
	Feed Conditions
F^a_r	100 L/s
$c^a_{r,i}$	0.58 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f^r_1 = k_1 c_A$$
$$f^r_2 = k_2 c_B$$
$$f^r_3 = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	110
No. of linear equalities	27
No. of nonlinear equalities	49

Best Known Solution

The best known solution is a network of the 5 CSTRs connected in series.

- Objective function: 0.4166031 mol/L
- Variables

$$F^{ad}_{r,l} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F^{d}_{l} = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F^{g}_{l} = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F^{gd}_{l,l'} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F^{gh}_{l,p} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F^{h}_{p} = 100.00$$

$$c^{d}_{l,i} = \begin{pmatrix} 0.580000 & 0.000000 & 0.0000000 & 0.00000000 \\ 0.365118 & 0.199499 & 0.0115306 & 0.00385254 \\ 0.234447 & 0.311496 & 0.0286909 & 0.00536656 \\ 0.151716 & 0.373396 & 0.0488990 & 0.00598941 \\ 0.098500 & 0.404599 & 0.0706506 & 0.00625021 \end{pmatrix}$$

$$c^{g}_{l,i} = \begin{pmatrix} 0.365118 & 0.199499 & 0.0115306 & 0.00385254 \\ 0.234447 & 0.311496 & 0.0286909 & 0.00536656 \\ 0.151716 & 0.373396 & 0.0488990 & 0.00598941 \\ 0.098500 & 0.404599 & 0.0706506 & 0.00625021 \\ 0.064040 & 0.416603 & 0.0929969 & 0.00636020 \end{pmatrix}$$

$$c^{h}_{p,i} = (0.064040, 0.416603, 0.0929969, 0.00636020)^T$$

$$V^{m}_{l} = (5.77978, 5.50900, 5.41197, 5.37610, 5.36393)^T$$

$$r^{m}_{l,j} = \begin{pmatrix} 3.65118 & 0.199499 & 0.0666554 \\ 2.34447 & 0.311496 & 0.0274827 \\ 1.51716 & 0.373396 & 0.0115088 \\ 0.98500 & 0.404599 & 0.0048512 \\ 0.64040 & 0.416603 & 0.0020505 \end{pmatrix}$$

8.4.9 Test Problem 4 : Isothermal Van de Vusse Reaction Case III

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$
$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:
Maximize the yield of **B**:

$$\max c_{1,B}^h$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Rate Constants	
k_1	10 s^{-1} (first order)
k_2	1 s^{-1} (first order)
k_3	0.5 L/(mol s) (second order)
Feed Conditions	
F_r^a	100 L/s
$c_{r,i}^a$	5.8 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f_1^r = k_1 c_A$$
$$f_2^r = k_2 c_B$$
$$f_3^r = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	110
No. of linear equalities	27
No. of nonlinear equalities	49

Best Known Solution

The best known solution is a network of the 5 CSTRs connected in series.

- Objective function: 3.579982 mol/L
- Variables

$$F_{r,l}^{ad} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_l^d = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_l^g = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_{l,l'}^{gd} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F_{l,p}^{gh} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F_p^h = 100.00$$

$$c_{l,i}^d = \begin{pmatrix} 5.80000 & 0.00000 & 0.000000 & 0.000000 \\ 2.18714 & 2.61064 & 0.353851 & 0.324187 \\ 1.42109 & 3.13347 & 0.501745 & 0.371845 \\ 0.98303 & 3.39459 & 0.639475 & 0.391450 \\ 0.69584 & 3.52700 & 0.775577 & 0.400792 \end{pmatrix}$$

$$c_{l,i}^g = \begin{pmatrix} 2.18714 & 2.61064 & 0.353851 & 0.324187 \\ 1.42109 & 3.13347 & 0.501745 & 0.371845 \\ 0.98303 & 3.39459 & 0.639475 & 0.391450 \\ 0.69584 & 3.52700 & 0.775577 & 0.400792 \\ 0.49779 & 3.57998 & 0.911252 & 0.405487 \end{pmatrix}$$

$$c_{p,i}^h = (0.49779, 3.57998, 0.911252, 0.405487)^T$$

$$V_l^m = (13.55421, 4.71981, 4.05734, 3.85885, 3.78984)^T$$

$$r_{l,j}^m = \begin{pmatrix} 21.87137 & 2.61064 & 2.39178 \\ 14.21093 & 3.13347 & 1.00975 \\ 9.83035 & 3.39459 & 0.48318 \\ 6.95837 & 3.52700 & 0.24209 \\ 4.97791 & 3.57998 & 0.12390 \end{pmatrix}$$

8.4.10 Test Problem 5 : Isothermal Van de Vusse Reaction Case IV

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_2} \mathbf{C}$$
$$\mathbf{2A} \xrightarrow{k_3} \mathbf{D}$$

Objective:
Maximize the yield of **B**:

$$\max c_{1,B}^{h}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	1 s^{-1} (first order)
k_2	2 s^{-1} (first order)
k_3	10 L/(mol s) (second order)
	Feed Conditions
F_r^a	100 L/s
$c_{r,i}^a$	1 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f_1^r = k_1 c_A$$
$$f_2^r = k_2 c_B$$
$$f_3^r = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	110
No. of linear equalities	27
No. of nonlinear equalities	49

Best Known Solution

The best known solution is a network of the 5 CSTRs connected in series.

- Objective function: 0.06911967 mol/L
- Variables

$$F_{r,l}^{ad} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_l^d = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_l^g = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_{l,l'}^{gd} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F_{l,p}^{gh} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F_p^h = 100.00$$

$$c_{l,i}^d = \begin{pmatrix} 1.000000 & 0.0000000 & 0.0000000 & 0.000000 \\ 0.307501 & 0.0594212 & 0.0374313 & 0.297823 \\ 0.242938 & 0.0645822 & 0.0432904 & 0.324595 \\ 0.204348 & 0.0671803 & 0.0482783 & 0.340097 \\ 0.176733 & 0.0685462 & 0.0530021 & 0.350859 \end{pmatrix}$$

$$c_{l,i}^g = \begin{pmatrix} 0.307502 & 0.0594212 & 0.0374313 & 0.297823 \\ 0.242938 & 0.0645822 & 0.0432904 & 0.324595 \\ 0.204348 & 0.0671803 & 0.0482783 & 0.340097 \\ 0.176733 & 0.0685462 & 0.0530021 & 0.350859 \\ 0.155418 & 0.0691197 & 0.0576168 & 0.358923 \end{pmatrix}$$

$$c_{p,i}^h = (0.155418, 0.0691197, 0.0576168, 0.358923)^T$$

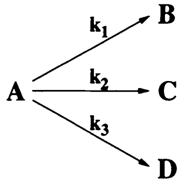
$$V_l^m = (31.49660, 4.53616, 3.71232, 3.44572, 3.33816)^T$$

$$r_{l,j}^m = \begin{pmatrix} 0.307502 & 0.118842 & 0.945572 \\ 0.242938 & 0.129164 & 0.590188 \\ 0.204348 & 0.134361 & 0.417581 \\ 0.176733 & 0.137092 & 0.312346 \\ 0.155418 & 0.138239 & 0.241549 \end{pmatrix}$$

8.4.11 Test Problem 6 : Isothermal Trambouze Reaction

Problem Information

Reaction Mechanism



Objective:
Maximize the selectivity of **C** to **A**

$$\max \frac{c^h_{1,C}}{1 - c^h_{1,A}}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & -1 & -1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	0.025 gmol/(L min) (first order)
k_2	0.2 min^{-1} (first order)
k_3	0.4 L/(mol min) (second order)
	Feed Conditions
F^a_r	100 L/min pure **A**
$c^a_{r,i}$	1 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f^r_1 = k_1$$
$$f^r_2 = k_2 c_A$$
$$f^r_3 = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	110
No. of linear equalities	27
No. of nonlinear equalities	49

Best Known Solution

- Objective function: 0.5
- Variables

$$F^{ad}_{r,l} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F^{d}_{l} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F^{g}_{l} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F^{gd}_{l,l'} = \begin{pmatrix} 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F^{gh}_{l,p} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F^{h}_{p} = 100.00$$

$$c^{d}_{l,i} = \begin{pmatrix} 1.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$c^{g}_{l,i} = \begin{pmatrix} 0.250011 & 0.187489 & 0.374994 & 0.187506 \\ 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$c^{h}_{p,i} = (0.2500113, 0.1874887, 0.3749944, 0.1875056)^T$$

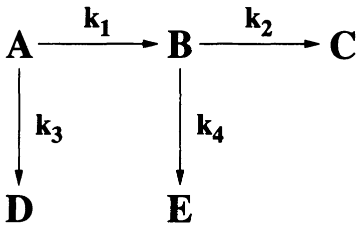
$$V^{m}_{l} = (749.9550, 0.00, 0.00, 0.00, 0.00)^T$$

$$r^{m}_{l,j} = \begin{pmatrix} 0.02500000 & 0.05000225 & 0.02500225 \\ 0.02500000 & 0.000000 & 0.000000 \\ 0.02500000 & 0.000000 & 0.000000 \\ 0.02500000 & 0.000000 & 0.000000 \\ 0.02500000 & 0.000000 & 0.000000 \end{pmatrix}$$

8.4.12 Test Problem 7 : Isothermal Denbigh Reaction Case I

Problem Information

Reaction Mechanism



Objective:
Maximize the selectivity of **B** to **D**:

$$\max \frac{c_{1,B}^{h}}{c_{1,D}^{h}}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -1 & 0 \\ 0.5 & -1 & 0 & -1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	1.0 L/(mol s) (second order)
k_2	0.6 s^{-1} (first order)
k_3	0.6 s^{-1} (first order)
k_4	0.1 L/(mol s) (second order)
	Feed Conditions
F_r^a	100 L/s
$c_{r,i}^a$	6.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0.6 mol/L **D**, 0 mol/L **E**

Rate Expressions

$$f_1^r = k_1 c_A^2$$
$$f_2^r = k_2 c_B$$
$$f_3^r = k_3 c_A$$
$$f_4^r = k_4 c_B^2$$

Problem Statistics

No. of continuous variables	126
No. of linear equalities	27
No. of nonlinear equalities	65

Best Known Solution

The best known solution is a network of the 5 CSTRs connected in series.

- Objective function: 1.232619
- Variables

$$F^{ad}_{r,l} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F^{d}_{l} = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F^{g}_{l} = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F^{gd}_{l,l'} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F^{gh}_{l,p} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F^{h}_{p} = 100.00$$

$$c^{d}_{l,i} = \begin{pmatrix} 6.00000 & 0.000000 & 0.0000000 & 0.600000 & 0.00000000 \\ 5.07454 & 0.405458 & 0.0078186 & 0.697855 & 0.00052835 \\ 4.31316 & 0.722212 & 0.0233875 & 0.790834 & 0.00240236 \\ 3.68278 & 0.966340 & 0.0465604 & 0.879148 & 0.00613451 \\ 3.15761 & 1.150582 & 0.0771169 & 0.963005 & 0.01199413 \end{pmatrix}$$

$$c^{g}_{l,i} = \begin{pmatrix} 5.07454 & 0.405458 & 0.0078186 & 0.697855 & 0.00052835 \\ 4.31316 & 0.722212 & 0.0233875 & 0.790834 & 0.00240236 \\ 3.68278 & 0.966340 & 0.0465604 & 0.879148 & 0.00613451 \\ 3.15761 & 1.150582 & 0.0771169 & 0.963005 & 0.01199413 \\ 2.71737 & 1.285165 & 0.1147744 & 1.042629 & 0.02006015 \end{pmatrix}$$

$$c_{p,i}^{h} = (2.71737, 1.285165, 0.1147744, 1.042629, 0.02006015)^{T}$$

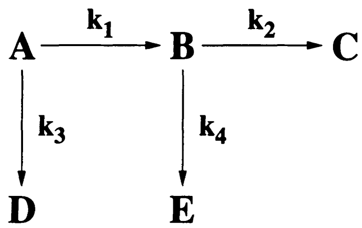
$$V_{l}^{m} = (3.21391, 3.59287, 3.99668, 4.42623, 4.88362)^{T}$$

$$r_{l,j}^{m} = \begin{pmatrix} 25.75090 & 0.243275 & 3.04472 & 0.016440 \\ 18.60339 & 0.433327 & 2.58790 & 0.052159 \\ 13.56289 & 0.579804 & 2.20967 & 0.093381 \\ 9.970488 & 0.690349 & 1.89457 & 0.132384 \\ 7.384113 & 0.771099 & 1.63042 & 0.165165 \end{pmatrix}$$

8.4.13 Test Problem 8 : Isothermal Denbigh ReactionCase II

Problem Information

Reaction Mechanism



Objective:
Maximize the production of **C** subject to 95% conversion of **A**

$$\max c_{1,C}^{h}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -1 & 0 \\ 1 & -1 & 0 & -1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	1.0 L/(mol s) (second order)
k_2	0.6 s^{-1} (first order)
k_3	0.6 s^{-1} (first order)
k_4	0.1 L/(mol s) (second order)
	Feed Conditions
F_r^a	100 L/s pure **A**
$c_{r,i}^a$	6.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**, 0 mol/L **E**

Rate Expressions

$$
\begin{aligned}
f_1^r &= k_1 c_A^2 \\
f_2^r &= k_2 c_B \\
f_3^r &= k_3 c_A \\
f_4^r &= k_4 c_B^2
\end{aligned}
$$

Additional Information

There is an additional constraint due to the requirement of 95% conversion of **A**:

$$c_{1,1}^h = 0.3 \text{mol/L}$$

Problem Statistics

No. of continuous variables	126
No. of linear equalities	28
No. of nonlinear equalities	65

Best Known Solution

- Objective function: 3.256119 mol/L
- Variables

$$F_{r,l}^{ad} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_l^d = (100.00, 94.2474, 94.2474, 94.2474, 94.2474, 94.2474)^T$$

$$F_l^g = (100.00, 94.2474, 94.2474, 94.2474, 94.2474, 94.2474)^T$$

$$F_{l,l'}^{gd} = \begin{pmatrix} 0.00 & 94.2474 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 94.2474 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 94.2474 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 94.2474 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F_{l,p}^{gh} = (5.75258, 0.00, 0.00, 0.00, 94.2474)^T$$

$$F_p^h = 100.00$$

$$c^d_{l,i} = \begin{pmatrix} 6.00000 & 0.00000 & 0.00000 & 0.00000 & 0.000000 \\ 5.12504 & 0.76777 & 0.01374 & 0.09170 & 0.001758 \\ 2.96703 & 2.19583 & 0.28238 & 0.45469 & 0.100073 \\ 1.67993 & 2.44890 & 0.77615 & 0.79341 & 0.301607 \\ 0.35851 & 0.81306 & 2.65204 & 1.62058 & 0.555808 \end{pmatrix}$$

$$c^g_{l,i} = \begin{pmatrix} 5.12504 & 0.76777 & 0.01374 & 0.09170 & 0.001758 \\ 2.96703 & 2.19583 & 0.28238 & 0.45469 & 0.100073 \\ 1.67993 & 2.44890 & 0.77615 & 0.79341 & 0.301607 \\ 0.35851 & 0.81306 & 2.65204 & 1.62058 & 0.555808 \\ 0.00549 & 0.01260 & 3.45402 & 1.97039 & 0.557492 \end{pmatrix}$$

$$c^h_{p,i} = (0.30000, 0.056039, 3.25612, 1.86232, 0.525523)^T$$

$$V^m_l = (2.98204, 19.2174, 31.6718, 362.412, 10000.0)^T$$

$$r^m_{l,j} = \begin{pmatrix} 26.2660 & 0.46066 & 3.075023 & 0.058947 \\ 8.80325 & 1.31750 & 1.780217 & 0.482166 \\ 2.82215 & 1.46934 & 1.007955 & 0.599713 \\ 0.12853 & 0.48784 & 0.215108 & 0.066107 \\ 0.00003 & 0.00756 & 0.003297 & 0.000016 \end{pmatrix}$$

8.4.14 Test Problem 9 : Isothermal Levenspiel Reaction

Problem Information

Reaction Mechanism

$$\mathbf{A} + \mathbf{B} \xrightarrow{\mathbf{k}} \mathbf{2B}$$

Objective:
Maximize the production of **B**

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$$

Rate Constants	
k_1	1.0 L/(mol s) (second order)
Rate Constants	
F^a_r	100 L/s
$c^a_{r,i}$	0.45 mol/L **A**, 0.55 mol/L **B**

Rate Expression

$$f_1^r = k_1 c_A c_B$$

Problem Statistics

No. of continuous variables	78
No. of linear equalities	18
No. of nonlinear equalities	27

Best Known Solution

- Objective function: 0.763002 mol/L
- Variables

$$F_{r,l}^{ad} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_l^d = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_l^g = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_{l,l'}^{gd} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F_{l,p}^{gh} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F_p^h = 100.00$$

$$c_{l,i}^d = \begin{pmatrix} 0.450000 & 0.550000 \\ 0.388501 & 0.611499 \\ 0.340633 & 0.659367 \\ 0.300790 & 0.699210 \\ 0.266667 & 0.733333 \end{pmatrix}$$

$$c_{l,i}^g = \begin{pmatrix} 0.388501 & 0.611499 \\ 0.340633 & 0.659367 \\ 0.300790 & 0.699210 \\ 0.266667 & 0.733333 \\ 0.236998 & 0.763002 \end{pmatrix}$$

$$c_{p,i}^{h} = (0.236998, 0.763002)^T$$

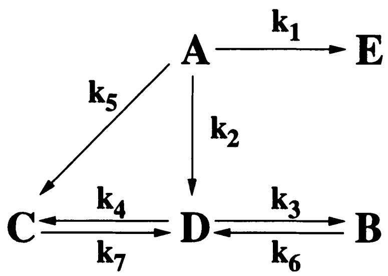
$$V_l^m = (25.8871, 21.3123, 18.9442, 17.4497, 16.4067)^T$$

$$r_{l,j}^m = (0.237568, 0.224602, 0.210315, 0.195555, 0.180830)^T$$

8.4.15 Test Problem 10 : α-Pinene Reaction

Problem Information

Reaction Mechanism



Objective:
Maximize the selectivity of **C** to **D**

$$\max \frac{c_{1,C}^h}{c_{1,D}^h}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & -1 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & -1 \\ 0 & 1 & -1 & -2 & 0 & 1 & 2 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

	Rate Constants
k_1	0.33384 min^{-1} (first order)
k_2	0.26687 min^{-1} (first order)
k_3	0.14940 min^{-1} (second order)
k_4	0.18957 L/(mol min) (second order)
k_5	0.009598 L/(mol min) (second order)
k_6	0.29425 min^{-1} (second order)
k_7	0.011932 min^{-1} (second order)
	Feed Conditions
F_r^a	100 L/min pure **A**
$c_{r,i}^a$	1.00 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**, 0 mol/L **E**

Rate Expressions

$$
\begin{aligned}
f_1^r &= k_1 c_A \\
f_2^r &= k_2 c_A \\
f_3^r &= k_3 c_D \\
f_4^r &= k_4 c_D^2 \\
f_5^r &= k_5 c_A^2 \\
f_6^r &= k_6 c_B \\
f_7^r &= k_7 c_C
\end{aligned}
$$

Problem Statistics

No. of continuous variables	78
No. of linear equalities	17
No. of linear inequalities	1
No. of nonlinear equalities	27

Best Known Solution

- Objective function: 1.546076
- Variables

$$F_{r,l}^{ad} = (89.74737, 10.25263, 0.00, 0.00, 0.00)^T$$

$$F_l^d = (89.74737, 10.25263, 10.25263, 10.25263, 10.25263)^T$$

$$F_l^g = (89.74737, 10.25263, 10.25263, 10.25263, 10.25263)^T$$

$$F_{l,l'}^{gd} = \begin{pmatrix} 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 10.25263 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 10.25263 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 10.25263 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F_{l,p}^{gh} = (89.74737, 0.00, 0.00, 0.00, 10.25263)^T$$

$$F_p^h = 100.00$$

$$c_{l,i}^d = \begin{pmatrix} 1.00000 & 0.000000 & 0.000000 & 0.000000 & 0.000000 \\ 1.00000 & 0.000000 & 0.000000 & 0.000000 & 0.000000 \\ 0.48804 & 0.029814 & 0.013609 & 0.174779 & 0.280150 \\ 0.00441 & 0.056105 & 0.139568 & 0.111465 & 0.548884 \\ 0.00004 & 0.050143 & 0.149973 & 0.098560 & 0.551315 \end{pmatrix}$$

$$c^g_{l,i} = \begin{pmatrix} 1.00000 & 0.000000 & 0.000000 & 0.000000 & 0.000000 \\ 0.48804 & 0.029814 & 0.013609 & 0.174779 & 0.280150 \\ 0.00441 & 0.056105 & 0.139568 & 0.111465 & 0.548884 \\ 0.00004 & 0.050143 & 0.149973 & 0.098560 & 0.551315 \\ 0.00000 & 0.049532 & 0.150798 & 0.097536 & 0.551335 \end{pmatrix}$$

$$c^h_{p,i} = (0.8974737, 0.005078374, 0.01546076, 0.01000000, 0.05652636)^T$$

$$V^m_l = (0.000000, 17.62920, 1871.154, 2051.577, 2059.640)^T$$

$$r^m_{l,j} = \begin{pmatrix} 0.33384 & 0.16293 & 0.001472 & 0.00001 & 0.00000 \\ 0.26687 & 0.13024 & 0.001177 & 0.00001 & 0.00000 \\ 0.00000 & 0.02611 & 0.016653 & 0.01472 & 0.01457 \\ 0.00000 & 0.00579 & 0.002355 & 0.00184 & 0.00180 \\ 0.00960 & 0.00229 & 0.000000 & 0.00000 & 0.00000 \\ 0.00000 & 0.00877 & 0.016509 & 0.01475 & 0.01457 \\ 0.00000 & 0.00016 & 0.001665 & 0.00179 & 0.00180 \end{pmatrix}^T$$

8.4.16 Test Problem 11 : Nonisothermal Van de Vusse Reaction Case II

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$

$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:
Maximize the yield of **B**

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	5.4×109 h^{-1}	15.84 kcal/mol	84 K L/mol
2	3.6×105 L/(mol h)	7.92 kcal/mol	108 K L/mol
3	1.6×1012 h^{-1}	23.76 kcal/mol	60 K L/mol
Feed Conditions			
F_r^a	100 L/s		
$c_{r,i}^a$	1.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**		

Rate Expressions

$$f_1^r = \hat{k}_1 e^{\frac{-E_1}{RT}} c_A$$
$$f_2^r = \hat{k}_2 e^{\frac{-E_2}{RT}} c_B$$
$$f_3^r = \hat{k}_3 e^{\frac{-E_3}{RT}} c_A^2$$

Additional Information

The temperatures in the reactors are bounded between 450 K and 810 K.

Problem Statistics

No. of continuous variables	115
No. of linear equalities	17
No. of nonlinear equalities	59

Best Known Solution

The best known solution is a network of the 5 CSTRs connected in series.

- Objective function: 0.8004376 mol/L
- Variables

$$F_{r,l}^{ad} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_l^d = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_l^g = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_{l,l'}^{gd} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F^{gh}_{l,p} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F^h_p = 100.00$$

$$c^d_{l,i} = \begin{pmatrix} 1.000000 & 0.000000 & 0.0000000 & 0.0000000 \\ 0.751524 & 0.217939 & 0.0142688 & 0.0081340 \\ 0.432529 & 0.480538 & 0.0397326 & 0.0236002 \\ 0.062313 & 0.769965 & 0.0765880 & 0.0455668 \\ 0.029024 & 0.793461 & 0.0844164 & 0.0465491 \end{pmatrix}$$

$$c^g_{l,i} = \begin{pmatrix} 0.751524 & 0.217939 & 0.0142688 & 0.0081340 \\ 0.432529 & 0.480538 & 0.0397326 & 0.0236002 \\ 0.062313 & 0.769965 & 0.0765880 & 0.0455668 \\ 0.029024 & 0.793461 & 0.0844164 & 0.0465491 \\ 0.014464 & 0.800438 & 0.0915585 & 0.0467697 \end{pmatrix}$$

$$c^h_{p,i} = (0.014464, 0.800438, 0.0915585, 0.0467697)^T$$

$$V^m_l = (0.0578041, 0.0175675, 0.00182321, 0.00037580, 0.000339863)^T$$

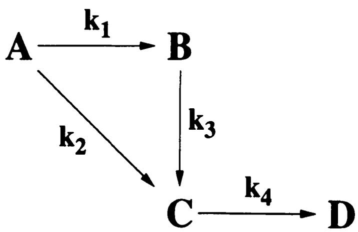
$$T^m_l = (494.276, 562.614, 810.000, 810.000, 810.000)^T$$

$$r^m_{l,j} = \begin{pmatrix} 401.72 & 24.685 & 28.143 \\ 1639.75 & 144.949 & 176.077 \\ 17896.06 & 2021.458 & 2409.663 \\ 8335.56 & 2083.146 & 522.770 \\ 4154.12 & 2101.461 & 129.837 \end{pmatrix}$$

8.4.17 Test Problem 12 : Nonisothermal Naphthalene Reaction

Problem Information

Reaction Mechanism



Objective:
Maximize the yield of **B**

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 1 & -1 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	2.0 $\times 10^{13}$ h^{-1}	38.00 kcal/mol	364 K L/mol
2	2.0 $\times 10^{13}$13 h^{-1}	38.00 kcal/mol	129 K L/mol
3	8.15 $\times 10^{17}$ h^{-1}	50.00 kcal/mol	108 K L/mol
4	2.1 $\times 10^{5}$ h^{-1}	20.00 kcal/mol	222 K L/mol
Feed Conditions			
F^a_r	100 L/h		
$c^a_{r,i}$	1.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**		

Rate Expressions

$$\begin{aligned} f^r_1 &= \hat{k}_1 e^{\frac{-E_1}{RT}} c_A \\ f^r_2 &= \hat{k}_2 e^{\frac{-E_2}{RT}} c_A \\ f^r_3 &= \hat{k}_3 e^{\frac{-E_3}{RT}} c_B \\ f^r_4 &= \hat{k}_4 e^{\frac{-E_4}{RT}} c_C \end{aligned}$$

Additional Information
The temperatures in the reactors are bounded between 900 K and 1500 K

Problem Statistics

No. of continuous variables	110
No. of linear equalities	27
No. of nonlinear equalities	49

Best Known Solution

The best known solution is a network of the 5 CSTRs connected in series.

- Objective function: 0.9993058 mol/L

- Variables

$$F_{r,l}^{ad} = (100.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$F_l^d = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_l^g = (100.00, 100.00, 100.00, 100.00, 100.00)^T$$

$$F_{l,l'}^{gd} = \begin{pmatrix} 0.00 & 100.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 100.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 100.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 100.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

$$F_{l,p}^{gh} = (0.00, 0.00, 0.00, 0.00, 100.00)^T$$

$$F_p^h = 100.00$$

$$c_{l,i}^d = \begin{pmatrix} 1.000000 & 0.00000000 & 0.000000 & 0.000000000 \\ 0.236839 & 0.00352521 & 0.759441 & 0.000194604 \\ 0.061809 & 0.00082200 & 0.937006 & 0.000362509 \\ 0.013153 & 0.00011647 & 0.986242 & 0.000488288 \\ 0.001184 & 0.00000439 & 0.998228 & 0.000583951 \end{pmatrix}$$

$$c_{l,i}^g = \begin{pmatrix} 0.236839 & 0.00352521 & 0.759441 & 0.000194604 \\ 0.061809 & 0.00082200 & 0.937006 & 0.000362509 \\ 0.013153 & 0.00011647 & 0.986242 & 0.000488288 \\ 0.001184 & 0.00000439 & 0.998228 & 0.000583951 \\ 0.000045 & 0.00000007 & 0.999306 & 0.000648867 \end{pmatrix}$$

$$c_{p,i}^h = (4.526830 \times 10^{-5}, 6.976425 \times 10^{-8}, 0.9993058, 0.0006488673)^T$$

$$V_l^m = (0.0053859, 0.0029219, 0.0010590, 0.00018950, 3.03094 \times 10^{-5})^T$$

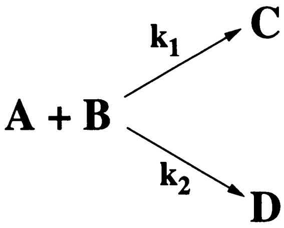
$$T_l^m = (941.126, 964.010, 1030.617, 1208.119, 1461.435)^T$$

$$r_{l,j}^m = \begin{pmatrix} 7084.837 & 7084.837 & 7019.384 & 3.613234 \\ 2995.179 & 2995.179 & 3087.696 & 5.746510 \\ 2297.241 & 2297.241 & 2363.862 & 11.87698 \\ 3158.110 & 3158.110 & 3217.256 & 50.48148 \\ 1877.826 & 1877.826 & 1892.068 & 214.1787 \end{pmatrix}$$

8.4.18 Test Problem 13 : Nonisothermal Parallel Reactions

Problem Information

Reaction Mechanism



Objective:
Maximize the yield of **C** while minimizing the volume of the reactor

$$\max 100c^h_{1,C} - \sum_{l \in L} v^m_l$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & -1 \\ -1 & -1 \\ 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	5.4 $\times 10^7$ h^{-1}	19.138 kcal/mol	10 K L/mol
2	3.6 $\times 10^5$ L/(mol h)	9.569 kcal/mol	20 K L/mol
Feed Conditions			
F^a_1	50 L/s pure **A**		
F^a_2	50 L/s pure **B**		
$c^a_{1,i}$	1.0 mol/L **A**, 0 mol/L **B**		
$c^a_{2,i}$	0 mol/L **A**, 1.0 mol/L **B**		

Rate Expressions

$$f^r_1 = \hat{k}_1 e^{\frac{-E_1}{RT}} c_A c_B^{0.3}$$
$$f^r_2 = \hat{k}_2 e^{\frac{-E_2}{RT}} c_A^{0.5} c_B^{1.8}$$

Additional Information
The temperatures in the reactors are bounded between 450 K and 800 K.

Problem Statistics

No. of continuous variables	115
No. of linear equalities	18
No. of nonlinear equalities	54

Best Known Solution

- Objective function: 43.08948
- Variables

$$F^{ad}_{r,l} = \begin{pmatrix} 50.00000 & 0.000000 & 0.000000 & 0.000000 & 0.000000 \\ 23.38640 & 13.09379 & 7.499338 & 4.505853 & 1.514625 \end{pmatrix}$$

$$F^d_l = (73.38640, 86.48018, 93.97952, 98.48538, 100.0000)^T$$

$$F^g_l = (73.38640, 86.48018, 93.97952, 98.48538, 100.0000)^T$$

$$F^{gd}_{l,l'} = \begin{pmatrix} 0.000000 & 73.38640 & 0.000000 & 0.000000 & 0.000000 \\ 0.000000 & 0.000000 & 86.48018 & 0.000000 & 0.000000 \\ 0.000000 & 0.000000 & 0.000000 & 93.97952 & 0.000000 \\ 0.000000 & 0.000000 & 0.000000 & 0.000000 & 98.48538 \\ 0.000000 & 0.000000 & 0.000000 & 0.000000 & 0.000000 \end{pmatrix}$$

$$F^{gh}_{l,p} = (0.000000, 0.000000, 0.000000, 0.000000, 100.0000)^T$$

$$F^h_p = 100.00$$

$$c^d_{l,i} = \begin{pmatrix} 0.681325 & 0.318675 & 0.000000 & 0.00000000 \\ 0.318264 & 0.161930 & 0.258306 & 0.00159743 \\ 0.158249 & 0.094187 & 0.370593 & 0.00318901 \\ 0.079973 & 0.064593 & 0.422854 & 0.00486290 \\ 0.040627 & 0.040627 & 0.452554 & 0.00681863 \end{pmatrix}$$

$$c^g_{l,i} = \begin{pmatrix} 0.3750494 & 0.0123990 & 0.304393 & 0.00188245 \\ 0.1719714 & 0.0156372 & 0.402730 & 0.00346555 \\ 0.0838071 & 0.0197455 & 0.443128 & 0.00509605 \\ 0.0412520 & 0.0258728 & 0.459514 & 0.00692349 \\ 0.0212265 & 0.0212265 & 0.470887 & 0.00788614 \end{pmatrix}$$

$$c^h_{p,i} = (0.0212265, 0.0212265, 0.470887, 0.00788614)^T$$

$$V_l^m = (0.697019, 0.792777, 0.827854, 0.821420, 0.860194)^T$$

$$T_l^m = (800.0000, 800.0000, 800.0000, 800.0000, 800.0000)^T$$

$$r_{l,j}^m = \begin{pmatrix} 32.04841 & 0.1981960 \\ 15.75456 & 0.2037839 \\ 8.234240 & 0.2164909 \\ 4.395426 & 0.2470580 \\ 2.131292 & 0.1241009 \end{pmatrix}$$

8.4.19 Test Problem 14 : Sulfur Dioxide Oxidation

Problem Information

Reaction Mechanism

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$$

Species 1 is SO_2, species 2 is O_2, species 3 is SO_3, and species 4 is N_2.

Objective:
Maximize the yield of SO_3

$$\max c_{1,3}^h$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 1 \\ -0.5 & 0.5 \\ 1 & -1 \\ 0 & 0 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	6.284×10^{11} mol/(hr kgcat)	15.500 kcal/mol	96.5 K kg/mol
2	2.732×10^{16} mol/(hr kgcat)	26.7995 kcal/mol	96.5 K kg/mol
Feed Conditions			
F_r^a	7731 kg/h		
$c_{r,i}^a$	2.5 mol/kg $\mathbf{SO_2}$, 3.46 mol/kg $\mathbf{O_2}$, 0 mol/kg $\mathbf{SO_3}$, 26.05 mol/kg $\mathbf{N_2}$		

Rate Expressions

The rates are given in terms of kg mol SO_3 per kg catalyst.

$$r_1 = \hat{k}_1 e^{\frac{-E_1}{T}} \cdot \frac{(c^g_{l,1})^{0.5} c^g_{l,2}}{\left(\sum_{i \in I} c^g_{l,i}\right)^{1.5}}$$

$$r_2 = \hat{k}_2 e^{\frac{-E_2}{T}} \frac{(c^g_{l,2})^{0.5} c^g_{l,3}}{(c^g_{l,1})^{0.5} \left(\sum_{i \in I} c^g_{l,i}\right)}$$

Additional Information

The temperatures in the reactors are bounded between 300 K and 1200 K.

Problem Statistics

No. of continuous variables	110
No. of linear equalities	17
No. of nonlinear equalities	54

Best Known Solution

- Objective function: 2.498196 mol/kg
- Variables

$$F^{ad}_{r,l} = (7731.000, 0.0000, 0.0000, 0.0000, 0.0000)^T$$

$$F^d_l = (7731.000, 7731.000, 7731.000, 7731.000, 7731.000)^T$$

$$F^g_l = (7731.000, 7731.000, 7731.000, 7731.000, 7731.000)^T$$

$$F^{gd}_{l,l'} = \begin{pmatrix} 0.0000 & 7731.000 & 0.0000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 7731.000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 7731.000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 7731.000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \end{pmatrix}$$

$$F^{gh}_{l,p} = (0.0000, 0.0000, 0.0000, 0.0000, 7731.000)^T$$

$$F^h_p = 7731.000$$

$$c_{l,i}^{d} = \begin{pmatrix} 2.500000 & 3.460000 & 0.000000 & 26.05000 \\ 0.150151 & 2.285075 & 2.349849 & 26.05000 \\ 0.024384 & 2.222192 & 2.475616 & 26.05000 \\ 0.007785 & 2.213892 & 2.492215 & 26.05000 \\ 0.003335 & 2.211668 & 2.496665 & 26.05000 \end{pmatrix}$$

$$c_{l,i}^{g} = \begin{pmatrix} 0.150151 & 2.285075 & 2.349849 & 26.05000 \\ 0.024384 & 2.222192 & 2.475616 & 26.05000 \\ 0.007785 & 2.213892 & 2.492215 & 26.05000 \\ 0.003335 & 2.211668 & 2.496665 & 26.05000 \\ 0.001804 & 2.210902 & 2.498196 & 26.05000 \end{pmatrix}$$

$$c_{p,i}^{h} = (0.001804, 2.210902, 2.498196, 26.05000)^T$$

$$V_l^m = (16783.9, 30239.2, 34328.8, 45139.1, 49155.4)^T$$

$$T_l^m = (739.297, 658.340, 617.072, 589.701, 571.340)^T$$

$$r_{l,j}^{m} = \begin{pmatrix} 2.549641 & 1.467253 \\ 0.07608014 & 0.04392624 \\ 0.008873133 & 0.005134993 \\ 0.001808408 & 0.001046388 \\ 0.0005712887 & 0.0003304261 \end{pmatrix}$$

8.5 Parameter Estimation problems

8.5.1 Introduction

The estimation of parameters in semi-empirical models is a common problem in the science and engineering fields. One statistical approach which has been widely studied from a computational point of view, is the maximum likelihood method. The method seeks to maximize the likelihood of the set of observed values occurring given a set of parameters for the model and the statistical distribution of the observations. In general, the error, i.e., the difference between the observed values and the unknown true values, is assumed to be normally distributed with zero mean and known diagonal covariance matrix. This assumption results in an optimization problem which seeks to minimize the weighted squared error between the observed data and the unknown true values obtained from the given model. A full treatment of the statistical aspects of the approach can be found in the book by Bard (1974).

Computational difficulties arise when the models used are nonlinear in nature because the optimization problem is then nonconvex. The resulting formulation may contain multiple minima in the area of interest and therefore result in inaccurate parameter estimates. The first global optimization approach for parameter estimation and data reconciliation problems was proposed recently by Esposito and Floudas (1998a,b). For detailed exposition to the theoretical and algorithmic aspects, the reader is directed to the book by Floudas (2000) and the articles by Esposito and Floudas (1998a,b).

First a general formulation of the problem will be presented. Second, a group of test problems will be given. The first three represent rather simple single equation models with only a few known local minima. The next three are also only single equation models, but add an extra layer of difficulty due to a larger number of known local minima. The last two problems are real examples of commonly encountered problems: a kinetic estimation from CSTR data, and a nonideal vapor-liquid equilibrium model. These two problems involve multiple equation models and a high degree of nonlinearity.

8.5.2 General formulation

A general formulation is presented below. Most of the examples in this section follow this general formulation. Exceptions to this will be noted.

Objective Function

$$\min_{\hat{\boldsymbol{z}}_\mu, \boldsymbol{\theta}} \sum_{\mu=1}^{r} \sum_{i=1}^{m} \frac{(\hat{z}_{\mu,i} - z_{\mu,i})^2}{\sigma_i^2}$$

Constraints

$$\boldsymbol{f}(\hat{\boldsymbol{z}}_\mu, \boldsymbol{\theta}) = \boldsymbol{0} \qquad \mu = 1, \ldots, m$$

Variable Bounds

$$\begin{aligned} \boldsymbol{z}_\mu - 3\boldsymbol{\sigma} \leq \hat{\boldsymbol{z}}_\mu \leq \boldsymbol{z}_\mu + 3\boldsymbol{\sigma} \\ \boldsymbol{\theta}^L \leq \boldsymbol{\theta} \leq \boldsymbol{\theta}^U \end{aligned}$$

Variable definitions

$\boldsymbol{f}$ is a system of l algebraic functions which represent the nonlinear model, $\boldsymbol{\theta}$ is a vector of p parameters, and $\hat{\boldsymbol{z}}_\mu$ is a vector of i fitted data variables at the μ^{th} data point. $\boldsymbol{z}_\mu$ is a vector of i experimentally observed values at the μ^{th} data point, and $\boldsymbol{\sigma}$ is a vector of i values which represent the experimental standard deviation of these observations.

8.5.3 Test Problem 1 : Linear Model

This example appears in Tjoa and Biegler (1992). The model represents the fitting of a straight line to a set of data, but due to the optimization domain, the model is in fact nonlinear. The reported global solution is from the work of Esposito and Floudas (1998a).

Formulation

Objective Function

$$\min_{\hat{z}_\mu, \boldsymbol{\theta}} \sum_{\mu=1}^{10} \sum_{i=1}^{2} \frac{(\hat{z}_{\mu,i} - z_{\mu,i})^2}{\sigma_i^2}$$

Constraints

$$z_{\mu,2} = \theta_1 + \theta_2 z_{\mu,1} \qquad \mu = 1, \dots, 10$$

Variable Bounds

$$\boldsymbol{z}_\mu - 0.5 \leq \hat{\boldsymbol{z}}_\mu \leq \boldsymbol{z}_\mu + 0.5$$
$$(0, -2) \leq \boldsymbol{\theta} \leq (10, 2)$$

Data

μ	1	2	3	4	5	6	7	8	9	10
$z_{\mu,1}$	0.0	0.9	1.8	2.6	3.3	4.4	5.2	6.1	6.5	7.4
$z_{\mu,2}$	5.9	5.4	4.4	4.6	3.5	3.7	2.8	2.8	2.4	1.5

$$\sigma = (1, 1)$$

Problem Statistics

No. of variables	12
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	10
No. of nonconvex inequalities	-

Global Solution

- Objective function: 0.61857
- Parameters
  $\boldsymbol{\theta} = (5.7084, -0.54556)^T$
- Fitted Data Variables

μ	1	2	3	4	5	6	7	8	9	10
$\hat{z}_{\mu,1}$	-0.049	0.86	1.97	2.50	3.50	4.27	5.26	5.96	6.43	7.50
$\hat{z}_{\mu,2}$	5.81	5.32	4.71	4.42	3.87	3.46	2.91	2.53	2.27	1.69

8.5.4 Test Problem 2 : Polynomial Model

This example also appears in Tjoa and Biegler (1992). The model represents the fitting of a third order polynomial to a set of data points. The reported global solution is from the work of Esposito and Floudas (1998a).

Formulation

Model

$$z_2 = \theta_1 + \theta_2 z_1 + \theta_3 z_1^2 + \theta_4 z_1^3$$

Variable Bounds

$$\boldsymbol{z}_\mu - 0.5 \leq \hat{\boldsymbol{z}}_\mu \leq \boldsymbol{z}_\mu + 0.5$$
$$(0, -2, -2, -2) \leq \boldsymbol{\theta} \leq (10, 2, 2, 2)$$

Data

The data is the same as in the previous example

Problem Statistics

No. of variables	14
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	10
No. of nonconvex inequalities	-
No. of known solutions	2

Global Solution

- Objective function: 0.485152
- Parameters
  $\boldsymbol{\theta} = (6.0153, -0.9998, 0.15247, -0.01324)^T$
- Fitted Data Variables

μ	1	2	3	4	5	6	7	8	9	10
$\hat{z}_{\mu,1}$	0.057	0.82	1.90	2.45	3.44	4.31	5.31	6.00	6.46	7.45
$\hat{z}_{\mu,2}$	5.95	5.29	4.58	4.29	3.84	3.48	3.02	2.64	2.35	1.55

8.5.5 Test Problem 3 : Non-linear Model

This example appears in Tjoa and Biegler (1992) and Rod and Hancil (1980). The reported global solution is from the work of Esposito and Floudas (1998a).

Formulation

Model

$$z_2 = \theta_1 + \frac{1}{z_1 - \theta_2}$$

Variable Bounds

$$\begin{aligned} \boldsymbol{z}_\mu - 0.05 \le \hat{\boldsymbol{z}}_\mu \le \boldsymbol{z}_\mu + 0.05 \\ (1,1) \le \boldsymbol{\theta} \le (10,10) \end{aligned}$$

Data

μ	1	2	3	4	5	6	7	8	9
$z_{\mu,1}$	0.113	0.126	0.172	0.155	0.219	0.245	0.274	0.264	0.312
$z_{\mu,2}$	1.851	1.854	1.849	1.815	1.828	1.847	1.804	1.832	1.838
μ	10	11	12	13	14	15	16	17	18
$z_{\mu,1}$	0.324	0.333	0.399	0.417	0.419	0.439	0.475	0.506	0.538
$z_{\mu,2}$	1.817	1.820	1.845	1.829	1.832	1.820	1.820	1.799	1.838
μ	19	20	21	22	23	24	25		
$z_{\mu,1}$	0.538	0.591	0.578	0.626	0.659	0.668	0.687		
$z_{\mu,2}$	1.835	1.811	1.794	1.825	1.801	1.810	1.802		

$$\sigma = (1,1)$$

Problem Statistics

No. of variables	52
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	25
No. of nonconvex inequalities	-

Global Solution

- Objective function: 4.64972×10^{-3}
- Parameters
  $\boldsymbol{\theta} = (2.06533, 4.51079)^T$
- Fitted Data Variables

μ	1	2	3	4	5	6	7	8	9
$\hat{z}_{\mu,1}$	0.112	0.125	0.171	0.156	0.219	0.244	0.276	0.264	0.312
$\hat{z}_{\mu,2}$	1.841	1.840	1.838	1.839	1.836	1.834	1.832	1.833	1.830

μ	10	11	12	13	14	15	16	17	18
$\hat{z}_{\mu,1}$	0.325	0.334	0.398	0.417	0.418	0.439	0.475	0.507	0.537
$\hat{z}_{\mu,2}$	1.830	1.829	1.825	1.824	1.824	1.823	1.821	1.819	1.816

μ	19	20	21	22	23	24	25
$\hat{z}_{\mu,1}$	0.537	0.591	0.579	0.625	0.660	0.668	0.687
$\hat{z}_{\mu,2}$	1.817	1.813	1.814	1.811	1.809	1.808	1.807

8.5.6 Test Problem 4: Respiratory Mechanical Model

This example appears in Csendes and Ratz (1995). The model is complex in nature, therefore the real and imaginary parts must be treated separately when applying a standard NLP algorithm. The reported global solution is from the work of Esposito and Floudas (1998a).

Formulation

Model

$$
\begin{aligned}
z_\mu &= \left(\theta_1 + \frac{\theta_2}{\omega_\mu^{\theta_3}}\right) + \jmath\left(\omega_\mu \theta_4 - \frac{\theta_5}{\omega_\mu^{\theta_3}}\right) \\
\omega_\mu &= \frac{\mu\pi}{20} \qquad \jmath = \sqrt{-1}
\end{aligned}
$$

Variable Bounds

$$
\begin{aligned}
z_\mu - (1+\jmath) \le \hat{z}_\mu \le z_\mu + (1+\jmath) \\
(0,0,1.1,0,0) \le \boldsymbol{\theta} \le (1.0,1.0,1.3,1.0,1.0)
\end{aligned}
$$

Data

μ	1	2	3	4	5	6
z_μ	5 - 5$\jmath$	3 - 2$\jmath$	2 - $\jmath$	1.5 - 0.5$\jmath$	1.2 - 0.2$\jmath$	1.1 - 0.1$\jmath$

$$\sigma = (1+\jmath)$$

Problem Statistics

No. of variables	17
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	12
No. of nonconvex inequalities	-

Global Solution

- Objective function: 0.212460

- Parameters
  $\boldsymbol{\theta} = (0.60630, 0.55676, 1.1318, 0.75020, 0.62190)^T$

- Fitted Data Variables

μ	1	2	3
$\hat{z}_\mu$	5.13 - 4.93$\jmath$	2.67 - 2.07$\jmath$	1.91 - 1.10$\jmath$

μ	4	5	6
$\hat{z}_\mu$	1.54 - 0.58$\jmath$	1.34 - 0.23$\jmath$	1.20 + 0.04$\jmath$

8.5.7 Test Problem 5: Kowalik Problem

This example appears in Moore et al. (1992). In the model only z_1 is assumed to contain error, z_2 is therefore treated as a constant and does not appear in the objective function. The reported global solution is from the work of Esposito and Floudas (1998a).

Formulation

Model

$$z_1 = \theta_1 \frac{z_2^2 + z_2\theta_2}{z_2^2 + z_2\theta_3 + \theta_4}$$

Variable Bounds

$$\begin{array}{c} z_{\mu,1} - 0.02 \le \hat{z}_{\mu,1} \le z_{\mu,1} + 0.02 \\ -0.2892 \le \boldsymbol{\theta} \le 0.2893 \end{array}$$

Data

μ	1	2	3	4	5	6
$z_{\mu,1}$	0.1957	0.1947	0.1735	0.1600	0.0844	0.0627
$1/z_{\mu,2}$	0.25	0.5	1	2	4	6

μ	7	8	9	10	11
$z_{\mu,1}$	0.0456	0.0342	0.0323	0.0235	0.0246
$1/z_{\mu,2}$	8	10	12	14	16

$$\sigma = 1$$

Problem Statistics

No. of variables	15
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	11
No. of nonconvex inequalities	-
No. of known solutions	7

Global Solution

- Objective function: 3.075×10^{-4}
- Parameters
  $\boldsymbol{\theta} = (0.19283, 0.19088, 0.12314, 0.13578)^T$
- Fitted Data Variables

μ	1	2	3	4	5	6
$\hat{z}_{\mu,1}$	0.1944	0.1928	0.1824	0.1489	0.0928	0.0624

μ	7	8	9	10	11
$\hat{z}_{\mu,1}$	0.0456	0.0355	0.0288	0.0241	0.0207

8.5.8 Test Problem 6: Pharmacokinetic Model

The model represents the fitting of kinetic data to a sum of three exponential terms. In the model only z_2 is assumed to contain error, z_1 is therefore treated as a constant and does not appear in the objective function. This example and the reported global solution is from the work of Esposito and Floudas (1998b).

Formulation

Model

$$z_2 = \sum_{j=1}^{3} \theta_{1,j} \exp\left[-\theta_{2,j}\, z_1\right]$$

Variable Bounds

$$0 \leq \hat{z}_{\mu,2} \leq 1$$
$$(-10, 0) \leq \boldsymbol{\theta}_j \leq (10, 0.5)$$

Data

μ	1	2	3	4	5	6	7	8
$z_{\mu,1}$	4	8	12	24	48	72	94	118
$z_{\mu,2}$	0.1622	0.6791	0.6790	0.3875	0.1822	0.1249	0.0857	0.0616

$$\sigma_2 = z_2$$

Problem Statistics

No. of variables	14
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	8
No. of nonconvex inequalities	-
No. of known solutions	4

Global Solution

- Objective function: 1.14×10^{-3}
- Parameters
  $\boldsymbol{\theta_1} = (0.3554, 2.007, -4.575)^T$
  $\boldsymbol{\theta_2} = (0.0149, 0.1102, 0.2847)^T$
- Fitted Data Variables

μ	1	2	3	4	5	6	7	8
$\hat{z}_{\mu,2}$	0.1622	0.6776	0.6817	0.3860	0.1838	0.1222	0.0875	0.0612

8.5.9 Test Problem 7: Steady-State CSTR

This model represents a steady state adiabatic CSTR with an irreversible first order reaction ($A \xrightarrow{k_1} B$). This model is presented by Kim et al. (1990). The reported global solution is from the work of Esposito and Floudas (1998a).

Formulation

Model

Mass Balances

$$\begin{aligned} \tfrac{1}{\tau}(z_1 - z_2) - k_1 z_2 &= 0 \\ -\tfrac{1}{\tau} z_3 + k_1 z_2 &= 0 \end{aligned}$$

Energy Balance

$$\frac{1}{\tau}(z_4 - z_5) + \frac{-\Delta H_r}{\rho C_p}(k_1 z_2) = 0$$

Kinetic Expression

$$k_1 = \theta_1 \exp\left[-\theta_2\left(\frac{T_r}{z_5} - 1\right)\right]$$

Variable Bounds

$$\begin{aligned} \boldsymbol{z}_\mu - 3\boldsymbol{\sigma} \leq \hat{\boldsymbol{z}}_\mu \leq \boldsymbol{z}_\mu + 3\boldsymbol{\sigma} \\ (0.0001, 5) \leq \boldsymbol{\theta} \leq (0.1, 15) \end{aligned}$$

Variable Definitions

z_1 and z_2 are the inlet and outlet concentrations respectively of component A, z_3 is the outlet concentration of component B, and z_4 and z_5 are the inlet and outlet temperatures (K) respectively. T_r is a reference temperature (800K), H_r is the heat of reaction (-4180 J/mol), τ is the residence time of the reactor (100s), ρ is the density of the reaction mixture (1.0 g/l), and C_p is the heat capacity of the reaction mixture (4.18 J/g K). The parameters θ_1 and θ_2 represent transformations of the Arrhenius parameters, with $\theta_1 = c_1 \exp \frac{-Q_1}{RT_r}$ and $\theta_2 = \frac{Q_1}{RT_r}$.

Data

μ	$z_{\mu,1}$	$z_{\mu,2}$	$z_{\mu,3}$	$z_{\mu,4}$	$z_{\mu,5}$
1	0.9871	0.8906	0.1157	547.47	663.48
2	1.0003	0.8350	0.1380	531.77	676.04
3	1.0039	0.8255	0.1850	512.21	684.81
4	0.9760	0.8020	0.2005	490.59	695.47
5	1.0129	0.7520	0.2420	464.67	703.69
6	1.0083	0.7193	0.2739	438.47	714.90
7	1.0075	0.6861	0.3215	408.04	726.09
8	0.9994	0.6388	0.3741	375.56	735.44
9	1.0007	0.5970	0.3926	340.26	745.70
10	0.9973	0.5580	0.4703	306.55	753.94
$\sigma = (0.01, 0.01, 0.01, 1.0, 1.0)$					

Problem Statistics

No. of variables	52
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	40
No. of nonconvex inequalities	-

Global Solution

- Objective function: 29.0473
- Parameters
  $\boldsymbol{\theta} = (0.0168, 12.4332)^T$
- Fitted Data Variables

μ	$\hat{z}_{\mu,1}$	$\hat{z}_{\mu,2}$	$\hat{z}_{\mu,3}$	$\hat{z}_{\mu,4}$	$\hat{z}_{\mu,5}$
1	0.9985	0.8826	0.1159	547.84	663.78
2	0.9878	0.8437	0.1441	531.49	675.63
3	1.0011	0.8282	0.1729	512.06	684.95
4	0.9920	0.7874	0.2046	490.84	695.44
5	1.0058	0.7660	0.2398	464.80	704.62
6	1.0005	0.7242	0.2763	438.34	714.62
7	0.9995	0.6822	0.3173	407.66	724.94
8	0.9997	0.6377	0.3600	375.35	735.32
9	1.0013	0.5962	0.4052	340.39	745.55
10	1.0071	0.5587	0.4484	306.56	754.96

8.5.10 Test Problem 8: Vapor-Liquid Equilibrium Model

A two parameter Van Laar equation is used to model binary vapor-liquid equilibrium data which consists of four measured qualtities (Pressure, Temperature, liquid and vapor mole fractions). The data is for the system consisting of methanol (component 1) and 1,2-dichloroethane (component 2). This model was studied by Kim et al. (1990) and Esposito and Floudas (1998a). The reported global solution is from the work of Esposito and Floudas (1998a).

Formulation

Model

Equilibrium Expressions

$$\begin{aligned} \gamma_1 z_1 p_1^o(T) \; - \; z_2 z_4 &= 0 \\ \gamma_2 (1 \; - \; z_1) p_2^o(T) \; - \; (1 \; - \; z_2) z_4 &= 0 \end{aligned}$$

Antoine Equation

$$p_i^o(T) \;=\; \exp\left[C_{i,1} \;-\; \frac{C_{i,2}}{T_r z_3 \;-\; C_{i,3}}\right] \qquad i = 1, 2$$

Two Parameter Van Laar Equation

$$\begin{aligned} \ln \gamma_1 &= \tfrac{\theta_1}{z_3}\left(1 \;+\; \tfrac{\theta_1}{\theta_2}\tfrac{z_1}{1 - z_1}\right)^{-2} \\ \ln \gamma_2 &= \tfrac{\theta_2}{z_3}\left(1 \;+\; \tfrac{\theta_2}{\theta_1}\tfrac{1 - z_1}{z_1}\right)^{-2} \end{aligned}$$

Variable Bounds

$$\begin{gathered} \boldsymbol{z}_\mu - 3\boldsymbol{\sigma} \;\le\; \hat{\boldsymbol{z}}_\mu \;\le\; \boldsymbol{z}_\mu + 3\boldsymbol{\sigma} \\ 1 \le \boldsymbol{\theta} \le 2 \end{gathered}$$

Variable Definitions

z_1 and z_2 are the liquid and vapor mole fractions respectively of component 1 (methanol), z_3 is the scaled system temperature, (scaled by T_r = 323.15 K), and z_4 is the system pressure (mmHg). The parameters θ_1 and θ_2 are scaled Van Laar coefficients, with $\theta_1 = \frac{A}{RT_r}$ and $\theta_2 = \frac{B}{RT_r}$. $p_i^o(T)$ is the vapor pressure of the pure component i, described by the Antoine Equation with coefficients, $C_{i,j}$. γ_i is the activity coefficient of component i.

Data

Antoine Coefficients

i	$C_{i,1}$	$C_{i,2}$	$C_{i,3}$
1	18.5875	3626.55	34.29
2	16.1764	2927.17	50.22

Observations

μ	$z_{\mu,1}$	$z_{\mu,2}$	$z_{\mu,3}$	$z_{\mu,4}$
1	0.30	0.591	1.00	483.80
2	0.40	0.602	1.00	493.20
3	0.50	0.612	1.00	499.90
4	0.70	0.657	1.00	501.40
5	0.90	0.814	1.00	469.70

$$\boldsymbol{\sigma} = (0.005, 0.015, 3.09 \times 10^{-4}, 0.75)$$

Problem Statistics

No. of variables	42
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	30
No. of nonconvex inequalities	-

Global Solution

- Objective function: 3.32185
- Parameters
  $\boldsymbol{\theta} = (1.9177, 1.6082)^T$
- Fitted Data Variables

μ	$\hat{z}_{\mu,1}$	$\hat{z}_{\mu,2}$	$\hat{z}_{\mu,3}$	$\hat{z}_{\mu,4}$
1	0.299	0.596	1.00	483.99
2	0.400	0.612	1.00	493.28
3	0.500	0.624	1.00	499.67
4	0.699	0.667	1.00	501.29
5	0.901	0.810	1.00	469.71

8.6 Phase and Chemical Equilibrium Problems - Equations of State

8.6.1 Introduction

The phase and chemical equilibrium problem is extremely important for predicting fluid phase behavior for most separation process applications. Process simulators must be able to reliably and efficiently predict the correct number and type of phases that exist at equilibrium and the distribution of components within those phases. The Gibbs free energy is the thermodynamic function most often used for equilibrium calculations because it can be applied at conditions of constant temperature and pressure. A global minimum of the Gibbs free energy corresponds to the true equilibrium solution. For many systems, the Gibbs free energy surface is nonconvex, therefore local optimization methods can provide no guarantees that the correct equilibrium solution has been located.

Despite the importance of the phase and chemical equilibrium problem, there has been relatively little work published on methods for solving the problem using equations of state. The use of equations of state results in more complicated expressions for thermodynamic quantities compared to activity coefficient equations, see Chapter 6. Most of the methods using equations of state that have appeared in the literature are confined to verifying the stability of a solution by use of the tangent plane stability criterion. Michelsen (1982) presented a local solution method that uses multiple, intelligently chosen initial guesses. Eubank et al. (1992) developed an "area" method. This method can be reliable, but provides no mathematical guarantee that the global minimum solution is found. Sun and Seider (1995) applied a homotopy-continuation method, and Hua et al. (1998) presented an interval Newton/generalized bisection method for finding all stationary points.

In this section, the phase and chemical equilibrium problem using equations of state is presented. Equations of state have a number of advantages over activity coefficient equations. First is that they are applicable over a wide range of pressures, while activity coefficient equations can be used only at low pressure. Second is that many equations of state can be used to represent the behavior of both liquid and vapor states.

When formulated using equations of state, the Gibbs free energy and tangent plane distance problems do not contain special structures and therefore they fall into the general class of twice-continuously differentiable nonlinear programming problems.

8.6.2 General formulation - Tangent Plane Distance Minimization

For a discussion of the general formulation of the tangent plane distance minimization problem, refer to Chapter 6.

Objective function

The objective is to minimize the distance between the Gibbs energy surface for an incipient phase and the tangent plane to the Gibbs energy surface constructed at the feed point $(\boldsymbol{x}^F, z^F)$. If a negative solution exists, then the feed composition corresponds to an unstable solution.

$$\min_{\boldsymbol{x},z} \sum_{i\in C} x_i \ln x_i + \sum_{i\in C} x_i \ln \hat{\phi}_i(x_i, z) - \sum_{i\in C} x_i \ln x_i^F \hat{\phi}_i^F$$

Constraints

Equation of State

$$E(\boldsymbol{x}, z) = 0$$

Mole balance

$$\sum_{i\in C} x_i = 1$$

Variable bounds

$$\begin{aligned} 0 \leq\ & x_i \leq 1 \quad \forall\, i \in C \\ 0 \leq\ & z \end{aligned}$$

Variable definition

- x_i - the mole fraction of component i in the incipient phase.
- z - the compressibility of the incipient phase.
- $\hat{\phi}_i$ - the fugacity coefficient of component i in the incipient phase.

8.6.3 Van der Waals Equation

One of the earliest and most famous equations of state developed for nonideal systems is that of van der Waals (1873). Despite its relative simplicity, the van der Waals equation is remarkably accurate for many systems. The equation of state in terms of the compressibility factor, and the fugacity coefficient term derived from it, are given below.

$$\begin{aligned}
\sum_{i \in C} x_i \ln \hat{\phi}_i(x_i, z) &= \frac{B}{z - B} - \ln(z - B) - \frac{2A}{z} \\
E(\boldsymbol{x}, z) &= z^3 - (B+1)z^2 + Az - AB
\end{aligned}$$

where,

$$\begin{aligned}
A &= \sum_{i \in C} \sum_{j \in C} \alpha_{ij} x_i x_j \\
B &= \sum_{i \in C} b_i x_i
\end{aligned}$$

8.6.4 Test Problem 1

Green et al. (1993) used this ternary system to demonstrate the failure of Newton's method to converge to the true equilibrium solution. For the feed composition given in this example, the van der Waals equation predicts three local extrema. The global minimum is negative, therefore the feed is an unstable solution.

Explicit Formulation

$$\begin{aligned}
\min \quad & x_1 \ln x_1 + x_2 \ln x_2 \\
& + \tfrac{B}{z-B} - \ln(z - B) - \tfrac{2A}{z} \\
& - x_1 \ln x_1^F \hat{\phi}_1^F - x_2 \ln x_2^F \hat{\phi}_2^F \\
\text{subject to} \quad & z^3 - (B+1)z^2 + Az - AB = 0 \\
& A - \alpha_{11} x_1^2 - 2\alpha_{12} x_1 x_2 - \alpha_{22} x_2^2 = 0 \\
& B - b_1 x_1 - b_2 x_2 = 0 \\
& x_1 + x_2 = 1 \\
& x_1, x_2, z \geq 0
\end{aligned}$$

Data

$$
\begin{aligned}
P &= 80 \text{ atm} \\
T &= 400 \text{ K} \\
R &= 82.06 \text{ cm}^3(\text{atm})\text{mol}^{-1}\text{K}^{-1} \\
z^F &= 0.55716 \\
\boldsymbol{x}^F &= (0.83, 0.085, 0.085)^T \\
\boldsymbol{b} &= (0.14998, 0.14998, 0.14998)^T \\
\ln \boldsymbol{\phi}_i^F &= (-0.244654, -1.33572, -0.457869)^T \\
\boldsymbol{\alpha} &= \begin{pmatrix} 0.37943 & 0.75885 & 0.48991 \\ 0.75885 & 0.88360 & 0.23612 \\ 0.48991 & 0.23612 & 0.63263 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	1
No. of nonconvex inequalities	-
No. of known solutions	3

Global Solution

- Objective function: -0.00988
- Continuous variables

$$
\begin{aligned}
z &= 0.26249 \\
\boldsymbol{x} &= (0.6967, 0.2090, 0.0943)^T
\end{aligned}
$$

8.6.5 Test Problem 2

This is the same ternary system as in Example 1. In this case the feed composition given is a stable solution.

Data

$$
\begin{aligned}
z^F &= 0.331438 \\
\boldsymbol{x}^F &= (0.69, 0.155, 0.155)^T \\
\ln \boldsymbol{\phi}_i^F &= (-0.214553, -1.67364, -0.319125)^T
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	1
No. of nonconvex inequalities	-
No. of known solutions	3

Global Solution

- Objective function: 0.0
- Continuous variables

$$\begin{aligned} z &= 0.284913 \\ \boldsymbol{x} &= (0.69, 0.155, 0.155)^T \end{aligned}$$

8.6.6 SRK Equation

The Redlick-Kwong equation has been used extensively since its introduction. It has a form similar to that of the van der Waals equation but the results are often a significant improvement. Soave (1972) proposed a modification of the Redlich-Kwong equation. The modified equation of state (SRK) is given below in terms of the compressibility factor.

$$\begin{aligned} \sum_{i \in C} x_i \ln \hat{\phi}_i(x_i, z) &= z - 1 - \ln(z - B) - \frac{A}{B} \ln\left(1 + \frac{B}{z}\right) \\ E(\boldsymbol{x}, z) &= z^3 - z^2 + (A - B^2 - B)z - AB \end{aligned}$$

where,

$$\begin{aligned} A &= \sum_{i \in C} \sum_{j \in C} \alpha_{ij} x_i x_j \\ B &= \sum_{i \in C} b_i x_i \end{aligned}$$

8.6.7 Test Problem 3

The binary system of hydrogen sulfide and methane has appeared frequently in the literature of phase equilibria. Michelsen (1982) has demonstrated that for certain feed composition, like the one given in this example, this problem can be difficult to solve because it contains multiple local minima.

Data

$$
\begin{aligned}
P &= 40.53 \text{ bar} \\
T &= 190 \text{ K} \\
R &= 83.14 \text{ cm}^3(\text{bar})\text{mol}^{-1}\text{K}^{-1} \\
z^F &= 0.531868 \\
\boldsymbol{x}^F &= (0.0187, 0.9813)^T \\
\ln \boldsymbol{\phi}_i^F &= (-1.0672, -0.3480)^T \\
\boldsymbol{b} &= (0.0771517, 0.0765784)^T \\
\boldsymbol{\alpha} &= \begin{pmatrix} 1.04633 & 0.579822 \\ 0.579822 & 0.379615 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	3
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	1
No. of nonconvex inequalities	-
No. of known solutions	5

Global Solution

- Objective function: -0.004
- Continuous variables

$$
\begin{aligned}
z &= 0.16436 \\
\boldsymbol{x} &= (0.0767, 0.9233)^T
\end{aligned}
$$

8.6.8 Test Problem 4

The binary system methane - propane was shown by Hua et al. (1998) to contain three stationary points for the feed condition given below.

Data

$$
\begin{aligned}
P &= 100 \text{ bar} \\
T &= 277.6 \text{ K} \\
R &= 83.14 \text{ cm}^3(\text{bar})\text{mol}^{-1}\text{K}^{-1} \\
z^F &= 0.439853 \\
\boldsymbol{x}^F &= (0.68, 0.32)^T \\
\ln \phi_i^F &= (0.0234027, -2.13584)^T \\
\boldsymbol{b} &= (0.12932, 0.271567)^T \\
\boldsymbol{\alpha} &= \begin{pmatrix} 0.352565 & 0.844083 \\ 0.844083 & 2.14335 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	3
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	1
No. of nonconvex inequalities	-
No. of known solutions	3

Global Solution

- Objective function: -0.00033
- Continuous variables

$$
\begin{aligned}
z &= 0.54594 \\
\boldsymbol{x} &= (0.7721, 0.2279)^T
\end{aligned}
$$

8.6.9 Peng-Robinson Equation

The Peng-Robinson cubic equation of state was developed in order to predict the behavior of the liquid phase more accurately than previous equations like van der Waals and SRK. The Peng-Robinson equation is slightly more complicated than its predecessors, due to the increased dependence on the mixing terms A and B. Both the equation of state and the fugacity coefficient expression derived from it are given below.

$$
\begin{aligned}
\sum_{i \in C} x_i \ln \hat{\phi}_i(x_i, z) &= z - 1 - \ln(z - B) - \frac{A}{2^{1.5}B} \ln\left(\frac{z + (1+\sqrt{2})B}{z + (1-\sqrt{2})B}\right) \\
E(\boldsymbol{x}, z) &= z^3 - (1-B)z^2 + (A - 3B^2 - 2B)z - AB + B^3 + B^2
\end{aligned}
$$

where,

$$\begin{aligned} A &= \sum_{i \in C} \sum_{j \in C} \alpha_{ij} x_i x_j \\ B &= \sum_{i \in C} b_i x_i \end{aligned}$$

8.6.10 Test Problem 5

The binary system, carbon dioxide - methane, was shown by Hua et al. (1998) to contain three stationary points for the feed condition given in this example problem. The global minimum tangent plane distance is negative, therefore the given feed condition is unstable.

Data

$$\begin{aligned} P &= 60.8 \text{ bar} \\ T &= 220 \text{ K} \\ R &= 83.14 \text{ cm}^3(\text{bar})\text{mol}^{-1}\text{K}^{-1} \\ z^F &= 0.445886 \\ \boldsymbol{x}^F &= (0.20, 0.80)^T \\ \ln \phi_i^F &= (-0.965195, -0.323254)^T \\ \boldsymbol{b} &= (0.0885973, 0.0890893)^T \\ \boldsymbol{\alpha} &= \begin{pmatrix} 0.884831 & 0.555442 \\ 0.555442 & 0.427888 \end{pmatrix} \end{aligned}$$

Problem Statistics

No. of continuous variables	3
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	1
No. of nonconvex inequalities	-
No. of known solutions	3

Global Solution

- Objective function: -0.007
- Continuous variables

$$\begin{aligned} z &= 0.15949 \\ \boldsymbol{x} &= (0.4972, 0.5028)^T \end{aligned}$$

8.6.11 Test Problem 6

This example is the ternary system of nitrogen - methane - ethane. For the feed condition given, the Peng-Robinson equation has three stationary points, as reported by Hua et al. (1998). The global minimum tangent plane distance is negative, therefore the feed composition is an unstable solution.

Data

$$\begin{aligned}
P &= 76 \text{ bar} \\
T &= 270 \text{ K} \\
R &= 83.14 \text{ cm}^3(\text{bar})\text{mol}^{-1}\text{K}^{-1} \\
z^F &= 0.448135 \\
\boldsymbol{x}^F &= (0.15, 0.30, 0.55)^T \\
\ln \phi_i^F &= (0.468354, -0.067012, -1.0288)^T \\
\boldsymbol{b} &= (0.0815247, 0.0907391, 0.13705)^T \\
\boldsymbol{\alpha} &= \begin{pmatrix} 0.142724 & 0.206577 & 0.342119 \\ 0.206577 & 0.323084 & 0.547748 \\ 0.342119 & 0.547748 & 0.968906 \end{pmatrix}
\end{aligned}$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	1
No. of convex inequalities	-
No. of nonlinear equalities	1
No. of nonconvex inequalities	-
No. of known solutions	3

Global Solution

- Objective function: -0.0012
- Continuous variables

$$\begin{aligned}
z &= 0.30572 \\
\boldsymbol{x} &= (0.097, 0.245, 0.658)^T
\end{aligned}$$

8.7 Clusters of Atoms and Molecules

8.7.1 Introduction

The theoretical prediction of the physical properties of materials is an important tool for understanding and interpreting experimental results at the atomistic level. Such properties are governed by the interatomic and intermolecular forces of the system, which can be studied through computational simulations of atomic and molecular clusters. For this reason, clusters have been the focus of many recent theoretical, as well as experimental, studies.

One important result of such studies will be the identification of the appropriate form of interatomic potentials for the prediction of bulk material properties. That is, the reliability of theoretical predictions is dependent on the choice of potential model. Accurate results can be obtained by solving the Schrödinger equation exactly, although the large computational effort associated with this problem greatly limits the size of system that can be considered. Therefore, empirical interatomic potentials have been developed in order to effectively address larger systems. As a first order approximation, these potentials can been modeled as pairwise interaction (two-body) terms (e.g., this is appropriate for rare gas clusters). However, when considering atoms without closed-shell structures, the use of more detailed potentials that incorporate many body terms (i.e., usually three-body) is required.

Once a potential has been chosen, a method for examining the potential energy surface must also be selected. The ability of these procedures to traverse complicated energy hypersurfaces must be measured, since this can greatly affect the quality of theoretical predictions. Particularly important is the efficiency of these methods in locating the global minimum energy configuration of the cluster. Typically, the identification of these global minimum energy structures is used to set benchmarks for global optimization algorithms.

A database of best known solutions for several classes of cluster problems (including Lennard-Jones and Morse potentials) can also be found at the following web address :

`http://brian.ch.cam.ac.uk/CCD.html`

8.7.2 General Formulation

A general formulation is presented below. This formulation represents a global minimization problem for a cluster system containing N particles. For completeness, the formulation includes up to N-body interaction terms, although most examples consider only two- and three-body interaction terms. The one-body term, which describes external forces on the system, is generally disregarded so that the expansion begins with the pair interaction terms.

Objective function

$$\min_{\boldsymbol{r}_1,\dots,\boldsymbol{r}_N} \quad \Phi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) \;=$$

$$\sum_{i<j} U_2(\boldsymbol{r}_i,\boldsymbol{r}_j) + \sum_{i<j<k} U_3(\boldsymbol{r}_i,\boldsymbol{r}_j,\boldsymbol{r}_k) + \ldots + U_N(\boldsymbol{r}_i,\boldsymbol{r}_j,\dots,\boldsymbol{r}_N)$$

Constraints

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0$$

Variable Bounds

$$\begin{array}{lrcl} x_i^L \le x_i \le x_i^U, & i & = & 2, \ldots, N \\ y_i^L \le y_i \le y_i^U, & i & = & 3, \ldots, N \\ x_i^L \le x_i \le x_i^U, & i & = & 4, \ldots, N \end{array}$$

Variable definitions

Φ represents the potential to be minimized, which is a function of the Cartesian coordinate vectors for the N individual atoms. The convention used for indexing the summations (which will be used in the following test problems) is to include all combinations of indices for which the imposed condition applies. For example, $\sum\limits_{i<j}$ implies that all combinations of i and j for which $i < j$ should be included in the summation. The Cartesian coordinate vector for atom i is given by $\boldsymbol{r}_i = (x_i,\ y_i,\ z_i)^T$. U_2, U_3 and U_N represent the two-, three- and N-body terms, respectively. In order to set the translational and rotational degrees of freedom, six constraints are added. These set the first atom at the origin, the second along the x-axis and the third in the x-y plane. Finally, x_i^L, y_i^L, z_i^L, x_i^U, y_i^U and z_i^U denote the lower and upper bounds for the x, y, and z Cartesian coordinates, respectively.

8.7.3 Lennard-Jones Potential

The global optimization of Lennard-Jones clusters is a two-body problem used to simulate heavy atom rare gas clusters such as argon, xenon and krypton. Computer simulations have been successful in predicting transitions from non-crystalline geometries to bulk face-centered cubic (fcc) crystalline forms (Leary (1997)). The problems are highly non-convex; that is, the number of distinct local minima is believed to grow exponentially as the number of atoms, N, increases (Hoare and McInnes (1983)).

The objective function is measured in units of energy, and interatomic distances are usually given in angstroms [Å]. Both values are easily scaled for homogeneous clusters of atoms. A plot of the scaled Lennard-Jones potential for a single atomic pair is given in Figure 8.3. The potential represents the difference between a strong, short-range repulsive term (r^{-12}) and a longer-range attractive term ($2r^{-6}$).

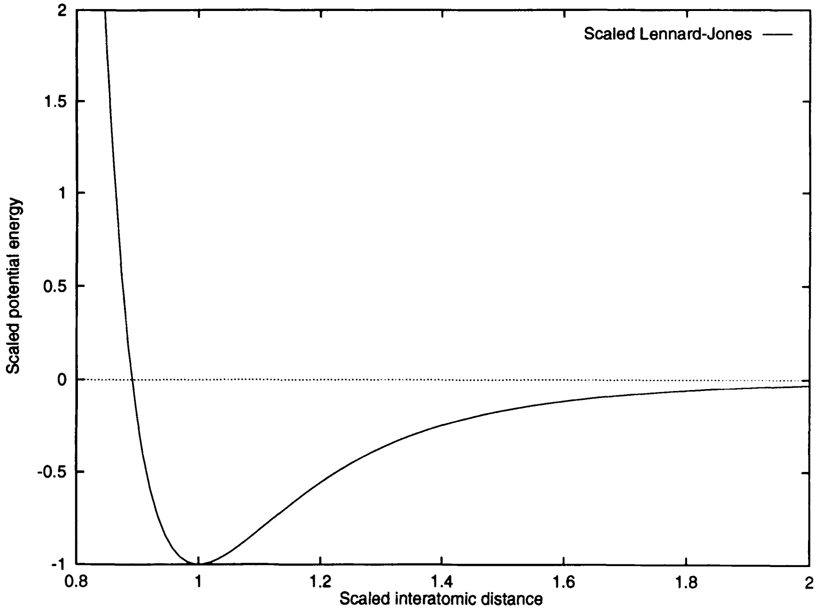


Figure 8.3: Scaled Lennard-Jones potential

Formulation

Objective function

$$\min_{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N} \quad \Phi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = 4\epsilon\sum_{i<j}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Constraints

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0$$

Variable definitions

ϵ and $2^{1/6}\sigma$ are the pair equilibrium well depth and separation, respectively. Typically, for homogeneous atom clusters, reduced units are used; that is $\epsilon = \sigma = 1$. After global minimum energy geometries have been found, the distances can be rescaled for various microcluster systems. It should also be noted that r_{ij} refers to the Euclidean distance between atoms i and j (i.e., $r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}$).

Problem Statistics

No. of continuous variables	$3N$-6
No. of linear equalities	6
No. of known solutions	Grows exponentially with N

Best Known Solutions

The following table provides the best known solutions for the scaled Lennard-Jones (homogeneous) microcluster problem. From left to right the columns indicate : number of atoms in the cluster, scaled energy, geometry of the cluster, and the earliest reference in which the solution was reported. The geometry classification codes include polytetrahedral structures (PT), face-centered cubic lattice structures (FCC), and two multilayer icosahedral lattice conformations : sublattices that comprise Mackay icosahedron (IC) and sublattices consisting of tetrahedrally bonded face-centered sites (FC).

N	Energy	Geometry	Reference
4	-6.000000	PT	Hoare and Pal (1971)
5	-9.103852	PT	Hoare and Pal (1971)
6	-12.712062	FCC	Hoare and Pal (1971)
7	-16.505384	PT	Hoare and Pal (1971)
8	-19.821489	PT	Hoare and Pal (1971)
9	-24.113360	PT	Hoare and Pal (1971)
10	-28.422532	PT	Hoare and Pal (1971)
11	-32.765970	PT	Hoare and Pal (1971)
12	-37.967600	PT	Hoare and Pal (1971)
13	-44.326801	IC	Hoare and Pal (1971)
14	-47.845157	FC	Hoare and Pal (1971)
15	-52.322627	FC	Hoare and Pal (1971)
16	-56.815742	FC	Hoare and Pal (1971)
17	-61.317995	FC	Freeman and Doll (1984)
18	-66.530949	FC	Hoare and Pal (1971)
19	-72.659782	FC	Hoare and Pal (1971)
20	-77.177043	FC	Hoare and Pal (1971)
21	-81.684571	FC	Hoare and Pal (1971)
22	-86.809782	FC	Northby (1987)
23	-92.844472	FC	Farges et al. (1985)
24	-97.348815	FC	Wille (1987)
25	-102.372663	FC	Hoare and Pal (1971)
26	-108.315616	FC	Hoare and Pal (1971)
27	-112.873584	FC	Northby (1987)
28	-117.822402	FC	Northby (1987)
29	-123.587371	FC	Hoare and Pal (1971)
30	-128.286571	FC	Northby (1987)

N	Energy	Geometry	Reference
31	-133.586422	IC	Northby (1987)
32	-139.635524	IC	Northby (1987)
33	-144.842719	IC	Northby (1987)
34	-150.044528	IC	Northby (1987)
35	-155.756643	IC	Northby (1987)
36	-161.825363	IC	Northby (1987)
37	-167.033672	IC	Northby (1987)
38	-173.928427	IC	Pillardy and Piela (1995), Doye et al. (1995)
39	-180.033185	IC	Northby (1987)
40	-185.249839	IC	Northby (1987)
41	-190.536277	IC	Northby (1987)
42	-196.277534	IC	Northby (1987)
43	-202.364664	IC	Northby (1987)
44	-207.688728	IC	Northby (1987)
45	-213.784862	IC	Northby (1987)
46	-220.680330	IC	Northby (1987)
47	-226.012256	IC	Northby (1987)
48	-232.199529	IC	Northby (1987)
49	-239.091864	IC	Northby (1987)
50	-244.549926	IC	Northby (1987)
51	-251.253964	IC	Northby (1987)
52	-258.229991	IC	Northby (1987)
53	-265.203016	IC	Northby (1987)
54	-272.208631	IC	Northby (1987)
55	-279.248470	IC	Hoare and Pal (1972)
56	-283.643105	IC	Northby (1987)
57	-288.342625	FC	Northby (1987)
58	-294.378148	FC	Northby (1987)
59	-299.738070	FC	Northby (1987)
60	-305.875476	FC	Northby (1987)
61	-312.008896	FC	Northby (1987)
62	-317.353901	FC	Northby (1987)
63	-323.489734	FC	Northby (1987)
64	-329.620147	FC	Northby (1987)
65	-334.971532	FC	Xue (1994)
66	-341.110599	FC	Coleman et al. (1994), Xue (1994)
67	-347.252007	FC	Northby (1987)
68	-353.394542	FC	Northby (1987)
69	-359.882566	FC	Wales and Doye (1997)

N	Energy	Geometry	Reference
70	-366.892251	FC	Northby (1987)
71	-373.349661	FC	Northby (1987)
72	-378.637253	FC	Coleman et al. (1994)
73	-384.789377	FC	Northby (1987)
74	-390.908500	FC	Northby (1987)
75	-397.492331	FC	Doye et al. (1995)
76	-402.894866	FC	Doye et al. (1995)
77	-409.083517	FC	Doye et al. (1995)
78	-414.794401	FC	Wales and Doye (1997)
79	-421.810897	FC	Northby (1987)
80	-428.083564	FC	Northby (1987)
81	-434.343643	FC	Northby (1987)
82	-440.550425	IC	Northby (1987)
83	-446.924094	IC	Northby (1987)
84	-452.657214	IC	Northby (1987)
85	-459.055799	FC	Northby (1987)
86	-465.384493	IC	Northby (1987)
87	-472.098165	IC	Northby (1987)
88	-479.032630	IC	Deaven et al. (1996)
89	-486.053911	IC	Northby (1987)
90	-492.433908	IC	Northby (1987)
91	-498.811060	IC	Northby (1987)
92	-505.185309	IC	Northby (1987)
93	-510.877688	IC	Northby (1987)
94	-517.264131	IC	Northby (1987)
95	-523.640211	IC	Northby (1987)
96	-529.879146	IC	Northby (1987)
97	-536.681383	IC	Northby (1987)
98	-543.642957	IC	Deaven et al. (1996)
99	-550.666526	IC	Northby (1987)
100	-557.039820	IC	Northby (1987)
101	-563.411308	IC	Northby (1987)
102	-569.363652	IC	Doye and Wales (1995)
103	-575.766131	IC	Doye and Wales (1995)
104	-582.086642	IC	Doye and Wales (1995)
105	-588.266501	IC	Northby (1987)
106	-595.061072	IC	Northby (1987)
107	-602.007110	IC	Wales and Doye (1997)
108	-609.033011	IC	Northby (1987)
109	-615.411166	IC	Northby (1987)
110	-621.788224	IC	Northby (1987)

N	Energy	Geometry	Reference
111	-628.068416	IC	Northby (1987)
112	-634.874626	IC	Northby (1987)
113	-641.794704	IC	Barrón et al. (1997)
114	-648.833100	IC	Northby (1987)
115	-655.756307	IC	Barrón et al. (1997)
116	-662.809353	IC	Northby (1987)
117	-668.282701	IC	Northby (1987)
118	-674.769635	IC	Northby (1987)
119	-681.419158	IC	Northby (1987)
120	-687.021982	IC	Northby (1987)
121	-693.819577	IC	Northby (1987)
122	-700.939379	IC	Northby (1987)
123	-707.802109	IC	Northby (1987)
124	-714.920896	IC	Northby (1987)
125	-721.303235	IC	Northby (1987)
126	-727.349853	IC	Northby (1987)
127	-734.479629	IC	Northby (1987)
128	-741.332100	IC	Northby (1987)
129	-748.460647	IC	Northby (1987)
130	-755.271073	IC	Northby (1987)
131	-762.441558	IC	Northby (1987)
132	-768.042203	IC	Northby (1987)
133	-775.023203	IC	Northby (1987)
134	-782.206157	IC	Xue (1994)
135	-790.278120	IC	Northby (1987)
136	-797.453259	IC	Northby (1987)
137	-804.631473	IC	Northby (1987)
138	-811.812780	IC	Northby (1987)
139	-818.993848	IC	Northby (1987)
140	-826.174676	IC	Northby (1987)
141	-833.358586	IC	Northby (1987)
142	-840.538610	IC	Northby (1987)
143	-847.721698	IC	Northby (1987)
144	-854.904499	IC	Northby (1987)
145	-862.087012	IC	Northby (1987)
146	-869.272573	IC	Northby (1987)
147	-876.461207	IC	Northby (1987)

8.7.4 Morse Potential

The Morse (1929) potential, like the Lennard-Jones potential, is used to model clusters by considering only two-body interaction terms. However, in this case a single variable parameter can be adjusted to shift the range of the potential. This diversity offers an increased probability of accurately predicting geometries of various metal clusters. This increased variability coupled with a rapid increase in the number of distinct local minima as cluster size increases, makes the Morse potential a rigorous test problem for global optimization algorithms. As with the Lennard-Jones potential, the objective function is measured in units of energy. A plot of the scaled Morse potential for a single atomic pair (for several values of its variable parameter) is given in Figure 8.4.

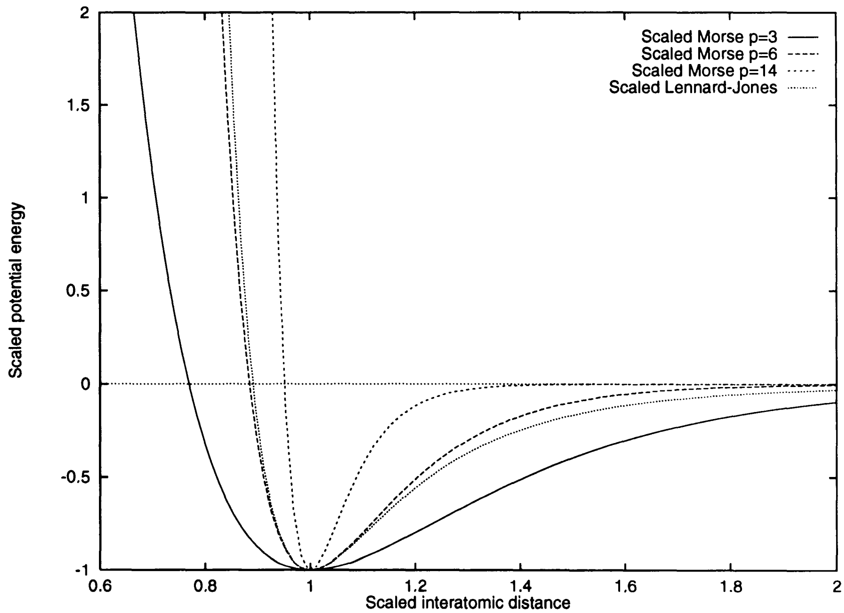


Figure 8.4: Scaled Morse potential

Formulation

Objective function

$$\min_{\boldsymbol{r}_1,\dots,\boldsymbol{r}_N} \quad \Phi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) = \epsilon \sum_{i<j} \left[\left(1 - e^{\rho\left[1-\frac{r_{ij}}{r_0}\right]} \right)^2 - 1 \right]$$

Constraints

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0$$

Variable definitions

ϵ and r_0 are the pair equilibrium well depth and separation, respectively. For homogeneous atom clusters, reduced units can be used (i.e., $\epsilon = \sigma = 1$), and then later rescaled. ρ is an adjustable parameter that broadens (small ρ) or narrows (large ρ) the range of the potential. It should also be noted that r_{ij} refers to the Euclidean distance between atoms i and j (i.e., $r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}$).

Problem Statistics

No. of continuous variables	$3N$-6
No. of linear equalities	6
No. of known solutions	Grows exponentially with N

Best Known Solutions

The following table provides the best known solutions for the reduced Morse potential microcluster problem. Results for ρ values of 3.0 and 6.0 are presented. This information was compiled from results presented in Doye and Wales (1997) and Doye et al. (1995).

N	Energy ($\rho = 3.0$)	Energy ($\rho = 6.0$)
5	-9.299500	-9.044930
6	-13.544229	-12.487810
7	-17.552961	-16.207580
8	-22.042901	-19.327420
9	-26.778449	-23.417190
10	-31.888630	-27.473283
11	-37.930817	-31.521880
12	-44.097880	-36.400278
13	-51.737046	-42.439863
14	-56.754744	-45.619277
15	-63.162119	-49.748409
16	-69.140648	-53.845835
17	-75.662417	-57.941386
18	-82.579266	-62.689245
19	-90.647461	-68.492285
20	-97.417393	-72.507782
21	-104.336946	-76.529139
22	-112.041223	-81.136735
23	-120.786879	-86.735494
24	-127.884549	-90.685398
25	-136.072704	-95.127899
26	-145.322134	-100.549598
27	-152.513867	-104.745275
28	-160.773356	-108.997831

N	Energy ($\rho = 3.0$)	Energy ($\rho = 6.0$)
29	-170.115560	-114.145949
30	-177.578647	-118.432844
31	-185.984248	-122.857743
32	-195.468461	-127.771395
33	-204.208737	-132.287431
34	-214.068392	-136.797544
35	-221.771452	-141.957188
36	-230.508264	-147.381965
37	-240.008130	-151.891203
38	-249.159174	-157.477108
39	-258.944962	-163.481990
40	-268.394773	-167.993097
41	-278.405573	-172.526828
42	-288.335415	-177.680222
43	-298.172449	-183.092699
44	-308.277011	-187.626292
45	-318.660653	-192.954739
46	-327.033118	-199.177751
47	-336.666189	-203.704178
48	-346.662788	-209.044000
49	-356.412817	-215.253702
50	-366.635589	-219.820229
51	-376.673413	-225.391240
52	-387.587332	-231.615013
53	-398.783184	-237.834976
54	-407.966010	-244.058174
55	-417.918562	-250.286609
56	-428.611289	-253.922955
57	-439.960320	-258.041717
58	-449.432282	-263.410755
59	-459.509280	-267.945226
60	-470.448485	-273.341243
61	-482.025765	-278.726626
62	-491.052378	-283.183002
63	-501.731893	-288.560948
64	-512.831683	-293.931716
65	-523.446427	-298.392345
66	-534.464040	-303.763297
67	-544.754257	-309.130322
68	-555.582496	-314.374880
69	-566.364140	-319.819905

N	Energy ($\rho = 3.0$)	Energy ($\rho = 6.0$)
70	-577.739782	-325.887749
71	-588.396687	-331.588748
72	-599.690310	-336.121753
73	-610.936684	-341.266253
74	-622.679870	-346.610834
75	-633.513370	-351.472365
76	-644.951602	-356.372708
77	-656.079789	-361.727086
78	-667.576295	-366.761455
79	-678.940231	-372.832290
80	-690.577890	-378.333471

8.7.5 Tersoff Potential

The Tersoff (1988) potential combines both two and three-body interaction terms together into one functional form. That is, for each pair of atoms i and j, a multi-body term, which depends on the positions and the neighbors of atom i, is also included into the pairwise potential formulation. As in the Morse potential, exponential functions are chosen to model the attractive and repulsive forces. This empirical many-body potential was originally employed to model the bulk properties of silicon (Si), but has since been applied to various metal cluster systems.

Formulation

Objective function

$$\min_{\boldsymbol{r}_1,\dots,\boldsymbol{r}_N} \quad \Phi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) = \sum_{i<j} f_c(r_{ij})\left[V_R(r_{ij}) + b_{ij}V_A(r_{ij})\right]$$

where

$$V_R(r_{ij}) = Ae^{-\lambda_1 r_{ij}}, \qquad V_A(r_{ij}) = Be^{-\lambda_2 r_{ij}},$$

$$b_{ij} = (1+\gamma^n \xi_{ij}^n)^{-1/2n}, \qquad \xi_{ij} = \sum_{k\neq i,j} f_c(r_{ik})g(\theta_{ijk}),$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - cos\theta)^2},$$

$$f_c(r) = \begin{cases} 1, & r < R - D, \\ \frac{1}{2} - \frac{1}{2}sin\left[\frac{\pi(r-R)}{2D}\right], & R - D < r < R + D, \\ 0, & r > R + D. \end{cases}$$

Constraints

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0$$

Variable definitions

V_R is a repulsive term, V_A is an attractive term, and b_{ij} is the multi-body term that depends on the positioning of atoms i and j, as well as the atoms neighboring atom i. The $f_c(r_{ij})$ term acts as a switching function so that the potential falls smoothly to zero at short distances. θ_{ijk} is the bond angle between bonds ij and ik. r_{ij} and r_{ik} refers to the Euclidean distance between atoms i and j, and i and k, respectively (i.e., $r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}$ and $r_{ik} = [(x_i - x_k)^2 + (y_i - y_k)^2 + (z_i - z_k)^2]^{\frac{1}{2}}$).

Data

Data are provided for two models of silicon.
Si(B):

$$\begin{array}{llll} A = 3264.7 \text{ eV} & B = 95.373 \text{ eV} & \lambda_1 = 3.2394 Å^{-1} & \lambda_2 = 1.3258 Å^{-1} \\ \gamma = 0.33675 & n = 22.956 & d = 2.0417 & h = 0.0000 \\ c = 4.8381 & R = 3.0 Å & D = 0.2 Å & \end{array}$$

Si(C):

$$\begin{array}{llll} A = 1830.8 \text{ eV} & B = 471.18 \text{ eV} & \lambda_1 = 2.4799 Å^{-1} & \lambda_2 = 1.7322 Å^{-1} \\ \gamma = 1.0999 \times 10^{-6} & n = 0.78734 & d = 16.218 & h = -0.59826 \\ c = 1.0039 \times 10^5 & R = 2.85 Å & D = 0.15 Å & \end{array}$$

Problem Statistics

No. of continuous variables	$3N$-6
No. of linear equalities	6
No. of known solutions	Grows exponentially with N

Best Known Solutions

The following table provides the best known solutions for small clusters of silicon modeled by the Tersoff potential. The second column provides energy values for the Si(B) clusters and the third column provides energy values for the Si(C) clusters. Results are compiled from Ali and Smith (1993) and Ali et al. (1997).

N	Si(B) Energy (eV)	Si(C) Energy (eV)
3	-7.87	-5.33
4	-15.71	-8.97
5	-20.80	-12.46
6	-26.82	-15.88

8.7.6 Brenner Potential

This potential was developed by Brenner (1990) for carbon clusters and is very similar in form to the Tersoff equation. Three-body terms are included by considering the neighboring atoms of i when considering pairwise interactions with atom j. Originally the potential energy function was applied to the calculation of properties for diamond and graphite. It has also been applied to the prediction of small carbon cluster geometries.

Formulation

Objective function

$$\min_{\boldsymbol{r}_1,\dots,\boldsymbol{r}_N} \quad \Phi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) \;=\; \sum_{i<j} f_c(r_{ij})\left[V_R(r_{ij}) + b_{ij}V_A(r_{ij})\right]$$

where

$$V_R(r_{ij}) = \tfrac{D_e}{S-1}e^{[-\beta\sqrt{2S}(r_{ij}-r_e)]}, \qquad V_A(r_{ij}) = \tfrac{SD_e}{S-1}e^{[-\beta\sqrt{2/S}(r_{ij}-r_e)]},$$

$$b_{ij} = (1+z_{ij})^{-n}, \qquad z_{ij} = \sum_{k\neq i,j} f_c(r_{ik})g(\theta_{ijk})e^{m(r_{ij}-r_{ik})},$$

$$g(\theta) = \alpha\left[1 + \frac{c^2}{d^2} - \frac{c^2}{d^2+(h+cos\theta)^2}\right],$$

$$f_c(r) = \begin{cases} 1, & r < R-D,\\ \frac{1}{2} - \frac{1}{2}sin\left[\frac{\pi(r-R)}{2D}\right], & R-D < r < R+D,\\ 0, & r > R+D.\end{cases}$$

Constraints

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0$$

Variable definitions

V_R is a repulsive term, V_A is an attractive term, and b_{ij} is the multi-body term that depends on the positioning of atoms i and j, as well as the atoms neighboring atom i. The $f_c(r_{ij})$ term acts as a switching function so that the potential falls smoothly to zero at short distances. θ_{ijk} is the bond angle between bonds ij and ik. r_{ij} and r_{ik} refers to the Euclidean distance between atoms i and j, and i and k, respectively (i.e., $r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}$ and $r_{ik} = [(x_i - x_k)^2 + (y_i - y_k)^2 + (z_i - z_k)^2]^{\frac{1}{2}}$).

Data

$D_e = 6.325$ eV	$r_e = 1.315Å$	$\beta = 1.5Å^{-1}$	$S = 1.29$
$n = 0.8047$	$\alpha = 0.0113$	$c = 19.0$	$d = 2.5$
$h = 1.0$	$m = 2.25Å^{-1}$	$R = 1.85Å$	$D = 0.15Å$

Problem Statistics

No. of continuous variables	$3N$-6
No. of linear equalities	6
No. of known solutions	Grows exponentially with N

Best Known Solutions

The following table provides the best known solution for small carbon cluster problems modeled by the Brenner potential. From left to right the columns indicate : number of atoms in the cluster, energy, and the geometry of the cluster. The geometries include, linear, mono- and poly-cyclic ring and fullerene conformations. The data is compiled from results presented in Hobday and Smith (1997).

N	Energy (eV)	Geometry
3	-12.40	linear
4	-18.58	linear
5	-26.33	m-cyclic ring
6	-33.96	m-cyclic ring
7	-41.10	m-cyclic ring
8	-47.91	m-cyclic ring
9	-54.50	m-cyclic ring
10	-60.95	m-cyclic ring
11	-67.32	m-cyclic ring
12	-73.61	m-cyclic ring
13	-79.90	m-cyclic ring
14	-86.11	m-cyclic ring
15	-92.34	m-cyclic ring
16	-98.61	m-cyclic ring
17	-140.80	m-cyclic ring
18	-111.38	p-cyclic ring

N	Energy (eV)	Geometry
19	-117.40	p-cyclic ring
20	-128.39	fullerene
21	-131.70	p-cyclic ring
22	-138.36	p-cyclic ring
23	-147.39	fullerene
24	-157.16	fullerene
25	-163.13	fullerene
26	-171.98	fullerene
27	-178.01	fullerene
28	-186.88	fullerene
29	-192.67	fullerene
30	-200.44	fullerene
31	-207.00	fullerene
32	-216.66	fullerene
33	-221.78	fullerene
34	-230.30	fullerene
35	-236.38	fullerene
36	-245.45	fullerene
37	-251.23	fullerene
38	-259.97	fullerene
39	-265.59	fullerene
40	-274.64	fullerene
41	-280.38	fullerene
42	-289.34	fullerene
43	-295.12	fullerene
44	-304.09	fullerene
45	-309.02	fullerene
46	-318.54	fullerene
47	-324.06	fullerene
48	-333.38	fullerene
49	-339.03	fullerene
50	-348.37	fullerene
51	-353.88	fullerene
52	-362.83	fullerene
53	-367.92	fullerene
54	-377.31	fullerene
55	-383.08	fullerene
56	-392.12	fullerene
57	-397.73	fullerene
58	-407.25	fullerene
59	-412.74	fullerene

N	Energy (eV)	Geometry
60	-422.55	fullerene

8.7.7 Bolding-Andersen Potential

The Bolding and Andersen (1990) potential intrinsically contains many multi-body effects in its formulation. Although it is similar to the Tersoff and Brenner potentials in that it contains only pairwise terms, complicated expressions are used to model up to four-body interaction energies. These expressions were developed by fitting parameters to a variety of data on silicon, including the structure and energy of small clusters and surface properties.

Formulation

Objective function

$$\min_{\boldsymbol{r}_1,\dots,\boldsymbol{r}_N} \quad \Phi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) = \sum_{i<j} f_c(r_{ij})\left[V_R(r_{ij}) + I_{ij}^{\pi} V_{\pi}(r_{ij}) + I_{ij}^{\sigma} V_{\sigma}(r_{ij})\right]$$

where

$$V_R(r) = \tfrac{1}{2}(V^{bond}(r) + V^{anti}(r)), \quad V_{\pi}(r) = -a_1 \tanh[a_2(r-a_3)] - 1,$$

$$V_{\sigma}(r) = \frac{1}{2}(V^{bond}(r) - V^{anti}(r)) - V_{\pi}(r),$$

$$V^{bond}(r) = -D_e\big(1 + \sum_{i=1}^{6} b_i \rho^i\big) e^{-b_1 \rho},$$

$$V^{anti}(r) = (b_8 + b_9\rho + b_{10}\rho^2)e^{-b_7\rho}, \qquad \rho = r - r_e, \qquad I_{ij}^{\sigma} = \tfrac{1}{I_1}\tfrac{1}{I_2},$$

$$I_1 = 1 + Z_{ij}^{a_6}\big(\sum_{k\neq i,j} a_4 S_{ik} S_{jk} + \sum_{k<l\neq i,j} a_5 S_{ik} S_{il} S_{jk} S_{jl} S_{kl}\big),$$

$$I_2 = 1 + Z_{ij}^{a_7}\big(\sum_{k\neq i,j} [S_{ik} P(\theta_{jik}) + S_{jk} P(\theta_{ijk})]\big),$$

$$P(\theta) = \sum_{n=0}^{6} d_n cos^n(\theta), \qquad Z_{ij} = \sum_{k\neq i,j} (S_{ik} + S_{jk}),$$

$$S_{ik} = S(r_{ik}) = S(r) = \begin{cases} 1, & r < r_e, \\ f_c(r)\frac{V_R(r)+V_{\sigma}(r)}{V_R(r_e)+V_{\sigma}(r_e)}, & r \geq r_e, \end{cases}$$

$$I^{\pi}_{ij} = S(Z^j_i)S(Z^i_j)e^{-I_3}, \qquad I_3 = \sum_{k \neq i,j} F_3 + \sum_{k,l \neq i,j} F_4 + \sum_{k,l,m \neq i,j} F_5,$$

$$S(Z) = \begin{cases} 1, & Z < 2, \\ c_1 + c_2 Z + c_3 Z^2 + c_4 Z^3, & 2 \leq Z \leq 2.5, \\ 0, & z > 2.5, \end{cases} \qquad Z^j_i = \sum_{k \neq i,j} S_{ik},$$

$$F_3 = a_8 S_{ik} S_{jk} + \frac{a_9}{1 + Z_{ij}} \left[S_{ik}(1 - S^4_{jk}) + S_{jk}(1 - S^4_{ik}) \right]$$

$$\begin{aligned} F_4 &= a_{10}(S_{ik}S_{il}S_{jk}S_{jl}) \\ &+ \tfrac{a_{11}}{1+Z^5_{ij}} \left[S_{ik}S_{jl}(1 - S_{il})(1 - S_{jk}) + S_{il}S_{jk}(1 - S_{ik})(1 - S_{jl}) \right] \\ &+ a_{12} \tfrac{\nu^2_{ijkl}}{r^2_{ij}} \left(\tfrac{S_{ik}S_{jl}}{r^2_{ik} r^2_{jl}} + \tfrac{S_{il}S_{jk}}{r^2_{il} r^2_{jk}} + \tfrac{S_{ik}S_{il}}{r^2_{ik} r^2_{il}} + \tfrac{S_{jk}S_{jl}}{r^2_{jk} r^2_{jl}} \right) \end{aligned}$$

$$\begin{aligned} F_5 &= a_{13}(S_{ik}S_{jk}S_{il}S_{jm}S_{kl}S_{km} + S_{ik}S_{jk}S_{im}S_{jl}S_{kl}S_{km}) \\ &+ a_{13}(S_{il}S_{jl}S_{ik}S_{jm}S_{kl}S_{lm} + S_{im}S_{jm}S_{il}S_{jk}S_{km}S_{lm}) \\ &+ a_{13}(S_{il}S_{jl}S_{im}S_{jk}S_{kl}S_{lm}S_{im}S_{jm}S_{ik}S_{jl}S_{km}S_{lm}) \end{aligned}$$

$$\nu_{ijkl} = \boldsymbol{r}_{ij} \cdot \boldsymbol{r}_{jl} \times \boldsymbol{r}_{ik}$$

$$f_c(r) = \begin{cases} 1, & r < R - D, \\ \frac{1}{2} - \frac{1}{2} sin\left[\frac{\pi(r-R)}{2D}\right], & R - D < r < R + D, \\ 0, & r > R + D. \end{cases}$$

Constraints

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0$$

Variable definitions

V_R is a repulsive term. The attractive term is broken up into two contributions, V_σ and V_π, which represent favorable interactions due to bonding of σ and π orbitals, respectively. These terms are modulated by the interference functions I^{σ}_{ij} and I^{π}_{ij}. There are two switching function, $f_c(r)$ and $S(Z)$, which are used to smooth the potential to zero. In addition, the bonding function $S(R)$ is used to measure the extent to which a pair of atoms are bonded. θ_{ijk} is the bond angle between bonds ij and ik. r_{ij} refers to the Euclidean distance between atoms i and j (i.e., $r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}$).

Data

$a_1 = 15.211 \frac{\text{kcal}}{\text{mol}}$	$a_2 = 4.0900\mathring{A}$	$a_3 = 2.3650\mathring{A}$
$a_4 = 0.0090$	$a_5 = 0.0100$	$a_6 = 1.0000$
$a_7 = 0.3333$	$a_8 = 0.4521$	$a_9 = -0.8763$
$a_{10} = 1.8387$	$a_{11} = 75.3470$	$a_{12} = 0.3425$
$a_{13} = 5.0000$	$b_1 = 2.3850\mathring{A}^{-1}$	$b_2 = 0.7296\mathring{A}^{-2}$
$b_3 = -2.2965\mathring{A}^{-3}$	$b_4 = -1.3677\mathring{A}^{-4}$	$b_5 = 2.0485\mathring{A}^{-5}$
$b_6 = -0.4745\mathring{A}^{-6}$	$b_7 = 3.4835\mathring{A}^{-1}$	$b_8 = 165.16 \frac{\text{kcal}}{\text{mol}}$
$b_9 = 96.70 \frac{\text{kcal}}{\text{mol}} \mathring{A}^{-1}$	$b_{10} = 495.73 \frac{\text{kcal}}{\text{mol}} \mathring{A}^{-2}$	$d_0 = 0.005387$
$d_1 = 0.007894$	$d_2 = -0.081615$	$d_3 = -0.083367$
$d_4 = 0.380043$	$d_5 = 0.374569$	$d_6 = 0.054232$
$c_1 = -175.0$	$c_2 = 240.0$	$c_3 = -108.0$
$c_4 = 16.0$	$r_e = 2.184\mathring{A}$	$D_e = 75.47 \frac{\text{kcal}}{\text{mol}}$

Problem Statistics

No. of continuous variables	$3N$-6
No. of linear equalities	6
No. of known solutions	Grows exponentially with N

Best Known Solutions

The following table provides the best known solutions for small clusters of silicon modeled by the Bolding-Andersen potential. Results are compiled from Bolding and Andersen (1990) and Niesse and Mayne (1996).

N	Energy (kcal/mol)
3	-186.1
4	-300.0
5	-382.7
6	-466.0
7	-568.2
8	-676.9
9	-789.2
10	-901.3

Chapter 9

Bilevel Programming Problems

9.1 Introduction

A problem where an optimization problem is constrained by another one is classified as a BiLevel Programming Problem, BLPP, and is of the general form:

$$
\begin{array}{ll}
\min\limits_{\boldsymbol{x},\,\boldsymbol{y}} & F(\boldsymbol{x},\boldsymbol{y}) \\
\text{s.t.} & \\
& \begin{array}{rcl} \boldsymbol{G}(\boldsymbol{x},\boldsymbol{y}) & \leq & \boldsymbol{0} \\ \boldsymbol{H}(\boldsymbol{x},\boldsymbol{y}) & = & \boldsymbol{0} \end{array} \\
& \min\limits_{\boldsymbol{y}} f(\boldsymbol{x},\boldsymbol{y}) \\
& \text{s.t.} \\
& \quad \begin{array}{rcl} \boldsymbol{g}(\boldsymbol{x},\boldsymbol{y}) & \leq & \boldsymbol{0} \\ \boldsymbol{h}(\boldsymbol{x},\boldsymbol{y}) & = & \boldsymbol{0} \end{array} \\
& \quad \boldsymbol{x} \in X \subseteq R^{n1}\ , \quad \boldsymbol{y} \in Y \subseteq R^{n2}
\end{array}
$$

where $f, F : R^{n1} \times R^{n2} \to R$, $\boldsymbol{g} = [g_1, .., g_J] : R^{n1} \times R^{n2} \to R^j$, $\boldsymbol{G} = [G_1, .., G_J] : R^{n1} \times R^{n2} \to R^{j'}$, $\boldsymbol{h} = [h_1, .., h_I] : R^{n1} \times R^{n2} \to R^i$, $\boldsymbol{H} = [H_1, .., H_{I'}] : R^{n1} \times R^{n2} \to R^{i'}$. F, $\boldsymbol{G}$ and $\boldsymbol{H}$ are the outer (planner's or leader's) problem objective function, inequality and equality constraints, and f, $\boldsymbol{g}$, and $\boldsymbol{h}$ are the inner (behavorial or follower's) problem objective, inequality and equality constraints, respectively. The decision variables of the outer problem are $\boldsymbol{x}$ and $\boldsymbol{y}$ and of the inner problem are $\boldsymbol{y}$.

The literature on the application of bilevel programming problems, BLPP, is quite extensive and diverse, such as economics, (Cassidy et al., 1971; Candler and Norton, 1977; Luh et al., 1982; Kolstad, 1985; Hobbs and Nelson, 1992; Suh and Kim, 1992; Onal et al., 1995; Mathur and Puri, 1995; Aiyoshi and

Shimizu, 1981; Bard et al., 1998), civil engineering, (Fisk, 1984; LeBlanc and Boyce, 1986; Ben-Ayed et al., 1988; Suh and Kim, 1992; Yang and Yagar, 1994; Yang et al., 1994; Yang and Yagar, 1995; Migdalas, 1995); chemical engineering (Grossmann and Floudas, 1987; Clark and Westerberg, 1990a,b, 1983; Gümüş and Ciric, 1997) or warfare (Bracken and McGill, 1973). Good reviews of bibliography on BLPP can be found in Vicente and Calamai (1994) and Kolstad (1985). Further algorithms and applications are presented in Bard (1998).

9.1.1 Terminology and Properties

The general terminology and basic properties of the BLPP are as follows:

- The relaxed BLPP feasible set (or constraint region):

  $\Omega \; = \; \{(\boldsymbol{x},\boldsymbol{y}) : G(\boldsymbol{x},\boldsymbol{y}) \leq \boldsymbol{0}, H(\boldsymbol{x},\boldsymbol{y}) = \boldsymbol{0}, \boldsymbol{g}(\boldsymbol{x},\boldsymbol{y}) \leq \boldsymbol{0}, \boldsymbol{h}(\boldsymbol{x},\boldsymbol{y}) = \boldsymbol{0}\}$

- For $\boldsymbol{x} \in X$, the inner problem feasible set (follower's solution set, or follower's feasible region):

  $\Omega(\boldsymbol{x}) \; = \; \{\boldsymbol{y} : \boldsymbol{y} \in Y, \boldsymbol{h}(\boldsymbol{x},\boldsymbol{y}) = \boldsymbol{0}, \boldsymbol{g}(\boldsymbol{x},\boldsymbol{y}) \leq \boldsymbol{0}\}$

- For $\boldsymbol{x} \in X$, inner rational reaction set (follower's rational reaction set):

  $RR(\boldsymbol{x}) \; = \{\boldsymbol{y} \in \text{argmin} f(\boldsymbol{x},\boldsymbol{y}) : \boldsymbol{y} \in \Omega(\boldsymbol{x})\}$

- The BLPP feasible set (the induced, or inducible region):

  $IR \; = \; \{(\boldsymbol{x},\boldsymbol{y}) : (\boldsymbol{x},\boldsymbol{y}) \in \Omega, \boldsymbol{y} \in RR(\boldsymbol{x})\}.$

For the BLPP to be well-posed, it is generally assumed that Ω is nonempty and compact, and $RR(\boldsymbol{x}) \neq \phi$.
Using the above terminology, the BLPP can be written as

$$\begin{aligned} &\min\ F(\boldsymbol{x},\boldsymbol{y}) \\ &\text{s.t. } (\boldsymbol{x},\boldsymbol{y}) \in IR. \end{aligned}$$

Several studies have proved that the solution of even the linear BLPP is an NP-hard problem (Jeroslow, 1985; Ben-Ayed and Blair, 1990; Bard, 1991). It has been further shown that the BLPP is strongly NP-hard (Hansen et al., 1992).

9.1.2 Solution Techniques

In general, there has been two basic techniques for the solution of the linear BLPP: enumeration and reformulation techniques.

Enumeration techniques are based on the property that the inducible region of the linear BLPP is composed of connected faces of Ω and that a solution lies at a vertex (Bard, 1984). The following approaches are of this type: Vertex enumeration (Candler and Townsley, 1982); K-th best algorithm; (Bialas, 1984); and branch and bound (Bard and Moore, 1990).

The reformulation techniques are based on the transformation of the bilevel problem into a single level one by replacing the inner problem with its Karush-Kuhn-Tucker optimality conditions. For the solution of the transformed problem, the following approaches have been proposed: mixed integer programming (Fortuny-Amat and McCarl, 1981); branch and bound (Hansen et al., 1992; Bard and Falk, 1982); penalty methods (Bard and Falk, 1982; Anandalingam and White, 1990; White and Anandalingam, 1993; Önal, 1993); parametric complementary pivoting (Judice and Faustino, 1992); and global optimization (Floudas and Zlobec, 1998; Visweswaran et al., 1996; Tuy et al., 1993; Al-Khayyal et al., 1992).

For the solution of the bilevel linear problems with quadratic objective functions, transformation based branch and bound (Bard, 1988; Edmunds and Bard, 1991), descent (Vicente et al., 1994), and global optimization (Visweswaran et al., 1996) methods have been proposed. More information on solution techniques can also be found in recent books by Bard (1998) and Shimizu et al. (1997).

Procedures for generating random BLPP test problems are presented in Calamai and Vicente (1993, 1994) and Moshirvaziri et al. (1996).

9.2 Bilevel Linear Programming Problems

When all the functions are linear, the resulting problem is a bilevel linear problem of the form:

$$
\begin{array}{ll}
\min\limits_{\boldsymbol{x},\, \boldsymbol{y}} & \boldsymbol{c}_1^T \boldsymbol{x} + \boldsymbol{d}_1^T \boldsymbol{y} \\
\text{s.t.} & \\
& \begin{array}{rcl} \boldsymbol{A}_1 \boldsymbol{x} + \boldsymbol{B}_1 \boldsymbol{y} & \leq & \boldsymbol{b}_1 \\ \boldsymbol{C}_1 \boldsymbol{x} + \boldsymbol{D}_1 \boldsymbol{y} & = & \boldsymbol{e}_1 \end{array} \\
& \min\limits_{\boldsymbol{y}} \boldsymbol{c}_2^T \boldsymbol{x} + \boldsymbol{d}_2^T \boldsymbol{y} \\
& \text{s.t.} \\
& \quad \begin{array}{rcl} \boldsymbol{A}_2 \boldsymbol{x} + \boldsymbol{B}_2 \boldsymbol{y} & \leq & \boldsymbol{b}_2 \\ \boldsymbol{C}_2 \boldsymbol{x} + \boldsymbol{D}_2 \boldsymbol{y} & = & \boldsymbol{e}_2 \end{array} \\
& \boldsymbol{x} \in X \subseteq R^{n1}\,, \quad \boldsymbol{y} \in Y \subseteq R^{n2}
\end{array}
$$

where we have $\boldsymbol{c}_1, \boldsymbol{c}_2 \in R^{n1}, \boldsymbol{d}_1, \boldsymbol{d}_2 \in R^{n2}, \boldsymbol{b}_1 \in R^{j}, \boldsymbol{b}_2 \in R^{j'}, \boldsymbol{e}_1 \in R^{i}, \boldsymbol{e}_2 \in R^{i'}, \boldsymbol{A}_1 \in R^{j\times n1}, \boldsymbol{B}_1 \in R^{j\times n2}, \boldsymbol{C}_1 \in R^{i\times n1}, \boldsymbol{D}_1 \in R^{i\times n2}, \boldsymbol{A}_2 \in R^{j'\times n1}, \boldsymbol{B}_2 \in R^{j'x\times n2}$, and $\boldsymbol{D}_2 \in R^{i'\times n2}$.

Detailed reviews of the properties of the linear BLPP and existing solution approaches can be found in Shimizu et al. (1997), Vicente and Calamai (1994), Ben-Ayed (1993) and Wen and Hsu (1991).

The examples presented in this chapter have all been solved by replacing the inner problem with its equivalent Karush-Kuhn-Tucker conditions. Therefore, a brief description follows.

9.2.1 Karush-Kuhn-Tucker Approach

Consider the bilevel linear programming problem. At fixed $\boldsymbol{x}$, the necessary and sufficient conditions for $(\boldsymbol{y}^*, \lambda^*, \mu^*)$ to be an optimal solution to the inner level problem is that the following set of optimality condition equations are satisfied:

$$\begin{aligned} \boldsymbol{A_2 x} + \boldsymbol{B_2 y}^* + \boldsymbol{s} &= \boldsymbol{b_2} \\ \boldsymbol{C_2 x} + \boldsymbol{D_2 y} &= \boldsymbol{e_2} \\ \boldsymbol{c_2} + \lambda^T \boldsymbol{B_2} + \mu^T \boldsymbol{D_2} &= \boldsymbol{0} \\ \lambda^{T*} \boldsymbol{s}^* &= \boldsymbol{0} \\ \lambda^*, \ \boldsymbol{s}^* &\geq \boldsymbol{0}. \end{aligned}$$

where λ^*, μ^* are, respectively, the KKT multiplier vectors of the inequality and equality constraints. It follows that the necessary and sufficient conditions for $(\boldsymbol{x}^*, \boldsymbol{y}^*, \lambda^*, \mu^*)$ to be the optimal solution of the BLPP, $(\boldsymbol{y}^*, \lambda^*, \mu^*)$ must satisfy the above conditions at fixed $\boldsymbol{x} = \boldsymbol{x}^*$ (Bard and Falk, 1982). From this line of reasoning, the bilevel programming problem can be transformed into a single level problem of the form:

$$\begin{aligned} \min_{\boldsymbol{x}\ \boldsymbol{y}} \quad & \boldsymbol{c_1^T x} + \boldsymbol{d_1^T y} \\ \text{s.t.} \quad & \\ & \boldsymbol{A_1 x} + \boldsymbol{B_1 y} \leq \boldsymbol{b_1} \\ & \boldsymbol{C_1 x} + \boldsymbol{D_1 y} = \boldsymbol{e_1} \\ & \boldsymbol{c_2} + \lambda^T \boldsymbol{B_2} + \mu^T \boldsymbol{D_2} = \boldsymbol{0} \\ & \boldsymbol{A_2 x} + \boldsymbol{B_2 y} + \boldsymbol{s} = \boldsymbol{b_2} \\ & \boldsymbol{C_2 x} + \boldsymbol{D_2 y} = \boldsymbol{e_2} \\ & \lambda^T \boldsymbol{s} = \boldsymbol{0}, \\ & \lambda, \ \boldsymbol{s} \geq \boldsymbol{0}, \\ & \ \boldsymbol{x} \in X, \ \boldsymbol{y} \in Y, \end{aligned}$$

Notice that even for the linear BLPP, the resulting problem is nonlinear and nonconvex due to the complementarity conditions. The complementarity conditions are difficult to handle by most of the commercial nonlinear codes.

9.2.2 Test Problem 1

This test problem is taken from Clark and Westerberg (1990a).

Formulation

Outer objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \; -x - 3y_1 + 2y_2$$

Inner objective function

$$\min_{\boldsymbol{y}} \; -y_1$$

Inner constraints

$$\begin{aligned} -y_1 &\leq 0 \\ y_1 &\leq 4 \\ -2x + y_1 + 4y_2 &\leq 16 \\ 8x + 3y_1 - 2y_2 &\leq 48 \\ -2x + y_1 - 3y_2 &\leq -12 \end{aligned}$$

Variable bounds

$$0 \leq x \leq 8$$
$$0 \leq \boldsymbol{y} \leq 4$$

Problem Statistics

No. of continuous variables	3
No. of inner variables	2
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	5
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: -13
- Inner objective function: -4
- Continuous variables

  $x = 5 \quad \boldsymbol{y} = (4, 2)^T$

9.2.3 Test Problem 2

This problem is taken from Liu and Hart (1994).

Formulation

Outer objective function

$$\min_{x,y} \ -x - 3y$$

Inner objective function

$$\min_{y} y$$

Inner Constraints

$$\begin{aligned} -y &\leq 0 \\ -x + y &\leq 3 \\ x + 2y &\leq 12 \\ 4x - y &\leq 12 \end{aligned}$$

Variable bounds

$$\begin{aligned} 0 &\leq x \\ 0 &\leq y \end{aligned}$$

Variable definition

Problem Statistics

No. of continuous variables	2
No. of inner variables	1
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	4
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: -16
- Inner objective function: 4
- Continuous variables

  $x = 4 \quad y = 4$
- Behavior

  The optimum is at a boundary feasible extreme point.

9.2.4 Test Problem 3

This problem is taken from Candler and Townsley (1982)

Outer objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \; 4y_1 - 40y_2 - 4y_3 - 8x_1 - 4x_2$$

Inner objective function

$$\min_{\boldsymbol{y}} \; y_1 + y_2 + 2y_3 + x_1 + 2x_2$$

Inner constraints

$$\begin{aligned} -\boldsymbol{y} &\leq 0 \\ \boldsymbol{H_1}^T\boldsymbol{y} + \boldsymbol{H_2}^T\boldsymbol{x} &= \boldsymbol{b} \end{aligned}$$

where

$$\boldsymbol{H}_1 = \begin{bmatrix} -1 & 1 & 1 & 1 & 0 & 0 \\ -1 & 2 & -0.5 & 0 & 1 & 0 \\ 2 & -1 & -0.5 & 0 & 0 & 1 \end{bmatrix}$$

$$\boldsymbol{H}_2 = \begin{bmatrix} 0 & 0 \\ 2 & 0 \\ 0 & 2 \end{bmatrix}$$

and $\boldsymbol{b}^T = (1, 1, 1)$.

Variable bounds

$$\begin{aligned} 0 &\leq \boldsymbol{x} \\ 0 &\leq \boldsymbol{y} \end{aligned}$$

Problem Statistics

No. of continuous variables	8
No. of inner variables	6
No. of outer variables	2
No. of linear inner equalities	3
No. of linear inner inequalities	6
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: 29.2
- Inner objective function: 3.2
- Continuous variables

$$\begin{aligned} \boldsymbol{x} &= (0, 0.9)^T \\ \boldsymbol{y} &= (0, 0.6, 0.4, 0, 0, 0)^T \end{aligned}$$

9.2.5 Test Problem 4

This test problem is taken from Clark and Westerberg (1988), and has been used for testing purposes in Chen and Florian (1995) and Yezza (1996).

Formulation

Outer objective function

$$\min_{x,y} \; x - 4y$$

Inner objective function

$$\min_{y} \; y$$

Inner constraints

$$\begin{aligned} -2x + y &\leq 0 \\ 2x + 5y - 108 &\leq 0 \\ 2x - 3y + 4 &\leq 0 \end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of inner variables	1
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	3
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: -37
- Inner objective function: 14
- Continuous variables

  $x = 19 \quad \mathrm{y} = 14$
- Behavior

  The global maximum of the problem occurs at $(1, 2)$.

9.2.6 Test Problem 5

This problem is taken from Bard (1991), and has also been used in Shimizu et al. (1997).

Outer objective function

$$\min_{x,\boldsymbol{y}} \; -x + 10y_1 - y_2$$

Inner objective function

$$\min_{\boldsymbol{y}} \; -y_1 - y_2$$

Inner constraints

$$\begin{aligned} x - y_1 &\leq 1 \\ x + y_2 &\leq 1 \\ y_1 + y_2 &\leq 1 \\ -y_1 &\leq 0 \\ -y_2 &\leq 0 \end{aligned}$$

Variable bounds

$$0 \le x$$
$$0 \le \boldsymbol{y}$$

Problem Statistics

No. of continuous variables	3
No. of inner variables	2
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	5
No. of outer equalities	0
No. of outer inequalities	-

Best Known Solution

- Outer objective function: -1
- Inner objective function: 0
- Continuous variables

  $x = 1 \quad \boldsymbol{y} = (0, 0)^T$

9.2.7 Test Problem 6

This test problem is taken from Anandalingam and White (1990), and is slightly different that its original version given by Bialas (1982).

Formulation

Outer objective function

$$\min_{x,y} \; -x - 3y$$

Inner objective function

$$\min_{y} \; -x + 3y$$

Inner constraints

$$\begin{aligned}
-x - 2y &\leq -10 \\
x + 2y &\leq 6 \\
2x - y &\leq 21 \\
x + 2y &\leq 38 \\
-x + 2y &\leq 18 \\
-y &\leq 0
\end{aligned}$$

Variable bounds

$$\begin{aligned}
0 &\leq x \\
0 &\leq y
\end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of inner variables	1
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	6
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: -49
- Inner objective function: 17
- Continuous variables

  $x = 16 \quad y = 11$

9.2.8 Test Problem 7

This test problem is taken from Bard and Falk (1982), and is also used in Shimizu et al. (1997) and Bard and Moore (1990).

Formulation

Outer objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \; -8x_1 - 4x_2 + 4y_1 - 40y_2 + 4y_3$$

Inner objective function

$$\min_{\boldsymbol{y}} \; x_1 + 2x_2 + y_1 + y_2 + 2y_3$$

Inner Constraints

$$\begin{aligned}
-y_1 + y_2 + y_3 &\leq 1 \\
2x_1 - y_1 + 2y_2 - 0.5y_3 &\leq 1 \\
2x_2 + 2y_1 - y_2 - 0.5y_3 &\leq 1 \\
-y_1 &\leq 0 \\
-y_2 &\leq 0 \\
-y_3 &\leq 0
\end{aligned}$$

Variable bounds

$$\begin{aligned}
0 &\leq \boldsymbol{x} \\
0 &\leq \boldsymbol{y}
\end{aligned}$$

Problem Statistics

No. of continuous variables	5
No. of inner variables	3
No. of outer variables	2
No. of linear inner equalities	-
No. of linear inner inequalities	6
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: -26.0
- Inner objective function: 3.2
- Continuous variables
  $\boldsymbol{x} = (0.0, 0.9)^T \quad \boldsymbol{y} = (0.0, 0.6, 0.4)^T$

9.2.9 Test Problem 8

This problem is taken from Bard and Falk (1982).

Formulation

Outer objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \; -2x_1 + x_2 + 0.5y_1$$

Inner objective function

$$\min_{\boldsymbol{y}} \; x_1 + x_2 - 4y_1 + y_2$$

Inner Constraints

$$\begin{aligned} -2x_1 + y_1 - y_2 &\leq -2.5 \\ x_1 - 3x_2 + y_2 &\leq 2 \\ x_1 + x_2 &\leq 2 \end{aligned}$$

Variable bounds

$$\begin{aligned} 0 &\leq \boldsymbol{x} \\ 0 &\leq \boldsymbol{y} \end{aligned}$$

Variable definition

Problem Statistics

No. of continuous variables	4
No. of inner continuous variables	2
No. of outer continuous variables	2
No. of outer equalities	-
No. of outer inequalities	-
No. of inner equalities	-
No. of inner inequalities	3

Optimum solution

- Outer objective function: -1.75
- Inner objective function: 0.0
- Continuous variables

  $\boldsymbol{x} = (1, 0)^T \quad \boldsymbol{y} = (0.5, 1)^T$

  Two other local solutions exist, each occuring at different vertices.

9.2.10 Test Problem 9

This test problem is taken from Visweswaran et al. (1996).

Outer objective function

$$\min_{x,y} \; x + y$$

Inner objective function

$$\min_{y} \; -5x - y$$

Inner Constraints

$$\begin{aligned} -x - 0.5y &\leq -2 \\ -0.25x + y &\leq 2 \\ x + 0.5y &\leq 8 \\ x - 2y &\leq 2 \\ -y &\leq 0 \end{aligned}$$

Variable bounds

$$\begin{aligned} 0 &\leq x \\ 0 &\leq y \end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of inner variables	1
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	5
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: 3.111
- Inner objective function: 6.667
- Continuous variables

  $x = 0.889 \quad y = 2.222$

9.2.11 Test Problem 10

This test problem is taken from Tuy et al. (1993).

Formulation

Outer objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \; -2x_1 + x_2 + 0.5y_1$$

Inner objective function

$$\min_{\boldsymbol{y}} \; -4y_1 + y_2 + x_1 + x_2$$

Inner constraints

$$\begin{aligned} -2x_1 + y_1 - y_2 &\leq -2.5 \\ x_1 - 3x_2 + y_2 &\leq 2 \\ -y_1 &\leq 0 \\ -y_2 &\leq 0 \end{aligned}$$

Variable bounds

$$\begin{gathered} 0 \leq \boldsymbol{x} \\ 0 \leq \boldsymbol{y} \end{gathered}$$

Problem Statistics

No. of continuous variables	4
No. of inner variables	2
No. of outer variables	2
No. of linear inner equalities	-
No. of linear inner inequalities	4
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: -3.25
- Inner objective function: -7.0

- Continuous variables

  $\boldsymbol{x} = (2,0)^T \quad \boldsymbol{y} = (1.5,0)^T$

- Behavior

  In the paper in which this problem is originally posed, a non-optimal solution is located at $\boldsymbol{x} = (1,0), \boldsymbol{y} = (0.5,1)$ with an outer objective function value of -1.75 (Bard and Falk, 1982).

9.3 Bilevel Quadratic Programming Problems

9.3.1 Introduction

The linear-quadratic and quadratic-quadratic bilevel optimization problems are of the form:

$$
\begin{aligned}
\min_{\boldsymbol{x},\, \boldsymbol{y}} \quad & F(\boldsymbol{x}, \boldsymbol{y}) \\
\text{s.t.} \quad & \\
& \boldsymbol{A_1 x} + \boldsymbol{B_1 y} \leq \boldsymbol{b_1} \\
& \boldsymbol{C_1 x} + \boldsymbol{D_1 y} = \boldsymbol{e_1} \\
& \min_{\boldsymbol{y}} \boldsymbol{c_2^T x} + \boldsymbol{d_2^T y} + \boldsymbol{x^T Q_1^2 y} + \boldsymbol{y^T Q_2^2 y} \\
& \text{s.t.} \\
& \qquad \boldsymbol{A_2 x} + \boldsymbol{B_2 y} \leq \boldsymbol{b_2} \\
& \qquad \boldsymbol{C_2 x} + \boldsymbol{D_2 y} = \boldsymbol{e_2} \\
& \quad \boldsymbol{x} \in X \subseteq R^{n1}, \quad \boldsymbol{y} \in Y \subseteq R^{n2}
\end{aligned}
$$

where for the linear-quadratic case $F(\boldsymbol{x}, \boldsymbol{y}) = \boldsymbol{c_1^T x} + \boldsymbol{d_1^T y}$ and for the quadratic-quadratic case $F(\boldsymbol{x}, \boldsymbol{y}) = \boldsymbol{c_1^T x} + \boldsymbol{d_1^T y} + \boldsymbol{x^T Q_1^1 y} + \boldsymbol{y^T Q_2^1 y}$ and the inner objective is assumed to be a convex quadratic function. Replacing the inner problem with the necessary and sufficient KKT optimality conditions results in the single level problem:

$$
\begin{aligned}
\min_{\boldsymbol{x},\, \boldsymbol{y}} \quad & F(\boldsymbol{x}, \boldsymbol{y}) \\
\text{s.t.} \quad & \\
& \boldsymbol{A_1 x} + \boldsymbol{B_1 y} \leq \boldsymbol{b_1} \\
& \boldsymbol{C_1 x} + \boldsymbol{D_1 y} = \boldsymbol{e_1} \\
& 2\boldsymbol{y^T Q_2^2} + \boldsymbol{x^T Q_1^2} + \boldsymbol{c_2} + \lambda^T \boldsymbol{B_2} + \mu^T \boldsymbol{D_2} = \boldsymbol{0} \\
& \boldsymbol{A_2 x} + \boldsymbol{B_2 y} + \boldsymbol{s} = \boldsymbol{b_2} \\
& \boldsymbol{C_2 x} + \boldsymbol{D_2 y} = \boldsymbol{e_2} \\
& \lambda^T \boldsymbol{s} = \boldsymbol{0}, \\
& \lambda, \ \boldsymbol{s} \geq \boldsymbol{0}, \\
& \ \boldsymbol{x} \in X, \ \boldsymbol{y} \in Y.
\end{aligned}
$$

9.3.2 Test Problem 1

This problem is the simplest version of the quadratic-quadratic BLPP, where F is strictly convex, G is convex, f is quadratic and g is affine (Shimizu et al., 1997).

Formulation

Outer objective function

$$\min_{x,y} \; (x-5)^2 + (2y+1)^2$$

Inner objective function

$$\min_{y} \; (y-1)^2 - 1.5xy$$

Inner constraints

$$\begin{aligned} -3x + y &\leq -3 \\ x - 0.5y &\leq 4 \\ x + y &\leq 7 \end{aligned}$$

Variable bounds

$$\begin{gathered} 0 \leq x \\ 0 \leq y \end{gathered}$$

Problem Statistics

No. of continuous variables	2
No. of continuous outer variables	1
No. of continuous inner variables	1
No. of linear outer equalities	-
No. of convex outer inequalities	-
No. of linear inner equalities	3
No. of linear inner inequalities	-
No. of convex inner inequalities	-

Best Known Solution

- Outer objective function: 17
- Inner objective function: 1
- Continuous variables

  $x = 1, y = 0$

9.3.3 Test Problem 2

This test problem is taken from Visweswaran et al. (1996), and is originally from Shimizu and Aiyoshi (1981).

Formulation

Outer objective function

$$\min_{x,y} \; x^2 + (y - 10)^2$$

Inner objective function

$$\min_{y} \; (x + 2y - 30)^2$$

Outer constraints

$$-x + y \leq 0$$

Inner constraints

$$\begin{aligned} x + y &\leq 20 \\ -y &\leq 0 \\ y &\leq 20 \end{aligned}$$

Variable bounds

$$\begin{gathered} 0 \leq x \leq 15 \\ 0 \leq y \leq 20 \end{gathered}$$

Problem Statistics

No. of continuous variables	2
No. of inner variables	1
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	3
No. of linear outer equalities	-
No. of linear outer inequalities	1

Best Known Solution

- Outer objective function: 100.0
- Inner objective function: 0.0
- Continuous variables

  $x = 10.0 \quad y = 10.0$

9.3.4 Test Problem 3

This test problem is taken from Visweswaran et al. (1996).

Formulation

Outer objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \ 2x_1 + 2x_2 - 3y_1 - 3y_2 - 60$$

Inner objective function

$$\min_{\boldsymbol{y}} \ (y_1 - x_1 + 20)^2 + (y_2 - x_2 + 20)^2$$

Outer constraints

$$x_1 + x_2 + y_1 - 2y_2 - 40 \ \leq \ 0$$

Inner constraints

$$\begin{aligned} -x_1 + 2y_1 &\leq -10 \\ -x_2 + 2y_2 &\leq -10 \\ -y_1 &\leq 10 \\ y1 &\leq 20 \\ -y_2 &\leq 10 \\ y_2 &\leq 20 \end{aligned}$$

Variable bounds

$$\begin{gathered} 0 \leq x_1 \leq 50 \\ 0 \leq x_2 \leq 50 \\ -10 \leq y_1 \leq 20 \\ -10 \leq y_2 \leq 20 \end{gathered}$$

Problem Statistics

No. of continuous variables	4
No. of inner variables	2
No. of outer variables	2
No. of linear inner equalities	-
No. of linear inner inequalities	6
No. of nonlinear equalities	-
No. of nonconvex inequalities	1

Best Known Solution

- Outer objective function: 0
- Inner objective function: 200
- Continuous variables

  $\boldsymbol{x} = (0,0)^T \quad \boldsymbol{y} = (-10,-10)^T$

- Behavior

  The problem has a local solution at $\boldsymbol{x} = (25,30)^T$, $\boldsymbol{y} = (5,10)^T$ for which the outer objective function is 5. The paper in which this problem is presented originally locates this local optimum solution (Aiyoshi and Shimizu, 1984). Shimizu et al. (1997) also report its local minimum as the solution of the problem.

9.3.5 Test Problem 4

This test problem is taken from Yezza (1996).

Formulation

Outer objective function

$$\min_{x,\boldsymbol{y}} \; 0.5((y_1 - 2)^2 + (y_2 - 2)^2)$$

Inner objective function

$$\min \; 0.5y_1^2 + y_2$$

Inner constraints

$$\begin{aligned} y_1 + y_2 &= x \\ -y_1 &\leq 0 \\ -y_2 &\leq 0 \end{aligned}$$

Variable bounds

$$0 \leq \boldsymbol{y}$$

Problem Statistics

No. of continuous variables	3
No. of inner variables	2
No. of outer variables	1
No. of linear inner equalities	1
No. of linear inner inequalities	2
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: 0.5
- Inner objective function: 2.5
- Continuous variables
  $x = 3 \quad \boldsymbol{y} = (1, 2)^T$

9.3.6 Test Problem 5

This problem is taken from Clark and Westerberg (1990a).

Formulation

Outer objective function

$$\min_{x,y} \; (x-3)^2 + (y-2)^2$$

Inner objective function

$$\min_{y} \; (y-5)^2$$

Inner constraints

$$\begin{aligned} -2x + y &\leq 1 \\ x - 2y &\leq 2 \\ x + 2y &\leq 14 \end{aligned}$$

Variable bounds

$$0 \leq x \leq 8$$

Problem Statistics

No. of continuous variables	2
No. of inner variables	1
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	3
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: 5
- Inner objective function: 4
- Continuous variables

  $x = 1 \quad y = 3$

9.3.7 Test Problem 6

This test problem is taken from Falk and Liu (1995).

Formulation

Outer objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} x_1^2 - 2x_1 + x_2^2 - 2x_2 + y_1^2 + y_2^2$$

Inner objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} (y_1 - x_1)^2 + (y_2 - x_2)^2$$

Inner constraints

$$\begin{aligned} -y_1 &\leq -0.5 \\ -y_2 &\leq -0.5 \\ y_1 &\leq 1.5 \\ y_2 &\leq 1.5 \end{aligned}$$

Variable bounds

$$0 \leq \boldsymbol{y}$$

Problem Statistics

No. of continuous variables	4
No. of inner variables	2
No. of outer variables	2
No. of linear inner equalities	-
No. of linear inner inequalities	4
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: -1
- Inner objective function: 0

- Continuous variables

  $\boldsymbol{x} = (0.5, 0.5)^T \quad \boldsymbol{y} = (0.5, 0.5)^T$

- Behavior

  The same problem with the outer problem objective:

$$\min_{\boldsymbol{x},\boldsymbol{y}} \; y_1^2 - 3y_1 + y_2^2 - 3y_2 + x_1^2 + x_2^2$$

  has its optimum solution at $\boldsymbol{x} = (0.5\sqrt{3}, 0.5\sqrt{3}, 0.5\sqrt{3}, 0.5\sqrt{3})^T$

9.3.8 Test Problem 7

This test problem is taken from Visweswaran et al. (1996).

Formulation

Outer objective function

$$\min_{x,y} \; (x-5)^2 + (2y+1)^2$$

Inner objective function

$$\min_{y} \; (y-1)^2 - 1.5xy$$

Inner constraints

$$\begin{aligned} -3x + y &\leq -3 \\ x - 0.5y &\leq 4 \\ x + y &\leq 7 \\ -y &\leq 0 \end{aligned}$$

Variable bounds

$$\begin{aligned} 0 &\leq x \\ 0 &\leq y \end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of inner variables	1
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	4
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: 17
- Inner objective function: 1
- Continuous variables

  $x = 1 \quad y = 0$

- Behavior

  The problem also has a local solution at (5, 2).

9.3.9 Test Problem 8

This test problem is taken from Yezza (1996).

Formulation

Outer objective function

$$\min_{x,y} \; -(4x-3)y + (2x+1)$$

Inner objective function

$$\min_{y} \; -(1-4x)y - (2x+2)$$

Inner constraints

$$\begin{aligned} -y &\leq 0 \\ y &\leq 1 \end{aligned}$$

Variable bounds

$$0 \leq x \leq 1$$
$$0 \leq y \leq 1$$

Problem Statistics

No. of continuous variables	2
No. of inner variables	1
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	2
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: 1.5
- Inner objective function: -2.5
- Continuous variables

  $x = 0.25 \quad y = 0$

9.3.10 Test Problem 9

This test problem is taken from Bard (1991).

Formulation

Outer objective function

$$\min_{x,\boldsymbol{y}} \; x + y_2$$

Inner objective function

$$\min_{\boldsymbol{y}} \; 2y_1 + xy_2$$

Inner constraints

$$\begin{aligned} x - y_1 - y_2 &\leq 0 \\ -y_1 &\leq 0 \\ -y_2 &\leq 0 \end{aligned}$$

<u>Variable bounds</u>

$$0 \leq x$$
$$0 \leq \boldsymbol{y}$$

Problem Statistics

No. of continuous variables	1
No. of inner variables	2
No. of outer variables	1
No. of linear inner equalities	-
No. of linear inner inequalities	3
No. of linear outer equalities	-
No. of linear outer inequalities	-

Best Known Solution

- Outer objective function: 2
- Inner objective function: 12
- Continuous variables

  $x = 2 \quad \boldsymbol{y} = (6, 0)^T.$

Chapter 10

Complementarity Problems

10.1 Introduction

A complementarity problem aims at determining $\boldsymbol{x} \in \Re^n$, such that

$$\boldsymbol{x} \geq \boldsymbol{0}, \quad \boldsymbol{F}(\boldsymbol{x}) \geq \boldsymbol{0}, \quad \perp$$

where $\boldsymbol{F} : \Re^n \rightarrow \Re^n$ and the symbol $\perp$ denotes orthogonality, that is,

$$\boldsymbol{x}^T \boldsymbol{F}(\boldsymbol{x}) = 0.$$

Applications of the complementarity problem are quite extensive and diverse, covering areas of mathematical programming, game theory, economics and engineering. The linear complementarity problem is applied to the development of theory and algorithms in linear programming, quadratic programming and bimatrix game problems, where the quadratic programming problems have been extensively used in science and engineering for the solution of the contact, porous flow, obstacle, journal bearing, elastic-plastic torsion, circuit simulation, and other free boundary problems (Luo et al., 1997; Isac, 1992; Cottle et al., 1992; Murty, 1988). The nonlinear complementarity problem applications include the solution of Nash equilibrium, traffic assignment or network equilibrium, spatial price equilibrium and the general or Walrasian equilibrium problems (Harker and Pang, 1990).

A large collection of complementarity test problems, referred as the Mixed Complementarity Problems LIBrary, MCPLIB, is publicly available via anonymous ftp from

`ftp.cs.wisc.edu:~/pub/mcplib/`

and are presented in GAMS modeling language (Brooke et al., 1988). The origin and structure of the problems in MCPLIB, and additional information is given in Dirkse and Ferris (1995). Furthermore, the standard GAMS distribution (Brooke et al., 1988) includes a library of test problems that is also available from

C. A. Floudas et al., *Handbook of Test Problems in Local and Global Optimization*

`http://www.gams.com/modlib/modlib.htm`

Both collections contain problems with known types of computational difficulties or real life applications. A testing environment consisting of many test problems from both libraries, along with GAMS and MATLAB interfaces, and a comparison of eight large mixed complementarity problem solution algorithm implementations is included in Billups et al. (1997). Selected test problems from both libraries are presented here.

10.2 Linear Complementarity Problems

Let $\boldsymbol{M}$ be a square matrix in $\Re^{n\times n}$ and $\boldsymbol{q}$ be a column vector in $\Re^n$. Then, the linear complementarity problem, LCP, is to find a vector $\boldsymbol{x} \in \Re^n$ such that

$$\boldsymbol{x}^T(\boldsymbol{q} + \boldsymbol{M}\boldsymbol{x}) = 0$$

$$\boldsymbol{x} \geq \boldsymbol{0}, \quad (\boldsymbol{q} + \boldsymbol{M}\boldsymbol{x}) \geq \boldsymbol{0}$$

and is denoted by the symbol $(\boldsymbol{q}, \boldsymbol{M})$. For each $\boldsymbol{q} \in \Re^n$, the LCP $(\boldsymbol{q}, \boldsymbol{M})$ has a unique solution if and only if all the principal minors of $\boldsymbol{M} \in \Re^{n\times n}$ are positive (i.e., $\boldsymbol{M}$ is a P-matrix).

For the solution of small to medium size linear complementarity problems, pivoting methods have been proposed, while for large scale LCPs, iterative methods have been developed. The pivoting algorithms include principal pivoting method (Dantzig and Cottle, 1967; Cottle and Dantzig, 1968; Graves, 1967) and Lemke and Howson's complementary pivoting algorithm (Lemke and Howson, 1964) that is originally developed for obtaining the Nash equilibrium points for bimatrix games. An extension of this algorithm addresses the solution of general linear complementarity problems (Lemke, 1968). Iterative methods have been applied to the analysis of elastic bodies in contact, free boundary problem for journal bearings and network equilibrium problems (Cottle et al., 1992). Most of the linear complementarity problem solution algorithms make use of the properties of the matrix $\boldsymbol{M}$.

10.2.1 Test Problem 1

This test problem is taken from MCPLIB (Dirkse and Ferris, 1995).

Formulation

$\boldsymbol{M}$ Matrix

$$M = \begin{bmatrix} 1 & 2 & 2 & \dots & 2 \\ 0 & 1 & 2 & \dots & 2 \\ & & \cdot & & \cdot & 2 \\ & & & \cdot & \cdot & 2 \\ & & & & 1 & 2 \\ & & & & & 1 \end{bmatrix}$$

$\underline{q \text{ vector}}$

$q_i = -1, \ i = 1, .., 16.$

Problem Statistics

No. of continuous variables	16
No. of linear functions	16
No. of known solutions	1

Best Known Solution

- Continuous variables

  $x = (0, 0, 0, .., 0, 1)^T.$

- Behavior

  It was proven by Murty (1988) that the number of pivots in Lemke's algorithm is exponential in the number of problem variables.

10.2.2 Test Problem 2

This test problem is taken from Cottle et al. (1992).

Formulation

$\underline{M \text{ Matrix}}$

$$M = \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}$$

$\underline{q \text{ vector}}$

$q_i = -1, i = 1, 2.$

Problem Statistics

No. of continuous variables	2
No. of linear functions	2
No. of known solutions	3

Best Known Solution

- Continuous variables

  Solution 1: $\boldsymbol{x} = (1, 0)^T$
  Solution 2: $\boldsymbol{x} = (0, 1)^T$
  Solution 3: $\boldsymbol{x} = (\frac{1}{2}, \frac{1}{2})^T$

- Behavior

  LCPs with positive semi-definite $\boldsymbol{M}$ may have multiple solutions. This problem has three solutions that are all given above.

10.2.3 Test Problem 3

This test problem is taken from Cottle et al. (1992).

Formulation

$\boldsymbol{M}$ Matrix

$$\boldsymbol{M} = \begin{bmatrix} 0 & -1 & 2 \\ 2 & 0 & -2 \\ -1 & 1 & 0 \end{bmatrix}$$

$\boldsymbol{q}$ vector

$$\boldsymbol{q} = (-3, 6, -1)^T$$

Problem Statistics

No. of continuous variables	3
No. of linear functions	3
No. of known solutions	1

Best Known Solution

- Continuous variables

  $\boldsymbol{x} = (0, 1, 3)^T$

- Behavior

  Note that the matrix $\boldsymbol{M}$ is sufficient.

10.2.4 Bimatrix Games

The LCP formulation is applied to the solution of bimatrix games.

Bimatrix Formulation

$$-\boldsymbol{e}_m + \boldsymbol{A}\boldsymbol{y} \geq \boldsymbol{0}, \quad \boldsymbol{x} \geq \boldsymbol{0}, \quad \perp$$

$$-\boldsymbol{e}_n + \boldsymbol{B}^T\boldsymbol{x} \geq \boldsymbol{0}, \quad \boldsymbol{y} \geq \boldsymbol{0}, \quad \perp.$$

where **A** and **B** are positive $m \times n$ matrices and $\boldsymbol{e}_m$ and $\boldsymbol{e}_n$ are vectors with every component equal to one.

LCP Formulation

$\underline{\boldsymbol{M}\text{ Matrix}}$

$$\boldsymbol{M} = \begin{bmatrix} \boldsymbol{0} & \boldsymbol{A} \\ \boldsymbol{B}^T & \boldsymbol{0} \end{bmatrix}$$

$\underline{\boldsymbol{q}\text{ vector}}$

$$\boldsymbol{q} = (-\boldsymbol{e}_m, -\boldsymbol{e}_n)^T.$$

10.2.5 Test Problem 4

This test problem is taken from Cottle et al. (1992) and is a bimatrix game with:

$$\boldsymbol{A} = \boldsymbol{B}^T = \begin{bmatrix} 10 & 20 \\ 30 & 15 \end{bmatrix}$$

LCP Formulation

$\underline{\boldsymbol{M}\text{ Matrix}}$

$$\boldsymbol{A} = \boldsymbol{B}^T = \begin{bmatrix} 0 & 0 & 10 & 20 \\ 0 & 0 & 30 & 15 \\ 10 & 20 & 0 & 0 \\ 30 & 15 & 0 & 0 \end{bmatrix}$$

$\underline{\boldsymbol{q}\text{ vector}}$

$$\boldsymbol{q}^T = (-1, -1, -1, -1)^T$$

Problem Statistics

No. of continuous variables	4
No. of linear functions	4
No. of known solutions	3

Best Known Solution

- Continuous variables

  Solution 1: $\boldsymbol{x} = (\frac{1}{10}, 0, \frac{1}{10}, 0)^T$
  Solution 2: $\boldsymbol{x} = (0, \frac{1}{15}, 0, \frac{1}{15})^T$
  Solution 3: $\boldsymbol{x} = (\frac{1}{90}, \frac{2}{45}, \frac{1}{90}, \frac{2}{45})^T$

- Behavior

  The third solution point can not be achieved by the application of the Lemke-Howson algorithm (Cottle et al., 1992).

10.2.6 Equilibrium Transportation Model

Dantzig's equilibrium transportation model at fixed supply and demand (Dantzig, 1963) can be reformulated as a LCP.

Formulation

Zero profit conditions

$$\forall i \in I,\ j \in J \quad w_i - p_j + C_{ij} \geq 0, \quad \boldsymbol{x} \geq \boldsymbol{0} \quad \perp$$

Supply limit at plant i

$$\forall i \in I \quad -\sum_{j=1}^{J} x_{ij} + a_i \geq 0, \quad \boldsymbol{w} \geq \boldsymbol{0} \quad \perp$$

Fixed demand at market j

$$\forall j \in J \quad \sum_{i=1}^{I} x_{ij} - b_j \geq 0, \quad \boldsymbol{p} \geq \boldsymbol{0} \quad \perp$$

Variable Definition

- w_i - shadow price at supply node i
- p_j - shadow price at demand node j
- x_{ij} - shipment quantities in cases from supply i to demand j

Parameter Definition

- a_i - capacity of plant i in cases at unit price
- b_j - demand at market j in cases at unit price
- c_{ij} - transportation cost in thousands of dollars per case
- f - freight in dollars per case per thousand miles

10.2.7 Test Problem 5

This test problem of Dantzig's equilibrium transportation model is taken from GAMSLIB.

Data

$$\boldsymbol{a} = (325, 575)^T$$

$$\boldsymbol{b} = (325, 300, 275)^T$$

$$\boldsymbol{D} = \begin{bmatrix} 2.5 & 1.7 & 1.8 \\ 7.5 & 1.8 & 1.4 \end{bmatrix}$$

$$f = 90$$

$$\boldsymbol{C} = \frac{f\ \boldsymbol{D}}{1000}$$

Problem Statistics

No. of continuous variables	11
No. of linear functions	11

Best Known Solution

- Continuous variables

$$\boldsymbol{p} = (0.225, 0.153, 0.126)^T$$

$$\boldsymbol{w} = (0.0, 0.0)^T$$

$$\boldsymbol{x} = \begin{bmatrix} 25.0 & 300.0 & 0.0 \\ 300.0 & 0.0 & 275.0 \end{bmatrix}$$

10.2.8 Traffic Equilibrium Problem

The simplified traffic equilibrium model is taken from Cottle et al. (1992) where the transportation network is modeled as a digraph with nodes N and arcs A. The problem is to move $D > 0$ units of flow from origin node i to destination node j via specific paths in the network.

Formulation

Feasible path demand condition

$$\sum_{k=1}^{n} F_k = D$$

Traffic congestion cost on each arc

$$c_a(f) = b_a + d_a f_a, \ \forall a \in A$$

Arc-path relationship

$$f_a = \sum_{k_a} F_{k_a}, \ \forall a \in A$$

Arc-path incidence matrix

$$\Delta = (\delta_{ak}) \text{ where } \delta_{ak} = \begin{cases} 1 & \text{if arc } a \text{ is contained in path } p_k \\ 0 & \text{otherwise.} \end{cases}$$

Path Costs

$$C(F) = \Delta^T c(f) = \Delta^T b + \Delta^T D \Delta$$

Parameter Definition

- A - set of arcs
- N - set of nodes
- a - index on arcs
- i, j - indices on nodes
- b_a, d_a - scalars
- D - diag(d_a)

Variable Definition

- F_k - traffic flow along the path p_k $(k = 1, .., n)$

- F - path flows vector
- c_a - cost function
- f_a - flow on arc a
- G - minimum cost between O-D pair (i,j)

Explicit Formulation

$$\begin{array}{rcl} & F \geq 0, & \\ \sum_{k=1}^{n} F_k & = & D \\ C(F) - Ge & \geq & 0 \\ F_k(C_k(F) - G) & = & 0 \; k = 1,..,n. \end{array}$$

which is a mixed complementarity problem with a single equality constraint and a free variable G. This formulation can be turned into an LCP by transforming the equality constraint into an inequality, restricting G to be nonnegative, and imposing a complementarity constraint between G and the demand constraint.

10.2.9 Test Problem 6

This test problem is taken from Cottle et al. (1992). The traffic network is given in figure 10.1. There are 3 paths that join the O-D pair and the demand D between the O-D pair is 6, and the cost on arc e_{32} is parametric.

$\boldsymbol{M}$ Matrix

$$\boldsymbol{M} = \begin{bmatrix} \Delta^T D \Delta & -e \\ e^T & 0 \end{bmatrix}$$

$$= \begin{bmatrix} 11 & 0 & 10 & -1 \\ 0 & 11 & 10 & -1 \\ 10 & 10 & 21 & -1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$$

$\boldsymbol{q}$ vector

$$\boldsymbol{q} = (\Delta^T b, -D)^T = (50, 50, \lambda, -6)^T$$

Problem Statistics

No. of continuous variables	4
No. of linear functions	4
No. of known solutions	parametric

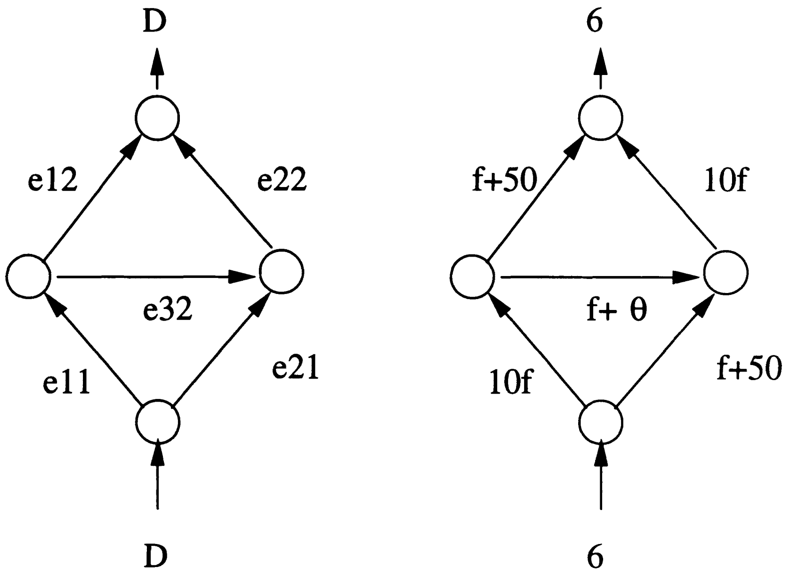


Figure 10.1: Traffic Network

Best Known Solution

- Continuous variables

  For $\lambda \in [0, 23]$
  $F_1 = F_2 = \frac{(\lambda+16)}{13}, F_3 = \frac{2(23-\lambda)}{13}, G = \frac{(1286-9\lambda)}{13}$
  For $\lambda \geq 23$,
  $F_1 = F_2 = 3, F_3 = 0, G = 83.$

10.3 Nonlinear Complementarity Problems

Let $F : \Re^n \to \Re^n$. Then, the Nonlinear Complementarity Problem , NCP, is the problem of finding $\boldsymbol{x} \in \Re^n$ that satisfies

$$\boldsymbol{x} \geq 0, \quad F(\boldsymbol{x}) \geq 0$$

$$\boldsymbol{x}^T F(\boldsymbol{x}) = 0.$$

For the solution of the nonlinear complementarity problems, reformulation of the original NCP as a minimization problem (Kanzow, 1996; Mangasarian and Solodov, 1993; More, 1996), as a nonlinear system of equations, or as a parametric problem have been proposed. Smoothing methods have also been developed for both linear and nonlinear complementarity problems (Chen and

Mangasarian, 1996). A review of theory, algorithms and applications of NCPs is given in Ferris and Pang (1997). For a brief description of many of NCP applications, see Luo et al. (1997), Harker and Pang (1990) and Nagurney (1993).

10.3.1 Test Problem 1

This test problem is taken from MCPLIB (Dirkse and Ferris, 1995) .

Formulation

Function

$$F(x) = \arctan(x - s)$$

$$s = 10$$

Problem Statistics

No. of continuous variables	1
No. of linear functions	-
No. of nonlinear functions	1
No. of known solutions	1

Best Known Solution

- Continuous variables

  $x = 10$

- Behavior

  If $s \geq$ 1.39174521, cycling may occur in Lemke's algorithm.

10.3.2 Test Problem 2

This problem is taken from Dirkse and Ferris (1995) and is originally from Kojima and Shindo (1986).

Formulation

Function

$$\boldsymbol{F}(\boldsymbol{x}) = \begin{bmatrix} 3x_1^2 + 2x_1x_2 + 2x_2^2 + x_3 + 3x_4 - 6 \\ 2x_1^2 + x_2^2 + x_1 + 10x_3 + 2x_4 - 2 \\ 3x_1^2 + x_1x_2 + 2x_2^2 + 2x_3 + 9x_4 - 9 \\ x_1^2 + 3x_2^2 + 2x_3 + 3x_4 - 3 \end{bmatrix}$$

Problem Statistics

No. of continuous variables	4
No. of linear functions	0
No. of nonlinear functions	4
No. of known solutions	2

Best Known Solution

- Continuous variables

  Solution 1: $\boldsymbol{x} = (\sqrt{6}/2, 0, 0, 0.5)^T$
  Solution 2: $\boldsymbol{x} = (1, 0, 3, 0)$

- Behavior

  The difficulty in solving this problem arises when a Newton-type method is used, since the LCP formed by linearizing F around $x = 0$ has no solution.

10.3.3 Test Problem 3

This problem is from Pang and Gabriel (1993), (originally by Mathiesen (1987)) and describes a simple Walrasian equilibrium model for testing purposes. Mangasarian and Solodov (1993) have also used this problem to test their solution method.

Formulation

Functions

$$\boldsymbol{F}(\boldsymbol{x}) = \begin{bmatrix} -x_1 + x_2 + x_3 \\ x_4 - 0.75(x_2 + \beta x_3) \\ 1 - x_4 - 0.25(x_2 + \beta x_3)/x_2 \\ \beta - x_4 \end{bmatrix} \tag{1}$$

Problem Statistics

No. of continuous variables	4
No. of linear functions	2
No. of nonlinear functions	2
No. of known solutions	multiple

Best Known Solution

- Functions: For $\beta = 0.5$ $\boldsymbol{F}(\boldsymbol{x}) = (0, 0, 0, 0)^T$

  For $\beta = 2$ $\boldsymbol{F}(\boldsymbol{x}) = (0, 0, 0, 1.25)^T$

- Continuous variables

  For $\beta = 0.5$, $\boldsymbol{x} = (0.5, 4.83201, 1.61067, 3.22134)^T$

  For $\beta = 2$, $\boldsymbol{x} = (0.75, 0.78425, 0.78425, 0)^T$

  This problem has multiple nondegenerate solutions, of which two are given in Pang and Gabriel (1993) and recited above.

10.3.4 Nash Equilibrium

The Nash equilibrium problem formulation is taken from Murphy et al. (1982).

Formulation

Find a vector x^* such that $\forall i$:

$$\min_{\boldsymbol{x}} -x_i P(x_i + \sum_{j \neq i} x_j^* - f_i(x_i))$$

$$x_i \geq 0$$

which, when replaced by the equivalent Karush-Kuhn-Tucker conditions can be reformulated as an NCP problem.

NCP Formulation

$$\forall i, \quad \nabla f_i(x_i) - P(Q) - x_i \nabla p(Q) \geq 0, \quad x_i \geq 0, \quad \perp$$

Functions

Inverse demand function for the market

$$P(Q) = 5000^{\frac{1}{\gamma}} Q^{-\frac{1}{\gamma}}$$

Total cost function for firm i

$$f_i(x_i) = c_i x_i + (\frac{\beta_i}{(1+\beta_i)}) L_i^{\frac{1}{\beta_i}}$$

Parameter Definition

- c_i,L_i, β_i - scalar parameters
- γ - elasticity of demand with respect to price

Variable Definition

- P - market price
- x_i - output of firm i
- Q - total quantity produced, such that $\sum_i x_i = Q$

10.3.5 Test Problem 4

This test problem is taken from GAMSLIB and is used for testing purposes in Harker (1988), where Nash equilibrium of a 5-firm noncooperative game is modeled (Murphy et al., 1982; Harker, 1984). Another Nash equilibrium problem of firms differentiated by the product they produce instead of production costs is given in Choi et al. (1990) and included in MCPLIB (Dirkse and Ferris, 1995).

Data

$$\begin{aligned} \boldsymbol{c} &= (10.0, 8.0, 6.0, 4.0, 2.0)^T \\ \boldsymbol{L} &= (5.0, 5.0, 5.0, 5.0, 5.0)^T \\ \boldsymbol{\beta} &= (1.2, 1.1, 1.0, 0.9, 0.8)^T \\ \gamma &= 1.1 \end{aligned}$$

Problem Statistics

No. of continuous variables	5
No. of linear functions	-
No. of nonlinear functions	5

Best Known Solution

- Continuous variables

  $\boldsymbol{x} = (36.933, 41.818, 43.707, 42.659, 39.179)^T$

- Behavior

  The solution reported above is taken from the GAMSLIB. The original paper by Murphy et al. (1982) reports very slightly different values.

10.3.6 Test Problem 5

This example problem is taken from MCPLIB (Dirkse and Ferris, 1995), and is also used for testing purposes in Harker (1988). This problem is the Cournot-Nash equilibrium problem with 10 firms.

Data

$$\begin{aligned} \boldsymbol{c} &= (5.0, 3.0, 8.0, 5.0, 1.0, 3.0, 7.0, 4.0, 6.0, 3.0)^T \\ \boldsymbol{L} &= (10.0, 10.0, 10.0, 10.0, 10.0, 10.0, 10.0, 10.0, 10.0, 10.0)^T \end{aligned}$$

$$\boldsymbol{\beta} = (1.2, 1.0, 0.9, 0.6, 1.5, 1.0, 0.7, 1.1, 0.95, 0.75)^T$$
$$\gamma = 1.2$$

Problem Statistics

No. of continuous variables	10
No. of linear functions	-
No. of nonlinear functions	10
No. of known solutions	1

Best Known Solution

- Continuous variables

  $\boldsymbol{x} = (7.442, 4.098, 2.591, 0.935, 17.949, 4.098, 1.305, 5.590, 3.222, 1.677)^T$

10.3.7 Invariant Capital Stock Problem

In the invariant capital capital stock problem, an economy is assumed to grow over an infinite number of time periods where the technology remains constant (Dirkse and Ferris, 1995). For more details on the problem, see Hansen and Koopmans (1972).

Formulation

$$\begin{aligned} \min_{\boldsymbol{x}_t, \boldsymbol{z}_t} - \sum_{t=0}^{\infty} \alpha^t v(\boldsymbol{x}_t) & \\ \text{s.t.} & \\ \boldsymbol{A}\boldsymbol{x}_t - \boldsymbol{z}_t & \leq \boldsymbol{0} \\ -\boldsymbol{B}\boldsymbol{x}_t + \boldsymbol{z}_{t+1} & \leq \boldsymbol{0} \\ \boldsymbol{C}\boldsymbol{x}_t - \boldsymbol{w} & \leq \boldsymbol{0} \\ \boldsymbol{x}_t \geq \boldsymbol{0}. & \end{aligned} \tag{2}$$

<u>NCP Formulation</u>

It is assumed that the objective function is convex and continuously differentiable.

$$\begin{aligned} -\nabla v(\boldsymbol{x}) + (\boldsymbol{A} - \alpha \boldsymbol{B})^T \boldsymbol{y} + \boldsymbol{C}^T \boldsymbol{u} \geq \boldsymbol{0}, &\quad \boldsymbol{x} \geq \boldsymbol{0}, \quad \perp \\ (\boldsymbol{B} - \boldsymbol{A})\boldsymbol{x} \geq \boldsymbol{0}, &\quad \boldsymbol{y} \geq \boldsymbol{0} \quad \perp \\ -\boldsymbol{C}\boldsymbol{x} + \boldsymbol{w} \geq \boldsymbol{0}, &\quad \boldsymbol{u} \geq \boldsymbol{0} \quad \perp \end{aligned}$$

<u>Parameter Definition</u>

- $\boldsymbol{A}$ - capital input matrix

- A_{ij} - units of capital good i required for running process j
- $\boldsymbol{B}$ - capital output matrix
- B_{ij} - units of capital good i produced for running process j
- $\boldsymbol{C}$ - resource input matrix
- C_{rj} - units of resource good r for running process j
- w - a constant on the resources available at the beginning of each time period
- α - discount factor $\alpha \in (0, 1)$.

Variable Definition

- x_j - activity level for production process j
- y_i - dual variable to capital input/output constraint on capital good i
- u_r - dual variable to resource constraint on resource type r
- v - utility function

10.3.8 Test Problem 6

This invariant capital stock problem is taken from MCPLIB (Dirkse and Ferris, 1995).

Data

$$v(\boldsymbol{x}) = (x_1 + 2.5x_2)^{0.2}(2.5x_3 + x_4)^{0.2}(2x_5 + 3x_6)^{0.2}$$

$$\boldsymbol{A} = \begin{pmatrix} 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 \\ 3 & 3 & 2 & 2 & 1 & 1 & 1 & 0.5 & 1 & 0.5 \end{pmatrix}$$

$$\boldsymbol{B} = \begin{pmatrix} 1.5 & 1.5 & 1.5 & 1.5 & 1.5 & 1.5 & 1.5 & 1.5 & 1.5 & 1.5 \\ 2.7 & 2.7 & 1.8 & 1.8 & 0.9 & 0.9 & 0.9 & 0.4 & 2 & 1.5 \end{pmatrix}$$

$$\boldsymbol{C} = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 0.5 & 1.5 & 1.5 & 0.5 & 0.5 & 1.5 & 1.5 & 0.5 & 0.5 & 1.5 \end{pmatrix}$$

$$p = 0.20$$
$$\alpha = 0.7$$
$$\boldsymbol{w} = (0.8, 0.8)^T$$

Problem Statistics

No. of continuous variables	14
No. of linear functions	4
No. of nonlinear functions	10

Best Known Solution

- Continuous variables

$\boldsymbol{x} = (0, 0.086, 0.111, 0, 0, 0.155, 0.107, 0, 0, 0.074)^T$
$\boldsymbol{y} = (0.359, 0.683)^T$
$\boldsymbol{u} = (0, 0.023)^T$

Chapter 11

Semidefinite Programming Problems

11.1 Introduction

Semidefinite programming involves the minimization of a linear function subject to the constraint that an affine combination of symmetric matrices is positive semidefinite. Several types of problems can be transformed to this form. This constraint is in general nonlinear and nonsmooth yet convex. Semidefinite programming can be viewed as an extension of linear programming and reduces to the linear programming case when the symmetric matrices are diagonal.

11.1.1 Problem formulation

The semidefinite programming problem can be expressed as:

$$\max_{\boldsymbol{y}} \boldsymbol{b}^T \boldsymbol{y}$$

$$\text{subject to} \quad \boldsymbol{A}_0 - \sum_{i=1}^{m} y_i \boldsymbol{A}_i \succeq \boldsymbol{0}$$

where the vector $\boldsymbol{y} \in \Re^m$ represents the decision variables, $\boldsymbol{b} \in \Re^m$ defines the objective function, and $\boldsymbol{A}_0, \ldots, \boldsymbol{A}_m$ are symmetric $n \times n$ matrices. The relation $\boldsymbol{A} \succeq \boldsymbol{B}$ where $\boldsymbol{A}$ and $\boldsymbol{B}$ are real symmetric matrices denotes $\boldsymbol{A} - \boldsymbol{B}$ as being positive semidefinite. The constraint in this problem is often referred to as a linear matrix inequality. Multiple linear matrix inequalities can be combined into a single block diagonal matrix inequality. The dual semidefinite programming problem can be expressed as:

C. A. Floudas et al., *Handbook of Test Problems in Local and Global Optimization*

$$\min_{\boldsymbol{X}} \boldsymbol{A}_0 \bullet \boldsymbol{X}$$

$$\text{subject to} \quad \boldsymbol{A}_i \bullet \boldsymbol{X} = b_i \quad \text{for } i = 1, \ldots, m$$

$$\boldsymbol{X} \succeq 0.$$

The $\bullet$ denotes the operation of taking the inner product of matrices, $\boldsymbol{A} \bullet \boldsymbol{B} := \sum_{i,j} A_{ij} B_{ij} = \text{trace } (\boldsymbol{A}^T \boldsymbol{B})$.

Provided both primal and dual programs are feasible and there is a strictly feasible point in either the primal or the dual, the optimal solution to the primal equals the optimal solution of the dual. In other words, if primal and dual optimal solutions are $\boldsymbol{X}^*$ and $(\boldsymbol{y}^*, \boldsymbol{S}^*)$ respectively, then $\boldsymbol{C} \bullet \boldsymbol{X}^* = \boldsymbol{b}^T \boldsymbol{y}^*$.

Approaches developed for the solution of SDP's include: the ellipsoid method (Yudin and Nemirovsky, 1977) (Nesterov, 1977), general methods for convex optimization (Hiriart-Urruty and Lemaréchal, 1993; Shor, 1985; Kiwiel, 1985) and interior point methods which are reviewed by Vandenberghe and Boyd (1996), Alizadeh (1995), and Pardalos and Wolkowicz (1998).

11.1.2 Semidefinite Programming Applications

The two main areas of application for semidefinite programming are in combinatorial optimization (Alizadeh, 1995; Ramana and Pardalos, 1996; Pardalos and Wolkowicz, 1998) and control theory (Boyd et al., 1994). Applications in combinatorial theory include:

- relaxation of the maximum cut problem;
- relaxation of the graph equipartition problem;
- relaxation of the maximum clique problem.

A set of maximum cut test problems generated by Helmberg and Rendl (1998) using G. Rinaldi's machine independent graph generator is available on the internet at:

`ftp://dollar.biz.uiowa.edu/pub/yyye/Gset`

These problems involve graphs having 800 to 3000 vertices.

Toh et al. (1998) provide MATLAB files to generate random instances of semidefinite programming applications. These files, available at:

`http://www.math.cmu.edu/~reha/sdpt3.html`

generate instances of the following problem types:

- maximum eigenvalue determination;
- matrix norm minimization;
- Chebychev approximation problem for a matrix;
- logarithmic Chebychev approximation;
- Chebychev approximation on the complex plane;
- control and system problem;
- relaxation of the maximum cut problem;
- relaxation of the stable set problem;
- the educational testing problem.

Other applications of semidefinite programming are (Vandenberghe and Boyd, 1996):

- pattern separation by ellipsoids;
- geometrical problems involving quadratic forms;
- truss topology design problems.

A library of semidefinite programming test problems SDPLIB can be found on the internet at

`http://www.nmt.edu/~borchers/sdplib.html`

A subclass of semidefinite programming problem is the second order cone problem:

$$\max_{\boldsymbol{y}} \boldsymbol{b}^T \boldsymbol{y}$$

$$\text{subject to } \|\boldsymbol{A}_i\boldsymbol{y} + \boldsymbol{f}_i\| \leq \boldsymbol{c}_i^T\boldsymbol{x} + d_i \quad i = 1, \dots, m,$$

where $\boldsymbol{x} \in \Re^n$, $\boldsymbol{b} \in \Re^n$, $\boldsymbol{A}_i \in \Re^{n_i \times n}$, $\boldsymbol{f} \in \Re^{n_i}$, and $\boldsymbol{c}_i \in \Re^n$. This type of problem may be posed as a semidefinite programming problem:

$$\max_{\boldsymbol{y}} \boldsymbol{b}^T \boldsymbol{y}$$

$$\text{subject to } \begin{bmatrix} (\boldsymbol{c}_i^T\boldsymbol{y} + d_i)\boldsymbol{I} & \boldsymbol{A}_i\boldsymbol{y} + \boldsymbol{f}_i \\ (\boldsymbol{A}_i\boldsymbol{y} + \boldsymbol{f}_i)^T & \boldsymbol{c}_i^T\boldsymbol{y} + d_i \end{bmatrix} \succeq \boldsymbol{0} \quad i = 1, \dots, m.$$

Applications of the second order cone problem include:

- antenna array weight design (Lebret and Boyd, 1997);

- robotic hand grasp force optimization (Buss et al., 1996);
- FIR filter design (Wu et al., 1996);
- portfolio optimization with loss risk constraints (Lobo et al., 1998);
- truss design (Ben-Tel and Bendsøe, 1993);
- equilibrium calculation of a system with piecewise linear springs (Lobo et al., 1998).

Second order cone programming test problems may be found on the internet at:

`http://www.princeton.edu/~rvdb/ampl/nlmodels/`

11.2 Educational Testing Problem

The educational testing problem (Fletcher, 1981a) involves the estimation of a measure of reliability of a student's total score in an examination that involves a number of subtests. Consider a class of n students who each take a set of m tests. Let X_{ij} represent the score obtained by student i on test j. As a measurement the score obtained will be subject to error:

$$X_{ij} = T_{ij} + N_{ij}.$$

Here T_{ij} and N_{ij} are respectively the "true" value and the "noise" associated with X_{ij}. Assume that the noise is uncorrelated with $\boldsymbol{T}$, has a zero mean and a diagonal covariance matrix $\boldsymbol{\Sigma}^{\boldsymbol{N}}$. The covariance matrix of $\boldsymbol{X}$, $\boldsymbol{\Sigma}^{\boldsymbol{X}}$, can then be written in terms of $\boldsymbol{\Sigma}$, the covariance matrix of $\boldsymbol{T}$ and, $\boldsymbol{\Sigma}^{\boldsymbol{N}}$:

$$\boldsymbol{\Sigma}^{\boldsymbol{X}} = \boldsymbol{\Sigma} + \boldsymbol{\Sigma}^{\boldsymbol{N}}.$$

The reliability of the examination is the quantity:

$$\rho = \frac{\boldsymbol{e}^T \boldsymbol{\Sigma} \boldsymbol{e}}{\boldsymbol{e}^T \boldsymbol{\Sigma}^{\boldsymbol{X}} \boldsymbol{e}},$$

where $\boldsymbol{e}$ is vector with all components equal to 1. If there is a large number of students we may estimate $\boldsymbol{\Sigma}^{\boldsymbol{X}}$. However $\boldsymbol{\Sigma}$ and $\boldsymbol{\Sigma}^{\boldsymbol{N}}$ are unknown. A lower bound on ρ may be obtained by using the fact that a covariance matrix is positive semidefinite and determining $\boldsymbol{\Sigma}^{\boldsymbol{N}}$ via the problem:

$$\begin{array}{ll} & \max\limits_{\boldsymbol{\Sigma}^{\boldsymbol{N}}} \ \mathrm{trace}(\boldsymbol{\Sigma}^{\boldsymbol{N}}) \\ \text{subject to} & \boldsymbol{\Sigma} - \boldsymbol{\Sigma}^{\boldsymbol{N}} \succeq \mathbf{0} \\ & \qquad \boldsymbol{\Sigma}^{\boldsymbol{N}} \succeq \mathbf{0}. \end{array}$$

11.2.1 General formulation

The test problems in this section are based on the tabulated data which originate from Woodhouse (1976). In the data table column j represents the scores obtained for subtest j and row i represents the scores obtained by student i.

Test problems are derived from this data by considering cases in which the overall examination is constituted by different subsets of tests. Let vector $\boldsymbol{v} = (v_1, \ldots, v_{m'})$, where $m' \leq m$, represent the subtests that are included in the overall examination. These problem definition vectors are given in the first column of the solution table. The covariance matrix $\boldsymbol{\Sigma}^{\boldsymbol{X}}$ for a given set of subtests $\boldsymbol{v}$ is defined as:

$$\Sigma_{jk}^{X} = \frac{1}{n-1} \sum_{i=1}^{n} (X_{iv_j} - \bar{X}_{v_k}) \tag{1}$$

where $\bar{X}_j = \sum_{i=1}^{n} x_{ij}/n$ is the mean score for subtest j.

Objective function

The objective function is the trace of the measurement noise covariance matrix.

$$\max_{\boldsymbol{y}} \boldsymbol{e}^T \boldsymbol{y}$$

where $\boldsymbol{e} \in \Re^m = (1, \ldots, 1)^T$ and $\boldsymbol{e}_i \in \Re^m$ is the ith unit vector.

Constraints

The covariance matrix $\boldsymbol{\Sigma}$ must be positive definite:

$$\boldsymbol{\Sigma}^{\boldsymbol{X}} - \sum_{i=1}^{m} y_i \boldsymbol{e}_i \boldsymbol{e}_i^T \succeq \boldsymbol{0}$$

where $\boldsymbol{e}_i \in \Re^m$ is the ith unit vector.

Variable bounds

The measurement noise covariance matrix $\boldsymbol{\Sigma}^{\boldsymbol{N}}$ must be positive semidefinite.

$$\boldsymbol{y} \geq \boldsymbol{0}$$

Variable definition

Scalar variable y_i represents the diagonal entry i of $\boldsymbol{\Sigma}^{\boldsymbol{N}}$.

Data

Data for all twelve educational testing problems is contained in the following table which defines the matrix $\boldsymbol{X}$ of the student scores for all the subtests.

Data for matrix X (student (i) by test (j))

15	25	20	28	35	50	21	18	22	28	28	12	15	40	18	23	14	16	15	10
21	27	32	32	41	42	30	35	33	32	64	16	24	38	34	13	15	17	28	18
23	35	40	22	55	48	36	40	46	18	38	18	26	37	24	24	17	20	19	26
23	29	50	36	42	52	44	32	24	19	32	24	20	46	32	23	11	12	40	38
34	37	42	19	36	46	17	26	35	28	39	54	21	47	29	42	18	18	30	20
36	60	70	45	55	54	32	30	32	29	41	28	20	47	36	28	20	20	18	24
36	35	46	27	50	40	60	34	39	46	48	63	20	48	40	19	21	24	40	22
38	70	44	50	45	42	20	28	29	16	55	40	22	49	42	25	23	26	30	28
39	46	52	24	37	60	53	30	46	43	54	54	23	46	44	22	35	22	48	30
40	74	65	60	72	41	33	36	24	52	64	36	28	50	46	26	25	23	30	30
40	48	32	23	58	52	23	40	37	24	58	38	29	54	44	28	11	27	41	34
41	12	24	50	47	48	41	42	37	28	56	57	32	51	43	25	17	24	32	39
46	52	76	48	70	58	20	50	28	42	76	58	28	58	45	34	27	35	18	56
46	73	84	63	38	57	33	56	42	18	72	77	21	52	48	32	35	32	32	19
47	42	74	28	60	57	36	42	48	52	63	46	36	53	49	53	29	30	42	40
47	82	72	70	39	64	21	25	44	26	44	44	37	51	46	33	38	35	37	42
47	40	42	50	48	61	40	40	26	29	61	44	30	56	47	52	46	27	48	40
48	70	65	48	42	57	35	58	50	46	60	32	34	58	54	35	36	31	16	18
49	65	60	55	62	56	52	50	52	28	50	48	34	58	53	41	45	40	38	52
50	30	35	28	62	54	41	46	50	21	65	33	32	58	54	38	50	44	43	50
52	42	54	33	42	64	40	40	56	44	64	38	34	60	44	34	38	30	44	38
52	72	70	65	72	68	62	38	56	44	58	46	56	58	46	36	55	20	48	47
52	44	64	72	44	62	35	44	56	46	62	39	30	61	46	38	40	42	24	80
53	25	42	28	68	52	41	45	44	26	28	43	51	62	47	35	42	48	50	40
54	48	60	58	36	51	63	41	64	29	63	49	32	58	47	39	43	58	48	49
55	64	62	30	42	57	34	47	52	34	57	37	43	63	48	38	47	20	54	65
58	30	24	62	51	51	44	36	43	25	36	54	41	65	48	43	40	35	50	42
58	16	40	45	42	58	44	42	58	36	58	52	40	64	49	36	18	45	53	28
58	44	56	51	68	68	46	48	72	38	62	34	32	68	49	42	47	47	28	70
39	58	58	50	74	52	36	58	60	28	44	56	34	72	51	33	48	58	54	58
60	32	35	48	40	56	52	32	40	37	72	57	36	61	52	51	42	46	17	51
60	78	80	62	52	54	58	47	80	32	64	39	45	66	53	42	70	40	50	18
60	38	55	66	42	52	30	54	62	42	90	38	38	63	56	46	62	48	55	44
61	48	64	68	70	53	42	40	38	45	73	56	50	64	54	46	45	42	50	22
62	86	94	50	49	62	48	56	74	33	84	36	52	67	52	47	41	70	57	53
63	35	38	55	38	58	46	59	63	48	62	58	38	68	53	47	48	75	44	25
64	79	65	76	68	57	32	33	52	46	72	62	52	54	54	48	55	35	60	54
64	50	52	35	60	56	52	64	76	36	63	44	48	56	52	49	63	38	48	46
65	37	42	70	50	58	58	62	66	34	53	64	62	72	53	50	74	45	62	57
65	82	74	63	36	62	60	58	60	38	57	63	58	70	51	51	55	55	64	58
67	44	46	54	52	58	55	68	80	40	28	65	50	71	54	52	65	70	74	68
67	48	56	80	44	64	62	35	70	62	58	72	56	72	60	41	78	38	75	68
68	62	78	56	50	53	62	54	80	64	62	48	54	74	62	76	58	45	80	36
69	39	30	42	38	62	40	32	68	56	68	71	58	73	56	43	79	47	73	70
70	52	20	76	69	61	64	56	69	54	64	66	58	78	52	72	32	47	71	71
72	54	72	38	54	51	66	65	76	72	54	49	60	74	57	42	68	62	22	46
72	42	48	70	70	57	42	40	68	53	62	74	60	78	58	52	55	48	72	75
74	64	66	70	42	60	40	78	53	48	69	67	76	77	59	68	58	55	16	60
78	68	62	63	35	56	63	80	74	43	71	78	62	76	59	68	70	75	72	75
79	37	42	28	64	52	40	38	72	72	56	52	58	82	60	61	75	66	58	58
80	62	30	65	59	51	68	57	74	48	78	71	42	54	61	62	78	69	78	58
82	85	80	52	44	57	70	69	64	71	85	76	64	56	63	67	44	70	60	26
82	40	74	52	52	64	74	64	76	46	64	46	51	80	63	68	65	55	70	67
84	42	76	70	55	61	90	80	56	41	58	82	72	72	67	73	85	60	76	78
84	42	54	60	42	58	42	60	52	70	77	68	68	74	59	71	79	65	44	75
86	85	88	80	37	63	80	72	79	42	73	42	68	82	65	73	85	62	80	82
87	53	51	62	68	56	60	42	78	42	62	74	62	84	65	75	63	75	68	83
89	41	60	40	60	54	88	88	83	57	84	64	64	80	62	65	90	78	88	52
90	73	78	77	52	42	56	50	58	59	72	84	70	84	62	63	82	85	78	87
90	81	74	64	48	38	86	52	80	63	66	68	60	62	63	74	75	81	84	94
96	85	88	90	72	44	58	62	70	74	64	74	72	64	64	84	85	78	88	54
97	56	55	35	68	70	78	76	56	72	83	69	65	86	65	76	82	89	92	90
99	75	65	88	54	42	80	90	88	58	78	88	70	88	63	82	72	71	98	80
100	65	75	70	70	60	83	85	70	62	72	90	72	84	64	78	88	80	80	72

The matrix Σ^X can be computed from the X matrix using equation 1.

Best known solution

The solutions shown in the following table are from Chu and Wright (1995).

Problem Vector v	Number of Variables		Optimal	Solution	y^*	Objective Value
1, 2, 5, 6	4	173	237	104	29	543
1, 3, 4, 5	4	156.232	240.935	128.742	107.248	633.158
1, 2, 3, 6,	6	0.000	102.020	19.877	31.461	305.482
8, 10		82.283	69.840			
1, 2, 4, 5,	6	59.623	214.032	69.805	115.733	564.463
6, 8		47.040	58.230			
1:6	6	152.706	54.476	82.631	99.643	535.362
		104.655	40.953			
1:8	8	14.032	38.542	95.099	158.901	641.839
		120.382	28.371	106.775	79.736	
1:10	10	0.000	43.892	80.717	132.887	690.781
		126.862	28.030	92.610	56.620	
		61.336	67.826			
1:12	12	18.633	61.863	63.427	127.568	747.489
		99.973	30.770	96.535	45.288	
		41.601	45.329	64.041	52.460	
1:14	14	0.000	59.499	62.912	109.924	671.275
		99.949	32.719	79.073	31.738	
		47.421	33.789	41.953	63.596	
		4.252	4.451			
1:16	16	0.000	63.487	52.389	108.192	663.4619
		92.395	34.562	85.755	21.957	
		37.549	32.967	28.511	54.571	
		12.930	4.104	6.706	27.387	
1:18	18	0.000	58.380	62.162	107.231	747.5058
		80.287	25.383	70.703	24.217	
		52.438	41.695	24.292	39.176	
		15.761	6.862	3.259	14.593	
		68.804	52.162			

Problem Vector v	Number of Variables		Optimal	Solution	y^*	Objective Value
1:20	20	0.000	47.373	76.582	101.002	820.343
		63.450	13.382	41.483	4.300	
		56.365	33.983	33.770	29.960	
		17.597	0.000	4.328	13.690	
		45.587	51.586	57.207	128.698	

11.3 Maximum Cut Problem

This section introduces the statement of the maximum cut problem, describes how an upper bound to the problem's optimal objective value can be obtained via a semidefinite programming relaxation and provides a set of such problems with their best known solutions. First some graph theoretic terminology is introduced.

A *graph* $G = (\mathcal{V}, \mathcal{E})$ consists of a finite nonempty set $\mathcal{V}$ of *nodes* and a finite set $\mathcal{E}$ of *edges*. An unordered pair of nodes (i, j) is associated with each edge. A *weighted* graph is one in which a scalar value w_{ij} is associated with each edge (i, j), when (i, j) is not an edge $w_{ij} = 0$. For a given graph G the *cut* $\delta(\mathcal{S})$ induced by the vertex set $\mathcal{S}$ consists of the set of edges with exactly one endpoint in $\mathcal{S}$. The *weight* of a cut, $w(\delta(\mathcal{S}))$ is the sum of the weights associated with the set of edges in the cut, $w(\delta(\mathcal{S})) = \sum_{(i,j)\in\delta(\mathcal{S})} w_{ij}$.

The maximum cut problem involves finding a cut $\delta(\mathcal{S})$ of maximum weight. The maximum cut problem can be formulated as an integer quadratic program.

$$\begin{aligned} \max_{\boldsymbol{x}} & \frac{1}{4}\sum_{i\in\mathcal{V}}\sum_{j\in\mathcal{V}} w_{ij}(1 - x_i x_j) \\ \text{subject to } & \boldsymbol{x} \in \{0, 1\}^n. \end{aligned}$$

In this formulation $x_i = 1$ if $i \in \mathcal{S}$ and $x_i = -1$ if $i \in \mathcal{V}\backslash\mathcal{S}$. The above formulation is equivalent to the following *continuous* quadratically constrained global optimization problem:

$$\begin{aligned} \max_{\boldsymbol{x},\boldsymbol{X}} \quad & \frac{1}{4}\boldsymbol{L} \bullet \boldsymbol{X} \\ \text{subject to} \quad & \boldsymbol{X}_{ii} = 1 \quad \text{for all } i \in \mathcal{V}. \\ & \boldsymbol{X} = \boldsymbol{x}\boldsymbol{x}^T, \end{aligned}$$

where $\boldsymbol{x} \in \Re^n$; $\boldsymbol{X} \in \Re^{n\times n}$, and the *weighted Laplacian* matrix $\boldsymbol{L} \in \Re^{n\times n}$ is composed of diagonal elements $L_{ii} = \sum_{j\in\mathcal{V}} w_{ij}$ for $i = 1, \ldots, n$, and off-diagonal elements $L_{ij} = -w_{ij}$ for $i = 1, \ldots, n$; $j = 1, \ldots, n$; $i \neq j$. This nonconvex problem can be approximated as a convex semidefinite programming problem by relaxing the constraint $\boldsymbol{X} = \boldsymbol{x}\boldsymbol{x}^T$ to $\boldsymbol{X} \succeq \boldsymbol{0}$.

11.3.1 General formulation

The dual formulation of the above maximum cut problem relaxation is presented in this section.

Objective function

$$\max_{\boldsymbol{y}} \boldsymbol{e}^T \boldsymbol{y}$$
$$\boldsymbol{e} \in \Re^n, e_i = 1, \; i = 1, \dots, n$$
$$\boldsymbol{y} \in \Re^n$$

Constraints

$$-\frac{1}{4}\boldsymbol{L} - \sum_{i=1}^{n} y_i \boldsymbol{E}_i \succeq \mathbf{0}.$$

$\boldsymbol{E}_i \in \Re^{n \times n}$ has all zero elements except $(\boldsymbol{E}_i)_{ii} = 1$.

Variables

The vector $\boldsymbol{y}$ is the variable in this problem.

Data

Tables 11.1 and 11.2, from Shor (1998), define the edges and weights of weighted graphs with 10 and 20 nodes respectively. Weights w_{ij} where (i, j) is not an edge are set to zero.

Best known solution

Table 11.3 provides data on the solutions to the maximum cut problems and their semidefinite programming relaxations.

In table 11.3 $w^{SDP}(\delta(\mathcal{S}))$ refers to the optimal objective function to the semidefinite relaxation of the maximum cut problem, as reported by Shor (1998). $\mathcal{S}^*$ refers to the set of nodes corresponding to the best known feasible solution to the maximum cut problem itself, and $w(\delta(\mathcal{S}^*))$ is the weight of this cut.

edge	weight w_{ij}								
(i,j)	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9
(1,2)	1	5	2	5	1	5	2	5	1
(1,5)	1	1	3	6	8	2	7	2	3
(1,10)	1	3	4	3	1	2	2	2	3
(2,3)	1	2	7	2	3	1	3	6	8
(2,9)	1	2	6	2	5	5	1	5	9
(3,4)	1	3	1	6	7	3	4	3	1
(3,8)	1	4	3	4	2	1	2	1	2
(4,5)	1	1	2	1	2	2	6	2	5
(4,7)	1	1	5	1	3	4	3	4	2
(5,6)	1	5	1	5	9	3	1	6	7
(6,8)	1	5	5	5	4	1	5	1	3
(6,9)	1	3	1	3	1	5	5	5	4
(7,9)	1	2	2	2	3	3	1	3	1
(7,10)	1	1	2	1	8	1	2	1	8
(8,10)	1	1	1	1	1	1	1	1	1

Table 11.1: Weighted graphs with 10 vertices and 15 edges

edge	weight w_{ij}					edge	weight w_{ij}				
(i,j)	T_1	T_2	T_3	T_4	T_5	(i,j)	T_1	T_2	T_3	T_4	T_5
(1,2)	1	7	7	2	6	(10,12)	1	7	1	2	1
(1,18)	1	7	7	3	5	(10,20)	1	9	7	4	2
(2,3)	1	7	7	5	4	(11,12)	1	1	7	5	5
(2,16)	1	7	9	4	3	(11,13)	1	7	1	6	5
(2,18)	1	7	9	1	3	(12,13)	1	7	7	1	4
(3,4)	1	7	7	5	4	(13,14)	1	7	7	1	4
(4,5)	1	1	7	5	5	(13,15)	1	9	1	1	1
(5,6)	1	7	7	3	6	(13,19)	1	9	1	3	1
(5,9)	1	1	1	2	1	(13,20)	1	7	9	4	2
(5,19)	1	7	9	2	3	(14,15)	1	9	7	2	2
(5,20)	1	7	9	4	4	(14,16)	1	7	1	3	5
(6,7)	1	7	7	5	6	(15,16)	1	1	7	2	3
(6,8)	1	1	1	1	3	(15,20)	1	9	9	4	2
(7,8)	1	7	7	3	3	(16,17)	1	7	7	2	1
(8,9)	1	1	7	3	2	(16,18)	1	9	9	3	3
(8,19)	1	7	7	2	1	(16,20)	1	9	7	2	2
(9,10)	1	7	7	1	2	(17,18)	1	7	7	1	1
(10,11)	1	1	7	1	1	(19,20)	1	9	9	3	3

Table 11.2: Weighted graphs with 20 vertices and 36 edges

Problem	$w^{SDP}(\delta(\mathcal{S}))$	$w(\delta(\mathcal{S}^*))$	$\mathcal{S}^*$	$\mathcal{V} \setminus \mathcal{S}^*$
P_1	12.71280	12.0	1,2,4,6,7,8	3,5,9,10
P_2	35.70171	35.0	2,4,5,8,9,10	1,3,6,7
P_3	40.91025	40.0	2,5,7,8,10	1,3,4,6,9
P_4	43.81359	43.0	1,3,6,7	2,4,5,8,9,10
P_5	52.76558	51.0	1,2,4,6,10	3,5,7,8,9
P_6	34.97500	34.0	2,3,5,6,7,10	1,4,8,9
P_7	40.13301	39.0	2,3,5,6,7,10	1,4,8,9
P_8	41.75555	41.0	1,3,5,7,8,9	2,4,6,10
P_9	52.99566	52.0	1,2,4,6,7,8	3,5,9,10
T_1	29.93753	29.0	1,3,5,7,8,10 13,15,16	2,4,6,9,11,12 14,17,18,19,20
T_2	192.08551	185.0	2,4,6,9,11,12, 14,17,18,19,20	1,3,5,7,8,10, 13,15,16
T_3	189.71114	181.0	1,2,4,6,8,10, 12,14,17,20	3,5,7,9,11,13, 15,16,18,19
T_4	88.07765	87.0	2,4,6,9,11,14, 17,18,19,20	1,3,5,7,8,10, 12,13,15,16
T_5	91.79930	90.0	2,4,6,9,11,12,14, 15,17,18,19,20	1,3,5,7,8,10, 13,16

Table 11.3: Solutions to the maximum cut problems

Chapter 12

Mixed-Integer Nonlinear Programming Problems (MINLPs)

12.1 Introduction

Mixed-integer problems are those that involve both continuous and integer variables. The introduction of integer variables allows the modeling of complex decisions through graph theoretic representations denoted as *superstructures* (Floudas, 1995). This representation leads to the simultaneous determination of the optimal structure of a network and its optimum operating parameters. Thus MINLPs find applications in engineering design such as heat exchanger network synthesis, reactor-separator-recycle network synthesis or pump network synthesis (Floudas, 1995; Grossmann, 1996), in metabolic pathway engineering (Hatzimanikatis *et al.*, 1996a,b; Dean and Dervakos, 1996), or in molecular design (Maranas, 1996; Churi and Achenie, 1996).

The solution of MINLPs is not a trivial matter. The presence of binary or integer variables results in a combinatorial explosion of the number of solutions, adding to the difficulties arising from the nonconvexity of the problem. Several techniques have been devised for convex MINLPs: branch-and-bound approaches (Beale, 1977; Gupta and Ravindran, 1985; Ostrovsky et al., 1990; Borchers and Mitchell, 1991; Quesada and Grossmann, 1992; Fletcher and Leyffer, 1998), the Generalized Benders Decomposition and its variants (Geoffrion, 1972; Paules and Floudas, 1989; Floudas et al., 1989), the Outer Approximation algorithm and its variants (Duran and Grossmann, 1986; Kocis and Grossmann, 1987; Viswanathan and Grossmann, 1990), and the Generalized Outer Approximation (Fletcher and Leyffer, 1994). While some of these techniques can also be used to find solutions of nonconvex MINLPs, global optimality cannot be guaranteed. In the last few years, several groups have concentrated on designing global optimization algorithms for MINLPs. The methods proposed, of varying applicability, include the interval-based ap-

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proach of Vaidyanathan and El-Halwagi (1996), the Extended Cutting Plane algorithm of Westerlund et al. (1998), and the branch-and-bound algorithms of Ryoo and Sahinidis (1995), Smith and Pantelides (1997) and Adjiman et al. (1998d).

The reported global solutions in this chapter are taken from the work of Adjiman et al. (1998d). A small set of test problems for mixed integer quadratic problems can be found in Fletcher and Leyffer (1998). For a description of the theoretical and algorithmic issues of global optimization approaches for nonconvex MINLP problems, the reader is directed to the article of Adjiman et al. (1998d), and the forthcoming book by Floudas (2000).

12.2 Literature Problems

12.2.1 Test Problem 1

This example was first proposed by Kocis and Grossmann (1988).

Formulation

Objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \quad 2x_1 + 3x_2 + 1.5y_1 + 2y_2 - 0.5y_3$$

Constraints

$$\begin{aligned} x_1^2 + y_1 &= 1.25 \\ x_2^{1.5} + 1.5y_2 &= 3 \\ x_1 + y_1 &\leq 1.6 \\ 1.333x_2 + y_2 &\leq 3 \\ -y_1 - y_2 + y_3 &\leq 0 \end{aligned}$$

Variable bounds

$$\begin{aligned} x_1, x_2 &\geq 0 \\ \boldsymbol{y} &\in \{0,1\}^3. \end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of binary variables	3
No. of convex inequalities	3
No. of nonlinear equalities	2
No. of known solutions	2

Global Solution

- Objective function: 7.6672
- Continuous variables: $\boldsymbol{x} = (1.12, 1.31)^T$.
- Binary variables: $\boldsymbol{y} = (0, 1, 1)^T$.

12.2.2 Test Problem 2

This example is example 6.6.5 from Floudas (1995).

Formulation

Objective function

$$\min_{\boldsymbol{x},y} \quad -0.7y + 5(x_1 - 0.5)^2 + 0.8$$

Constraints

$$\begin{aligned}
-e^{(x_1-0.2)} - x_2 &\leq 0 \\
x_2 + 1.1y &\leq 1 \\
x_1 - 1.2y &\leq 0.2
\end{aligned}$$

Variable bounds

$$\begin{array}{rcl}
0.2 \leq & x_1 & \leq 1 \\
-2.22554 \leq & x_2 & \leq -1 \\
y & \in & \{0, 1\}
\end{array}$$

Problem Statistics

No. of continuous variables	2
No. of binary variables	1
No. of convex inequalities	2
No. of nonconvex inequalities	1
No. of known solutions	1

Global Solution

- Objective function: 1.0765.
- Continuous variables: $\boldsymbol{x} = (0.9419, -2.1)^T$.
- Binary variables: $y = 1$.

12.2.3 Test Problem 3

This example was proposed by Yuan et al. (1988).

Formulation

Objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \quad (y_1-1)^2+(y_2-2)^2+(y_3-1)^2-\ln(y_4+1) \\ +(x_1-1)^2+(x_2-2)^2+(x_3-3)^2$$

Constraints

$$\begin{aligned} y_1+y_2+y_3+x_1+x_2+x_3 &\le 5 \\ y_3^2+x_1^2+x_2^2+x_3^2 &\le 5.5 \\ y_1+x_1 &\le 1.2 \\ y_2+x_2 &\le 1.8 \\ y_3+x_3 &\le 2.5 \\ y_4+x_1 &\le 1.2 \\ y_2^2+x_2^2 &\le 1.64 \\ y_3^2+x_3^2 &\le 4.25 \\ y_2^2+x_3^2 &\le 4.64 \end{aligned}$$

Variable bounds

$$\begin{aligned} x_1,x_2,x_3 &\ge 0 \\ \boldsymbol{y} &\in \{0,1\}^4. \end{aligned}$$

Problem Statistics

No. of continuous variables	3
No. of binary variables	4
No. of convex inequalities	5
No. of nonconvex inequalities	4
No. of known solutions	2

Global Solution

- Objective function: 4.5796.
- Continuous variables: $\boldsymbol{x} = (0.2, 0.8, 1.908)^T$.
- Binary variables: $\boldsymbol{y} = (1, 1, 0, 1)^T$.

12.2.4 Test Problem 4

This example was first presented by Berman and Ashrafi (1993).

Formulation

Objective function

$$\min_{\boldsymbol{x},\boldsymbol{y}} \quad -x_1x_2x_3$$

Constraints

$$\begin{aligned}
x_1 + 0.1^{y_1}0.2^{y_2}0.15^{y_3} &= 1\\
x_2 + 0.05^{y_4}0.2^{y_5}0.15^{y_6} &= 1\\
x_3 + 0.02^{y_7}0.06^{y_8} &= 1\\
-y_1 - y_2 - y_3 &\leq -1\\
-y_4 - y_5 - y_6 &\leq -1\\
-y_7 - y_8 &\leq -1\\
3y_1 + y_2 + 2y_3 + 3y_4 + 2y_5 + y_6 + 3y_7 + 2y_8 &\leq 10
\end{aligned}$$

Variable bounds

$$0 \leq x_1, x_2, x_3 \leq 1$$
$$\boldsymbol{y} \in \{0,1\}^8.$$

Problem Statistics

No. of continuous variables	3
No. of binary variables	8
No. of convex inequalities	4
No. of nonlinear equalities	3
No. of known solutions	3

Global Solution

- Objective function: -0.94347
- Continuous variables: $\boldsymbol{x} = (0.97, 0.9925, 0.98)^T$.
- Binary variables: $\boldsymbol{y} = (0,1,1,1,0,1,1,0)^T$.

12.2.5 Test Problem 5

This example is a purely integer nonconvex problem presented in Pörn et al. (1997).

Formulation

Objective function

$$\min_{\boldsymbol{y}} 7y_1 + 10y_2$$

Constraints

$$\begin{aligned} y_1^{1.2}y_2^{1.7} - 7y_1 - 9y_2 &\le 24 \\ -y_1 - 2y_2 &\le 5 \\ -3y_1 + y_2 &\le 1 \\ 4y_1 - 3y_2 &\le 11 \end{aligned}$$

Variable bounds

$$y_1, y_2 \in [1, 5] \cap \mathcal{N}$$

Problem Statistics

No. of integer variables	2
No. of convex inequalities	3
No. of nonconvex inequalities	1
No. of known solutions	2

Global Solution

- Objective function: 31.
- Integer variables: $\boldsymbol{y} = (3, 1)^T$.

12.2.6 Test Problem 6

This example is also taken from Pörn et al. (1997).

Formulation

Objective function

$$\min_{x,y} \quad 3y - 5x$$

Constraints

$$\begin{aligned} 2y^2 - 2y^{0.5} - 2x^{0.5}y^2 + 11y + 8x &\le 39 \\ -y + x &\le 3 \\ 2y + 3x &\le 24 \end{aligned}$$

Variable bounds

$$1 \leq x \leq 10$$
$$y \in [1, 6] \cap \mathcal{N}$$

Problem Statistics

No. of continuous variables	1
No. of integer variables	1
No. of convex inequalities	2
No. of nonconvex inequalities	1
No. of known solutions	1

Global Solution

- Objective function: -17.
- Continuous variable: $x = 4$.
- Integer variable: $y = 1$.

12.3 Heat Exchanger Network Synthesis with the Chen Approximation

12.3.1 Introduction

The goal of heat exchanger network synthesis problems is to minimize the annualized cost of a heat exchanger network by determining which hot stream/cold stream, hot stream/cold utility and cold stream/hot utility matches should take place and what heat loads should be assigned to each heat exchanger. Binary variables are used to represent the existence of each heat exchanger. A variety of models based on this principle have been studied in the literature (Floudas et al., 1986; Floudas and Ciric, 1988; Gundersen and Naess, 1988; Yee and Grossmann, 1991; Quesada and Grossmann, 1993; Zamora and Grossmann, 1998). Several expressions have been used to compute the area of a heat exchanger which enters into the calculation of the capital cost of the network. In the present problem, taken from Yee and Grossmann (1991), the logarithmic mean temperature difference which appears in the exact area expression is approximated with the formula derived by Chen (1987).

The design of a heat exchanger network involving two hot streams, two cold streams, one hot and one cold utility is given. There are two temperature intervals. The superstructure for this problem is shown in Figure 12.1. The annualized cost of the network is expressed as the summation of the utility costs, the fixed charges for the required heat-exchangers and an area-based cost for each heat-exchanger. Since the Chen approximation for the logarithmic

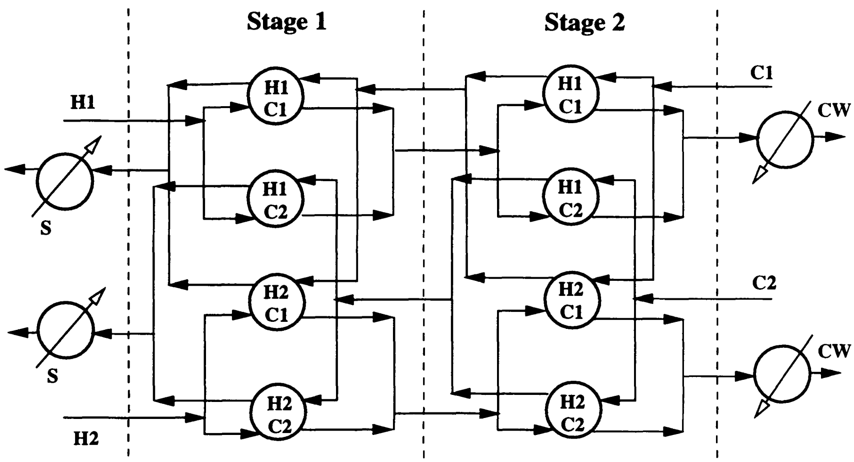


Figure 12.1: Superstructure for the heat exchanger network problem with the Chen approximation.

mean of the temperature difference is used Chen (1987), the area is a highly nonlinear function of the heat duty and the temperature differences at both ends of the heat exchanger.

12.3.2 General Formulation

Objective function

$$
\begin{aligned}
\min_{\boldsymbol{T},\boldsymbol{Q},\boldsymbol{\Delta T},\boldsymbol{z}} \quad & \sum_{i\in HP} C_{CU} Q_{CU,i} + \sum_{j\in CP} C_{HU} Q_{HU,j} \\
&+ \sum_{i\in HP}\sum_{j\in CP}\sum_{k\in SI} CF_{ij} z_{ijk} + \sum_{i\in HP} CF_{i,CU} z_{CU,i} + \sum_{j\in CP} CF_{j,HU} z_{HU,j} \\
&+ \sum_{i\in HP}\sum_{j\in CP}\sum_{k\in SI} \frac{C_{ij} Q_{ijk}}{U_{ij}\left[\Delta T_{ijk}\Delta T_{ijk+1}\left(\Delta T_{ijk}+\Delta T_{ijk+1}\right)/2\right]^{\frac{1}{3}}} \\
&+ \sum_{i\in HP} \frac{C_{i,CU} Q_{CU,i}}{U_{CU,i}\left[\Delta T_{CU,i}\left(T_{out,i}-T_{in,CU}\right)\left(\Delta T_{CU,i}+T_{out,i}-T_{in,CU}\right)/2\right]^{\frac{1}{3}}} \\
&+ \sum_{j\in CP} \frac{C_{j,HU} Q_{HU,j}}{U_{HU,j}\left[\Delta T_{HU,j}\left(T_{in,HU}-T_{out,j}\right)\left(\Delta T_{HU,j}+T_{in,HU}-T_{out,j}\right)/2\right]^{\frac{1}{3}}}
\end{aligned}
$$

Constraints

$$
\begin{aligned}
\sum_{k\in SI}\sum_{j\in CP} Q_{ijk} + Q_{CU,i} &= \left(T_{in,i} - T_{out,i}\right) Fcp_i, \quad \forall i \in HP \\
\sum_{k\in SI}\sum_{i\in HP} Q_{ijk} + Q_{HU,j} &= \left(T_{out,j} - T_{in,j}\right) Fcp_j, \quad \forall j \in CP
\end{aligned}
$$

$$
\begin{aligned}
(T_{i,k} - T_{i,k+1})\, Fcp_i - \sum_{j \in CP} Q_{ijk} &= 0, \ \ \forall\, k \in SI, \ \forall\, i \in HP \\
(T_{j,k} - T_{j,k+1})\, Fcp_j - \sum_{i \in HP} Q_{ijk} &= 0, \ \ \forall\, k \in SI, \ \forall\, j \in CP \\
T_{i,1} &= T_{in,i}, \ \ \forall\, i \in HP \\
T_{j,NS+1} &= T_{in,j}, \ \ \forall\, j \in CP \\
T_{i,k} - T_{i,k+1} &\geq 0, \ \ \forall\, k \in SI, \ \forall\, i \in HP \\
T_{j,k} - T_{j,k+1} &\geq 0, \ \ \forall\, k \in SI, \ \forall\, j \in CP \\
T_{i,NS+1} &\geq T_{out,i}, \ \ \forall\, i \in HP \\
T_{j,1} &\leq T_{out,j}, \ \ \forall\, j \in CP \\
Fcp_i\, T_{i,NS+1} - Q_{CU,i} &= Fcp_i\, T_{out,i}, \ \ \forall\, i \in HP \\
Fcp_j\, T_{j,1} + Q_{HU,j} &= Fcp_j\, T_{out,j}, \ \ \forall\, j \in CP \\
Q_{ijk} - Q_{ij}^{max} z_{ijk} &\leq 0, \\
&\quad \ \forall\, k \in SI, \ \forall\, i \in HP, \ \forall\, j \in CP \\
Q_{CU,i} - Q_{i,CU}^{max} z_{CU,i} &\leq 0, \ \ \forall\, i \in HP \\
Q_{HU,j} - Q_{HU,j}^{max} z_{HU,j} &\leq 0, \ \ \forall\, j \in CP \\
\Delta T_{ijk} - T_{i,k} + T_{j,k} + \Delta T_{ij}^{max} z_{ijk} &\leq \Delta T_{ij}^{max}, \\
&\quad \ \forall\, k \in SI, \ \forall\, i \in HP, \ \forall\, j \in CP \\
\Delta T_{ijk+1} - T_{i,k+1} + T_{j,k+1} + \Delta T_{ij}^{max} z_{ijk} &\leq \Delta T_{ij}^{max}, \\
&\quad \ \forall\, k \in SI, \ \forall\, i \in HP, \ \forall\, j \in CP \\
\Delta T_{CU,i} - T_{i,NS+1} + \Delta T_{i,CU}^{max} z_{CU,i} &\leq \Delta T_{i,CU}^{max} - T_{out,CU}, \ \ \forall\, i \in HP \\
\Delta T_{HU,j} + T_{j,1} + \Delta T_{HU,j}^{max} z_{HU,j} &\leq \Delta T_{HU,j}^{max} + T_{out,HU}, \ \ \forall\, j \in CP
\end{aligned}
$$

where $\Delta T_{ij}^{max} = \max\{0, T_{j,in} - T_{i,in}, T_{j,in} - T_{i,out}, T_{j,out} - T_{i,in}, T_{j,out} - T_{i,out}\}$, for all $i \in HP \cup \{HU\}$ and $j \in CP \cup \{CU\}$; and $Q_{ij}^{max} = \min\{(T_{in,i} - T_{out,i})\, Fcp_i, (T_{out,j} - T_{in,j})\, Fcp_j\}$, for all $i \in HP \cup \{HU\}$ and $j \in CP \cup \{CU\}$.

Variable bounds

$$
\begin{array}{rcl}
0 \leq & Q_{ijk} & \leq Q_{ij}^{max}, \forall\, k \in SI, \ \forall\, i \in HP, \ \forall\, j \in CP \\
0 \leq & Q_{CU,i} & \leq Q_{i,CU}^{max}, \forall\, i \in HP \\
0 \leq & Q_{HU,j} & \leq Q_{HU,j}^{max}, \forall\, j \in CP \\
T_{i,out} \leq & T_{ik} & \leq T_{i,in}, \forall\, k \in ST, \ \forall\, i \in HP \\
T_{j,in} \leq & T_{jk} & \leq T_{j,out}, \forall\, k \in ST, \ \forall\, j \in CP \\
\Delta T_{mapp} \leq & \Delta T_{ijk} & \leq \Delta T_{ij}^{max}, \forall\, k \in ST, \ \forall\, i \in HP, \ \forall\, j \in CP \\
\Delta T_{mapp} \leq & \Delta T_{CU,i} & \leq \Delta T_{i,CU}^{max}, \forall\, i \in HP \\
\Delta T_{mapp} \leq & \Delta T_{HU,j} & \leq \Delta T_{HU,j}^{max}, \forall\, j \in CP \\
z_{ijk}, z_{CU,i}, z_{HU,j} & \in \{0,1\}, & \forall\, k \in SI, \ \forall\, i \in HP, \ \forall\, j \in CP
\end{array}
$$

Variable definitions

SI is the set of temperature intervals or stages, NS is the number of stages, HP is the set of hot process streams, CP is the set of cold process streams, and ST is the set of temperature locations.

The continuous variables are T_{ik}, the temperature of hot stream i at the temperature location k; T_{jk}, the temperature of cold stream j at the temperature location k; Q_{ijk}, the heat exchanged between hot stream i and cold stream j in stage k; $Q_{CU,i}$, the heat exchanged between hot stream i and the cold utility; $Q_{HU,j}$, the heat exchanged between cold stream j and the hot utility; ΔT_{ijk}, the temperature approach for the match of hot stream i and cold stream j at temperature location k; $\Delta T_{CU,i}$, the temperature approach for the match of hot stream i and the cold utility; $\Delta T_{HU,j}$, the temperature approach for the match of cold stream j and the hot utility. The binary variables are z_{ijk}, for the existence of a match between hot stream i and cold stream j in stage k; $z_{CU,i}$, for the existence of a match between hot stream i and the cold utility; $z_{HU,j}$, for the existence of a match between cold stream j and the hot utility.

The parameters are T_{in}, the inlet temperature of a stream; T_{out}, the outlet temperature; Fcp, the heat capacity flowrate of a stream; Q^{max}, the upper bound on heat exchange; ΔT^{max}, the upper bound on the temperature difference; C_{HU}, the steam utility cost; C_{CU}, the cooling water cost; CF_{ij}, the fixed charge for the heat exchanger between hot stream i and cold stream j; $CF_{i,CU}$, the fixed charge for the heat exchanger between hot stream i and the cold utility; $CF_{j,HU}$, the fixed charge for the heat exchanger between cold stream j and the hot utility; C_{ij}, the coefficient for the area-dependent cost of the heat exchanger between hot stream i and cold stream j; $C_{i,CU}$, the coefficient for the area-dependent cost of the heat exchanger between hot stream i and the cold utility; $C_{j,HU}$, the coefficient for the area-dependent cost of the heat exchanger between cold stream j and the hot utility; U_{ij}, the overall heat transfer coefficient for the hot stream i-cold stream j unit; $U_{CU,i}$, the overall heat transfer coefficient for the hot stream i-cold utility exchanger; $U_{HU,j}$, the overall heat transfer coefficient for the hot utility-cold stream j unit; ΔT_{mapp}, the minimum approach temperature.

12.3.3 Test Problem 1

A specific formulation for heat exchanger network synthesis using the Chen approximation is as follows.

Formulation

Objective function

$$
\begin{aligned}
\min_{T,Q,\Delta T,z} \quad & 15Q_{CU,H1} + 15Q_{CU,H2} + 80Q_{HU,C1} + 80Q_{HU,C2} + 5500z_{H1,C1,1} \\
& +5500z_{H1,C1,2} + 5500z_{H1,C1,3} + 5500z_{H1,C2,1} + 5500z_{H1,C2,2} \\
& +5500z_{H1,C2,3} + 5500z_{H2,C1,1} + 5500z_{H2,C1,2} + 5500z_{H2,C1,3} \\
& +5500z_{H2,C2,1} + 5500z_{H2,C2,2} + 5500z_{H2,C2,3} + 5500z_{CU,H1} \\
& +5500z_{CU,H2} + 5500z_{HU,C1} + 5500z_{HU,C2} \\
& + \frac{300Q_{H1,C1,1}}{0.5\left[\Delta T_{H1,C1,1}\Delta T_{H1,C1,2}\left(\Delta T_{H1,C1,1} + \Delta T_{H1,C1,2}\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{H1,C1,2}}{0.5\left[\Delta T_{H1,C1,2}\Delta T_{H1,C1,3}\left(\Delta T_{H1,C1,2} + \Delta T_{H1,C1,3}\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{H1,C2,1}}{0.5\left[\Delta T_{H1,C2,1}\Delta T_{H1,C2,2}\left(\Delta T_{H1,C2,1} + \Delta T_{H1,C2,2}\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{H1,C2,2}}{0.5\left[\Delta T_{H1,C2,2}\Delta T_{H1,C2,3}\left(\Delta T_{H1,C2,2} + \Delta T_{H1,C2,3}\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{H2,C1,1}}{0.5\left[\Delta T_{H2,C1,1}\Delta T_{H2,C1,2}\left(\Delta T_{H2,C1,1} + \Delta T_{H2,C1,2}\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{H2,C1,2}}{0.5\left[\Delta T_{H2,C1,2}\Delta T_{H2,C1,3}\left(\Delta T_{H2,C1,2} + \Delta T_{H2,C1,3}\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{H2,C2,1}}{0.5\left[\Delta T_{H2,C2,1}\Delta T_{H2,C2,2}\left(\Delta T_{H2,C2,1} + \Delta T_{H2,C2,2}\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{H2,C2,2}}{0.5\left[\Delta T_{H2,C2,2}\Delta T_{H2,C2,3}\left(\Delta T_{H2,C2,2} + \Delta T_{H2,C2,3}\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{CU,H1}}{0.83333\left[70\Delta T_{CU,H1}\left(\Delta T_{CU,H1} + 70\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{CU,H2}}{0.83333\left[70\Delta T_{CU,H2}\left(\Delta T_{CU,H2} + 70\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{HU,C1}}{0.5\left[30\Delta T_{HU,C1}\left(\Delta T_{HU,C1} + 30\right)/2\right]^{\frac{1}{3}}} \\
& + \frac{300Q_{HU,C2}}{0.5\left[180\Delta T_{HU,C2}\left(\Delta T_{HU,C2} + 180\right)/2\right]^{\frac{1}{3}}}
\end{aligned}
$$

Constraints

$$
\begin{aligned}
Q_{H1,C1,1} + Q_{H1,C2,1} + Q_{H1,C1,2} + Q_{H1,C2,2} + Q_{CU,H1} &= 2800 \\
Q_{H2,C1,1} + Q_{H2,C2,1} + Q_{H2,C1,2} + Q_{H2,C2,2} + Q_{CU,H2} &= 4400 \\
Q_{H1,C1,1} + Q_{H2,C1,1} + Q_{H1,C1,2} + Q_{H2,C1,2} + Q_{HU,C1} &= 3600 \\
Q_{H1,C2,1} + Q_{H2,C2,1} + Q_{H1,C2,2} + Q_{H2,C2,2} + Q_{HU,C2} &= 1950 \\
10(T_{H1,1} - T_{H1,2}) - Q_{H1,C1,1} - Q_{H1,C2,1} &= 0 \\
10(T_{H1,2} - T_{H1,3}) - Q_{H1,C1,2} - Q_{H1,C2,2} &= 0 \\
20(T_{H2,1} - T_{H2,2}) - Q_{H2,C1,1} - Q_{H2,C2,1} &= 0 \\
20(T_{H2,2} - T_{H2,3}) - Q_{H2,C1,2} - Q_{H2,C2,2} &= 0 \\
15(T_{C1,1} - T_{C1,2}) - Q_{H1,C1,1} - Q_{H2,C1,1} &= 0 \\
15(T_{C1,2} - T_{C1,3}) - Q_{H1,C1,2} - Q_{H2,C1,2} &= 0 \\
13(T_{C2,1} - T_{C2,2}) - Q_{H1,C2,1} - Q_{H2,C2,1} &= 0 \\
13(T_{C2,2} - T_{C2,3}) - Q_{H1,C2,2} - Q_{H2,C2,2} &= 0 \\
T_{H1,1} &= 650 \\
T_{H2,1} &= 590 \\
T_{C1,3} &= 410 \\
T_{C2,3} &= 350 \\
-T_{H1,1} + T_{H1,2} &\leq 0 \\
-T_{H1,2} + T_{H1,3} &\leq 0 \\
-T_{H2,1} + T_{H2,2} &\leq 0 \\
-T_{H2,2} + T_{H2,3} &\leq 0 \\
-T_{C1,1} + T_{C1,2} &\leq 0 \\
-T_{C1,2} + T_{C1,3} &\leq 0 \\
-T_{C2,1} + T_{C2,2} &\leq 0 \\
-T_{C2,2} + T_{C2,3} &\leq 0 \\
-T_{H1,3} &\leq -370 \\
-T_{H2,3} &\leq -370 \\
T_{C1,1} &\leq 650 \\
T_{C2,1} &\leq 500 \\
10T_{H1,3} - Q_{CU,H1} &= 3700 \\
20T_{H2,3} - Q_{CU,H2} &= 7400 \\
15T_{C1,1} + Q_{HU,C1} &= 9750 \\
13T_{C2,1} + Q_{HU,C2} &= 6500
\end{aligned}
$$

$$\begin{aligned}
Q_{H1,C1,1} - 2800 z_{H1,C1,1} &\leq 0 \\
Q_{H1,C1,2} - 2800 z_{H1,C1,2} &\leq 0 \\
Q_{H1,C2,1} - 1950 z_{H1,C2,1} &\leq 0 \\
Q_{H1,C2,2} - 1950 z_{H1,C2,2} &\leq 0 \\
Q_{H2,C1,1} - 3600 z_{H2,C1,1} &\leq 0 \\
Q_{H2,C1,2} - 3600 z_{H2,C1,2} &\leq 0 \\
Q_{H2,C2,1} - 1950 z_{H2,C2,1} &\leq 0 \\
Q_{H2,C2,2} - 1950 z_{H2,C2,2} &\leq 0 \\
Q_{CU,H1} - 2800 z_{CU,H1} &\leq 0 \\
Q_{CU,H2} - 4400 z_{CU,H2} &\leq 0 \\
Q_{HU,C1} - 3600 z_{HU,C1} &\leq 0 \\
Q_{HU,C2} - 1950 z_{HU,C2} &\leq 0 \\
\Delta T_{H1,C1,1} - T_{H1,1} + T_{C1,1} + 280 z_{H1,C1,1} &\leq 280 \\
\Delta T_{H1,C1,2} - T_{H1,2} + T_{C1,2} + 280 z_{H1,C1,1} &\leq 280 \\
\Delta T_{H1,C1,2} - T_{H1,2} + T_{C1,2} + 280 z_{H1,C1,2} &\leq 280 \\
\Delta T_{H1,C1,3} - T_{H1,3} + T_{C1,3} + 280 z_{H1,C1,2} &\leq 280 \\
\Delta T_{H1,C2,1} - T_{H1,1} + T_{C2,1} + 300 z_{H1,C2,1} &\leq 300 \\
\Delta T_{H1,C2,2} - T_{H1,2} + T_{C2,2} + 300 z_{H1,C2,1} &\leq 300 \\
\Delta T_{H1,C2,2} - T_{H1,2} + T_{C2,2} + 300 z_{H1,C2,2} &\leq 300 \\
\Delta T_{H1,C2,3} - T_{H1,3} + T_{C2,3} + 300 z_{H1,C2,2} &\leq 300 \\
\Delta T_{H2,C1,1} - T_{H2,1} + T_{C1,1} + 280 z_{H2,C1,1} &\leq 280 \\
\Delta T_{H2,C1,2} - T_{H2,2} + T_{C1,2} + 280 z_{H2,C1,1} &\leq 280 \\
\Delta T_{H2,C1,2} - T_{H2,2} + T_{C1,2} + 280 z_{H2,C1,2} &\leq 280 \\
\Delta T_{H2,C1,3} - T_{H2,3} + T_{C1,3} + 280 z_{H2,C1,2} &\leq 280 \\
\Delta T_{H2,C2,1} - T_{H2,1} + T_{C2,1} + 240 z_{H2,C2,1} &\leq 240 \\
\Delta T_{H2,C2,2} - T_{H2,2} + T_{C2,2} + 240 z_{H2,C2,1} &\leq 240 \\
\Delta T_{H2,C2,2} - T_{H2,2} + T_{C2,2} + 240 z_{H2,C2,2} &\leq 240 \\
\Delta T_{H2,C2,3} - T_{H2,3} + T_{C2,3} + 240 z_{H2,C2,2} &\leq 240 \\
\Delta T_{CU,H1} - T_{H1,3} + 350 z_{CU,H1} &\leq -670 \\
\Delta T_{CU,H2} - T_{H2,3} + 290 z_{CU,H2} &\leq -610 \\
\Delta T_{HU,C1} + T_{C1,1} + 270 z_{HU,C1} &\leq 950 \\
\Delta T_{HU,C2} + T_{C2,1} + 330 z_{HU,C2} &\leq 1010
\end{aligned}$$

Variable bounds

$$
\begin{array}{rcl}
0 \leq & Q_{H1,C1,k} & \leq 2800, \ \forall k \in \{1,2\} \\
0 \leq & Q_{H1,C2,k} & \leq 1950, \ \forall k \in \{1,2\} \\
0 \leq & Q_{H2,C1,k} & \leq 3600, \ \forall k \in \{1,2\} \\
0 \leq & Q_{H2,C2,k} & \leq 1950, \ \forall k \in \{1,2\} \\
0 \leq & Q_{CU,H1} & \leq 2800 \\
0 \leq & Q_{CU,H2} & \leq 4400 \\
0 \leq & Q_{HU,C1} & \leq 3600 \\
0 \leq & Q_{HU,C2} & \leq 1950 \\
370 \leq & T_{H1,k} & \leq 650, \forall k \in \{1,2,3\} \\
370 \leq & T_{H2,k} & \leq 590, \forall k \in \{1,2,3\} \\
410 \leq & T_{C1,k} & \leq 650, \forall k \in \{1,2,3\} \\
350 \leq & T_{C1,k} & \leq 500, \forall k \in \{1,2,3\} \\
10 \leq & \Delta T_{H1,C1,k} & \leq 280, \forall k \in \{1,2,3\} \\
10 \leq & \Delta T_{H1,C2,k} & \leq 300, \forall k \in \{1,2,3\} \\
10 \leq & \Delta T_{H2,C1,k} & \leq 280, \forall k \in \{1,2,3\} \\
10 \leq & \Delta T_{H2,C2,k} & \leq 240, \forall k \in \{1,2,3\} \\
10 \leq & \Delta T_{CU,H1} & \leq 350 \\
10 \leq & \Delta T_{CU,H2} & \leq 290 \\
10 \leq & \Delta T_{HU,C1} & \leq 270 \\
10 \leq & \Delta T_{HU,C1} & \leq 330 \\
z_{ijk}, z_{CU,i}, z_{HU,j} & \in \{0,1\}, & \forall k \in \{1,2\}, \ \forall i \in \{H1, H2\}, \ \forall j \in \{C1, C2\}
\end{array}
$$

Data

Stream	T_{in} (K)	T_{out} (K)	Fcp (kW/K)
Hot 1	650	370	10.0
Hot 2	590	370	20.0
Cold 1	410	650	15.0
Cold 2	350	500	13.0
Steam	680	680	—
Water	300	320	—

CF_{ij}	= \$5500/yr	$CF_{i,CU}$	= \$5500/yr	$CF_{j,HU}$	= \$5500/yr
C_{ij}	= \$300/yr	$C_{i,CU}$	= \$300/yr	$C_{j,HU}$	= \$300/yr
U_{ij}	= 0.5 kW/m^{2}K	$U_{CU,i}$	= 0.83333 kW/m^{2}K	$U_{HU,j}$	= 0.5 kW/m^{2}K
C_{HU}	= \$80/kW-yr	C_{CU}	= \$15/kW-yr	ΔT_{mapp}	= 10 K

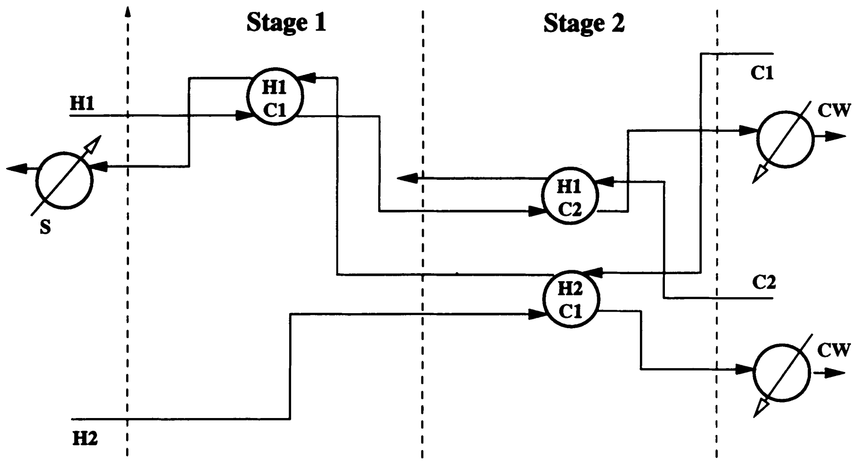


Figure 12.2: Optimum configuration for the heat exchanger network problem with the Chen approximation.

Problem Statistics

No. of continuous variables	40
No. of binary variables	12
No. of linear equalities	20
No. of convex inequalities	44
No. of known solutions	9

Global Solution

The global optimum configuration involves six heat exchangers and is shown in Figure 12.2 (see also Adjiman et al. (1998d)).

- Objective function: \$ 154,997/yr.
- Continuous variables

	$k=1$	$k=2$	$k=3$
$T_{H1,k}$	650.00 K	581.77 K	386.77 K
$T_{H2,k}$	590.00 K	590.00 K	468.67 K
$T_{C1,k}$	617.26 K	571.77 K	410.00 K
$T_{C2,k}$	500.00 K	500.00 K	350.00 K

$Q_{H1,C1,1} = 682.30$ kW	$Q_{H2,C1,1} = 0$
$Q_{H1,C1,2} = 0$	$Q_{H2,C1,2} = 2426.55$ kW
$Q_{H1,C2,1} = 0$	$Q_{H2,C2,1} = 0$
$Q_{H1,C2,2} = 1950.00$ kW	$Q_{H2,C2,2} = 0$

$Q_{CU,H1} = 167.70$ kW	$Q_{CU,H2} = 1973.45$ kW
$Q_{HU,C1} = 491.15$ kW	$Q_{HU,C2} = 0$

$\Delta T_{H1,C1,1} = 32.74$ K	$\Delta T_{H2,C1,1} = -$
$\Delta T_{H1,C1,2} = 10.00$ K	$\Delta T_{H2,C1,2} = 18.23$ K
$\Delta T_{H1,C1,3} = -$	$\Delta T_{H2,C1,3} = 58.67$ K
$\Delta T_{H1,C2,1} = -$	$\Delta T_{H2,C2,1} = -$
$\Delta T_{H1,C2,2} = 81.77$ K	$\Delta T_{H2,C2,2} = -$
$\Delta T_{H1,C2,3} = 36.77$ K	$\Delta T_{H2,C2,3} = -$

$\Delta T_{CU,H1} = 66.77$ K	$\Delta T_{CU,H2} = 148.67$ K
$\Delta T_{HU,C1} = 62.74$ K	$\Delta T_{HU,C2} = -$

- Binary variables

$z_{H1,C1,1} = 1$	$z_{H1,C2,1} = 0$	$z_{H2,C1,1} = 0$	$z_{H2,C2,1} = 0$
$z_{H1,C1,2} = 0$	$z_{H1,C2,2} = 1$	$z_{H2,C1,2} = 1$	$z_{H2,C2,2} = 0$
$z_{CU,H1} = 1$	$z_{CU,H2} = 1$	$z_{HU,C1} = 1$	$z_{HU,C2} = 0$

12.4 Heat Exchanger Network Synthesis with Arithmetic Mean Temperature Difference

12.4.1 Introduction

The general formulation for these test problem is taken from Zamora and Grossmann (1998). It is similar to that of the Chen approximation. The greatest difference lies in the expression used for the area of the heat exchangers, which is based on the arithmetic mean temperature difference rather than the Chen approximation. In addition, the assumption of no stream splitting is imposed by adding two new sets of linear constraints.

12.4.2 General Formulation

Objective function

$$
\begin{aligned}
\min_{\boldsymbol{T},\boldsymbol{Q},\boldsymbol{\Delta T},\boldsymbol{z}} \quad & \sum_{i\in HP} C_{CU}Q_{CU,i} + \sum_{j\in CP} C_{HU}Q_{HU,j} \\
& + \sum_{i\in HP}\sum_{j\in CP}\sum_{k\in SI} CF_{ij}z_{ijk} + \sum_{i\in HP} CF_{i,CU}z_{CU,i} + \sum_{j\in CP} CF_{j,HU}z_{HU,j} \\
& + \sum_{i\in HP}\sum_{j\in CP}\sum_{k\in SI} \frac{C_{ij}Q_{ijk}}{\frac{U_{ij}}{2}\left(\Delta T_{ijk}+\Delta T_{ijk+1}\right)} \\
& + \sum_{i\in HP} \frac{C_{i,CU}Q_{CU,i}}{\frac{U_{CU,i}}{2}\left(\Delta T_{CU,i}+T_{out,i}-T_{in,CU}\right)} \\
& + \sum_{j\in CP} \frac{C_{j,HU}Q_{HU,j}}{\frac{U_{HU,j}}{2}\left(\Delta T_{HU,j}+T_{in,HU}-T_{out,j}\right)}.
\end{aligned}
$$

<u>Constraints</u>

$$
\begin{aligned}
\sum_{k\in SI}\sum_{j\in CP} Q_{ijk} + Q_{CU,i} &= (T_{in,i} - T_{out,i})\, Fcp_i, \;\; \forall\, i \in HP \\
\sum_{k\in SI}\sum_{i\in HP} Q_{ijk} + Q_{HU,j} &= (T_{out,j} - T_{in,j})\, Fcp_j, \;\; \forall\, j \in CP \\
(T_{i,k} - T_{i,k+1})\, Fcp_i - \sum_{j\in CP} Q_{ijk} &= 0, \;\; \forall\, k \in SI, \; \forall\, i \in HP \\
(T_{j,k} - T_{j,k+1})\, Fcp_j - \sum_{i\in HP} Q_{ijk} &= 0, \;\; \forall\, k \in SI, \; \forall\, j \in CP \\
T_{i,1} &= T_{in,i}, \;\; \forall\, i \in HP \\
T_{j,NS+1} &= T_{in,j}, \;\; \forall\, j \in CP \\
T_{i,k} - T_{i,k+1} &\geq 0, \;\; \forall\, k \in SI, \; \forall\, i \in HP \\
T_{j,k} - T_{j,k+1} &\geq 0, \;\; \forall\, k \in SI, \; \forall\, j \in CP \\
T_{i,NS+1} &\geq T_{out,i}, \;\; \forall\, i \in HP \\
T_{j,1} &\leq T_{out,j}, \;\; \forall\, j \in CP \\
Fcp_i \; T_{i,NS+1} - Q_{CU,i} &= Fcp_i \; T_{out,i}, \;\; \forall\, i \in HP \\
Fcp_j \; T_{j,1} + Q_{HU,j} &= Fcp_j \; T_{out,j}, \;\; \forall\, j \in CP \\
Q_{ijk} - Q_{ij}^{max} z_{ijk} &\leq 0, \\
&\quad \forall\, k \in SI, \; \forall\, i \in HP, \; \forall\, j \in CP \\
Q_{CU,i} - Q_{i,CU}^{max} z_{CU,i} &\leq 0, \;\; \forall\, i \in HP \\
Q_{HU,j} - Q_{HU,j}^{max} z_{HU,j} &\leq 0, \;\; \forall\, j \in CP \\
\Delta T_{ijk} - T_{i,k} + T_{j,k} + \Delta T_{ij}^{max} z_{ijk} &\leq \Delta T_{ij}^{max}, \\
&\quad \forall\, k \in SI, \; \forall\, i \in HP, \; \forall\, j \in CP \\
\Delta T_{ijk+1} - T_{i,k+1} + T_{j,k+1} + \Delta T_{ij}^{max} z_{ijk} &\leq \Delta T_{ij}^{max}, \\
&\quad \forall\, k \in SI, \; \forall\, i \in HP, \; \forall\, j \in CP \\
\Delta T_{CU,i} - T_{i,NS+1} + \Delta T_{i,CU}^{max} z_{CU,i} &\leq \Delta T_{i,CU}^{max} - T_{out,CU}, \;\; \forall\, i \in HP \\
\Delta T_{HU,j} + T_{j,1} + \Delta T_{HU,j}^{max} z_{HU,j} &\leq \Delta T_{HU,j}^{max} + T_{out,HU}, \;\; \forall\, j \in CP \\
\sum_{j\in CP} z_{i,j,k} &\leq 1, \;\; \forall\, i \in HP, \; \forall k \in SI \\
\sum_{i\in HP} z_{i,j,k} &\leq 1, \;\; \forall\, j \in CP, \; \forall k \in SI
\end{aligned}
$$

where $\Delta T_{ij}^{max} = \max\{0, T_{j,in} - T_{i,in}, T_{j,in} - T_{i,out}, T_{j,out} - T_{i,in}, T_{j,out} - T_{i,out}\}$, with $i \in HP \cup \{HU\}$ and $j \in CP \cup \{CU\}$; and
$Q_{ij}^{max} = \min\{(T_{in,i} - T_{out,i})\, Fcp_i, (T_{out,j} - T_{in,j})\, Fcp_j\}, \forall i \in HP \cup \{HU\}, \forall j \in$

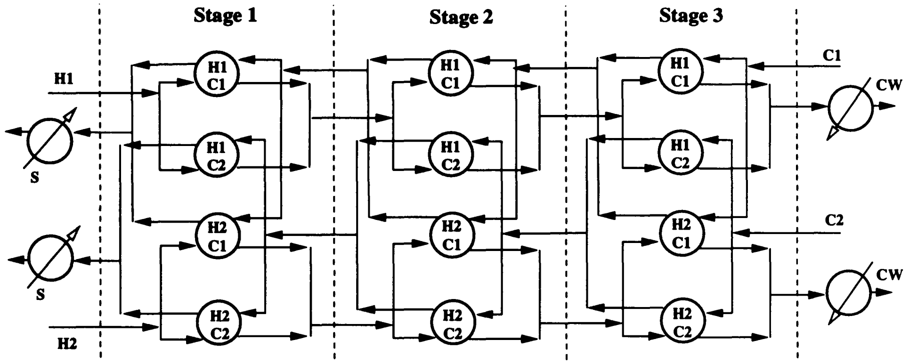


Figure 12.3: Superstructure for the heat exchanger network problem with the arithmetic mean temperature difference – Test problem 1.

$CP \cup \{CU\}$.

<u>Variable bounds</u>

$$
\begin{array}{rcl}
0 \leq & Q_{ijk} & \leq Q_{ij}^{max}, \forall k \in SI,\ \forall i \in HP,\ \forall j \in CP \\
0 \leq & Q_{CU,i} & \leq Q_{i,CU}^{max}, \forall i \in HP \\
0 \leq & Q_{HU,j} & \leq Q_{HU,j}^{max}, \forall j \in CP \\
T_{i,out} \leq & T_{ik} & \leq T_{i,in}, \forall k \in ST,\ \forall i \in HP \\
T_{j,in} \leq & T_{jk} & \leq T_{j,out}, \forall k \in ST,\ \forall j \in CP \\
\Delta T_{mapp} \leq & \Delta T_{ijk} & \leq \Delta T_{ij}^{max}, \forall k \in ST,\ \forall i \in HP,\ \forall j \in CP \\
\Delta T_{mapp} \leq & \Delta T_{CU,i} & \leq \Delta T_{i,CU}^{max}, \forall i \in HP \\
\Delta T_{mapp} \leq & \Delta T_{HU,j} & \leq \Delta T_{HU,j}^{max}, \forall j \in CP \\
z_{ijk}, z_{CU,i}, z_{HU,j} & \in \{0,1\}, & \forall k \in SI,\ \forall i \in HP,\ \forall j \in CP
\end{array}
$$

<u>Variable definitions</u>
The sets, variables and paramaters have the same meaning as for the Chen approximation formulation.

12.4.3 Test Problem 1

This corresponds to example 4 of Zamora and Grossmann (1998). Two hot streams and two cold streams are considered in a network with three temperature intervals. The superstructure is shown in Figure 12.3.

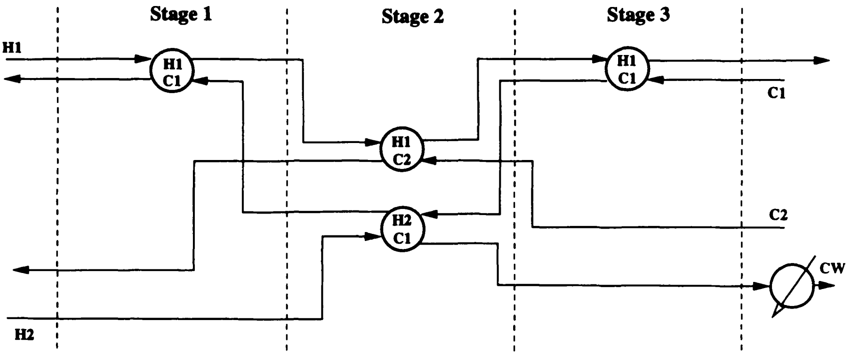


Figure 12.4: Optimum configuration for the heat exchanger network problem with the arithmetic mean temperature difference – Test problem 1.

Data

Stream	T_{in} (K)	T_{out} (K)	Fcp (kW/K)
H1	443	333	30
H2	423	303	15
C1	293	408	20
C2	353	413	40
Steam	450	450	—
Water	293	313	—

CF_{ij}	= \$6250/yr	$CF_{i,CU}$	= \$6250/yr	$CF_{j,HU}$	= \$6250/yr
C_{ij}	= \$83.26/yr	$C_{i,CU}$	= \$83.26/yr	$C_{j,HU}$	= \$99.91/yr
U_{ij}	= 0.8 kW/m^{2}K	$U_{CU,i}$	= 0.8 kW/m^{2}K	$U_{HU,j}$	= 1.2 kW/m^{2}K
C_{HU}	= \$80/kW-yr	C_{CU}	= \$20/kW-yr	ΔT_{mapp}	= 1 K

Problem Statistics

No. of continuous variables	52
No. of binary variables	16
No. of linear equalities	24
No. of convex inequalities	72
No. of known solutions	3

Global Solution

The global optimum configuration involves five heat exchangers and is shown in Figure 12.4.

- Objective function: \$74711/yr.
- Continuous variables

	$k=1$	$k=2$	$k=3$	$k=4$
$T_{H1,k}$	443.00 K	436.64 K	356.64 K	333.00 K
$T_{H2,k}$	423.00 K	423.00 K	329.67 K	329.67 K
$T_{C1,k}$	408.00 K	398.45 K	328.45 K	293.00 K
$T_{C2,k}$	413.00 K	413.00 K	353.00 K	353.00 K

$Q_{H1,C1,1} = 190.93$ kW	$Q_{H2,C1,1} = 0$
$Q_{H1,C1,2} = 0$	$Q_{H2,C1,2} = 1400.00$ kW
$Q_{H1,C1,3} = 709.07$ kW	$Q_{H2,C1,3} = 0$
$Q_{H1,C2,1} = 0$	$Q_{H2,C2,1} = 0$
$Q_{H1,C2,2} = 2400.00$ kW	$Q_{H2,C2,2} = 0$
$Q_{H1,C2,3} = 0$	$Q_{H2,C2,3} = 0$

$Q_{CU,H1} = 0$	$Q_{CU,H2} = 400$ kW
$Q_{HU,C1} = 0$	$Q_{HU,C2} = 0$

$\Delta T_{H1,C1,1} = 35.00$ K	$\Delta T_{H2,C1,1} = -$
$\Delta T_{H1,C1,2} = 38.18$ K	$\Delta T_{H2,C1,2} = 24.55$ K
$\Delta T_{H1,C1,3} = 28.18$ K	$\Delta T_{H2,C1,3} = 1.21$ K
$\Delta T_{H1,C1,4} = 40.00$ K	$\Delta T_{H2,C1,4} = -$
$\Delta T_{H1,C2,1} = -$	$\Delta T_{H2,C2,1} = -$
$\Delta T_{H1,C2,2} = 23.64$ K	$\Delta T_{H2,C2,2} = -$
$\Delta T_{H1,C2,3} = 36.36$ K	$\Delta T_{H2,C2,3} = -$
$\Delta T_{H1,C2,4} = -$	$\Delta T_{H2,C2,4} = -$

$\Delta T_{CU,H1} = -$	$\Delta T_{CU,H2} = 16.67$ K
$\Delta T_{HU,C1} = -$	$\Delta T_{HU,C2} = -$

- Binary variables

$z_{H1,C1,1} = 1$	$z_{H1,C2,1} = 0$	$z_{H2,C1,1} = 0$	$z_{H2,C2,1} = 0$
$z_{H1,C1,2} = 0$	$z_{H1,C2,2} = 1$	$z_{H2,C1,2} = 1$	$z_{H2,C2,2} = 0$
$z_{H1,C1,3} = 1$	$z_{H1,C2,3} = 0$	$z_{H2,C1,3} = 0$	$z_{H2,C2,3} = 0$
$z_{CU,H1} = 0$	$z_{CU,H2} = 1$	$z_{HU,C1} = 0$	$z_{HU,C2} = 0$

12.4.4 Test Problem 2

This corresponds to example 5 of Zamora and Grossmann (1998). This time, three hot streams and two cold streams are considered over three temperature intervals. The superstructure is shown in Figure 12.5.

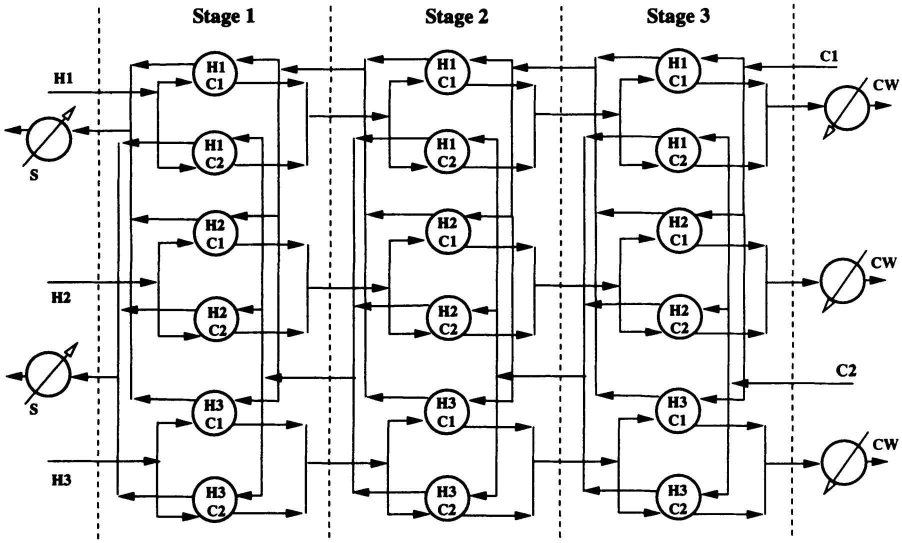


Figure 12.5: Superstructure for the heat exchanger network problem with the arithmetic mean temperature difference – Test problem 2.

Data

Stream	T_{in} (^oC)	T_{out} (^oC)	Fcp (kW/^oC)	h (kW/(m^2 ^oC))
H1	159	77	2.285	0.10
H2	267	80	0.204	0.04
H3	343	90	0.538	0.50
C1	26	127	0.933	0.01
C2	118	265	1.961	0.50
Steam	300	300	—	0.05
Water	20	60	—	0.20

The overall heat transfer coefficients are computed based on the film heat transfer coefficients h, listed in the above table. Thus, $U_{ij} = \left(\frac{1}{h_i} + \frac{1}{h_j}\right)^{-1}$.

CF_{ij}	= \$7400/yr	$CF_{i,CU}$	= \$7400/yr	$CF_{j,HU}$	= \$7400/yr
C_{ij}	= \$80/yr	$C_{i,CU}$	= \$80/yr	$C_{j,HU}$	= \$80/yr
C_{HU}	= \$110/kW-yr	C_{CU}	= \$10/kW-yr	ΔT_{mapp}	= 1^{o}C

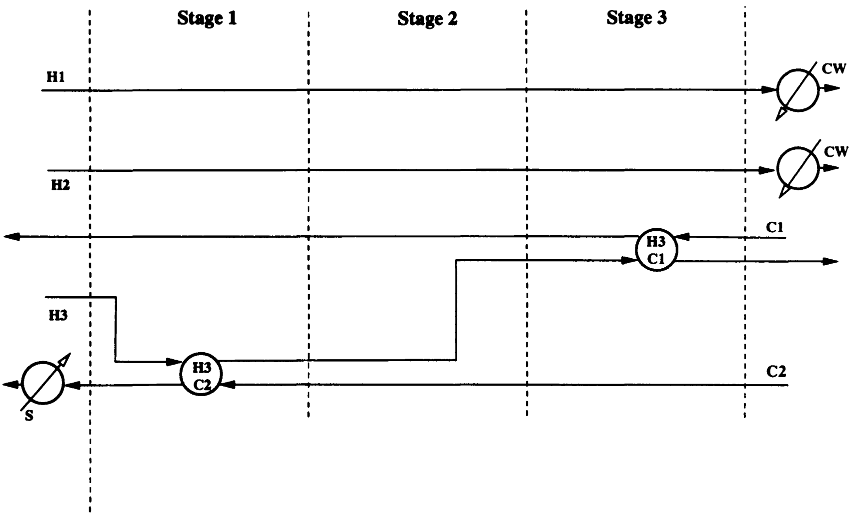


Figure 12.6: Optimum configuration for the heat exchanger network problem with the arithmetic mean temperature difference – Test problem 2.

Problem Statistics

No. of continuous variables	72
No. of binary variables	23
No. of linear equalities	30
No. of convex inequalities	99
No. of known solutions	7

Global Solution

The global optimum configuration involves five heat exchangers and is shown in Figure 12.6. There exists another solution with the same objective function but a different network structure.

- Objective function: \$82043/yr.

- Continuous variables

	$k=1$	$k=2$	$k=3$	$k=4$
$T_{H1,k}$	159.00 K	159.64 K	159.64 K	159.00 K
$T_{H2,k}$	267.00 K	267.00 K	267.00 K	267.00 K
$T_{H3,k}$	343.00 K	265.15 K	265.15 K	90.00 K
$T_{C1,k}$	127.00 K	127.00 K	127.00 K	26.00 K
$T_{C2,k}$	139.36 K	118.00 K	118.00 K	118.00 K

$Q_{H1,C1,1} = 0$	$Q_{H2,C1,1} = 0$	$Q_{H3,C1,1} = 0$
$Q_{H1,C1,2} = 0$	$Q_{H2,C1,2} = 0$	$Q_{H3,C1,2} = 0$
$Q_{H1,C1,3} = 0$	$Q_{H2,C1,3} = 0$	$Q_{H3,C1,3} = 94.23$ kW
$Q_{H1,C2,1} = 0$	$Q_{H2,C2,1} = 0$	$Q_{H3,C2,1} = 41.88$ kW
$Q_{H1,C2,2} = 0$	$Q_{H2,C2,2} = 0$	$Q_{H3,C2,2} = 0$
$Q_{H1,C2,3} = 0$	$Q_{H2,C2,3} = 0$	$Q_{H3,C2,3} = 0$

$Q_{CU,H1} = 187.37$ kW	$Q_{CU,H2} = 38.15$ kW	$Q_{CU,H3} = 0$
$Q_{HU,C1} = 0$	$Q_{HU,C2} = 246.39$ kW	

$\Delta T_{H1,C1,1} = -$	$\Delta T_{H2,C1,1} = -$	$\Delta T_{H3,C1,1} = -$
$\Delta T_{H1,C1,2} = -$	$\Delta T_{H2,C1,2} = -$	$\Delta T_{H3,C1,2} = -$
$\Delta T_{H1,C1,3} = -$	$\Delta T_{H2,C1,3} = -$	$\Delta T_{H3,C1,3} = 138.15$ K
$\Delta T_{H1,C1,4} = -$	$\Delta T_{H2,C1,4} = -$	$\Delta T_{H3,C1,4} = 64$ K
$\Delta T_{H1,C2,1} = -$	$\Delta T_{H2,C2,1} = -$	$\Delta T_{H3,C2,1} = 203.64$ K
$\Delta T_{H1,C2,2} = -$	$\Delta T_{H2,C2,2} = -$	$\Delta T_{H3,C2,2} = 147.15$ K
$\Delta T_{H1,C2,3} = -$	$\Delta T_{H2,C2,3} = -$	$\Delta T_{H3,C2,3} = -$
$\Delta T_{H1,C2,4} = -$	$\Delta T_{H2,C2,4} = -$	$\Delta T_{H3,C2,4} = -$

$\Delta T_{CU,H1} = 99.00$ K	$\Delta T_{CU,H2} = 207.00$ K	$\Delta T_{CU,H3} = -$
$\Delta T_{HU,C1} = -$	$\Delta T_{HU,C2} = 160.64$ K	

- Binary variables

$z_{H1,C1,1} = 0$	$z_{H2,C1,2} = 0$	$z_{H3,C1,1} = 0$
$z_{H1,C1,2} = 0$	$z_{H2,C1,2} = 0$	$z_{H3,C1,2} = 0$
$z_{H1,C1,3} = 0$	$z_{H2,C1,3} = 0$	$z_{H3,C1,3} = 1$
$z_{H1,C2,1} = 0$	$z_{H2,C2,1} = 0$	$z_{H3,C2,1} = 1$
$z_{H1,C2,2} = 0$	$z_{H2,C2,2} = 0$	$z_{H3,C2,2} = 0$
$z_{H1,C2,3} = 0$	$z_{H2,C2,3} = 0$	$z_{H3,C2,3} = 0$
$z_{CU,H1} = 1$	$z_{CU,H2} = 1$	$z_{CU,H3} = 0$
$z_{HU,C1} = 0$	$z_{HU,C2} = 1$	

12.5 Pump network synthesis

12.5.1 Introduction

In this example, taken from Westerlund et al. (1994), the aim is to identify the least costly configuration of centrifugal pumps that achieves a pre-specified pressure rise based on a given total flowrate. Figure 12.7 shows a schematic representation of a three level pump network superstructure, where each level corresponds to a different pump type. A major hurdle in solving this problem stems from the nonconvex participation of integer variables which leads to the presence of many local minima.

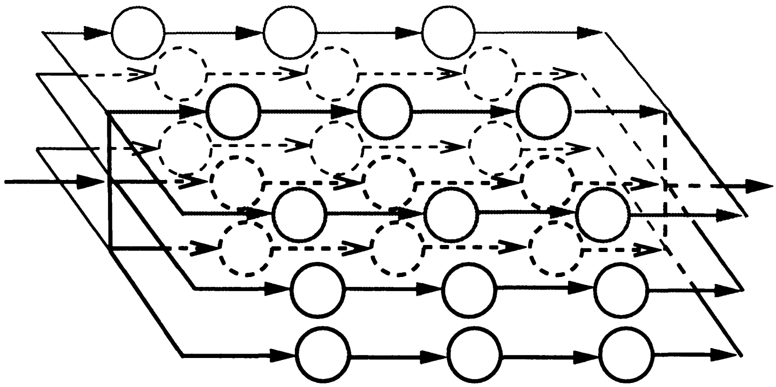


Figure 12.7: Superstructure for the pump network synthesis problem

12.5.2 Test Problem 1

Formulation

The goal is to minimize the annualized network cost given three different pump types.

Objective function

$$\min_{\boldsymbol{x},\dot{\boldsymbol{v}},\boldsymbol{\omega},\boldsymbol{P},\boldsymbol{\Delta p},\boldsymbol{Np},\boldsymbol{Ns},\boldsymbol{z}} \quad \sum_{i=1}^{3} (C_i + C_i' P_i) Np_i Ns_i z_i$$

Constraints

$$\begin{aligned}
P_1 - 19.9(\frac{\omega_1}{\omega_{max}})^3 - 0.1610(\frac{\omega_1}{\omega_{max}})^2\dot{v}_1 + 0.000561(\frac{\omega_1}{\omega_{max}})\dot{v}_1^2 &= 0 \\
P_2 - 1.21(\frac{\omega_2}{\omega_{max}})^3 - 0.0644(\frac{\omega_2}{\omega_{max}})^2\dot{v}_2 + 0.000564(\frac{\omega_2}{\omega_{max}})\dot{v}_2^2 &= 0 \\
P_3 - 6.52(\frac{\omega_3}{\omega_{max}})^3 - 0.1020(\frac{\omega_3}{\omega_{max}})^2\dot{v}_3 + 0.000232(\frac{\omega_3}{\omega_{max}})\dot{v}_3^2 &= 0 \\
\Delta p_1 - 629(\frac{\omega_1}{\omega_{max}})^2 - 0.696(\frac{\omega_1}{\omega_{max}})\dot{v}_1 + 0.0116\dot{v}_1^2 &= 0 \\
\Delta p_2 - 215(\frac{\omega_2}{\omega_{max}})^2 - 2.950(\frac{\omega_2}{\omega_{max}})\dot{v}_2 + 0.115\dot{v}_2^2 &= 0 \\
\Delta p_3 - 361(\frac{\omega_3}{\omega_{max}})^2 - 0.530(\frac{\omega_3}{\omega_{max}})\dot{v}_3 + 0.00946\dot{v}_3^2 &= 0 \\
x_1 + x_2 + x_3 &= 1 \\
\dot{v}_i N p_i - x_i V_{tot} &= 0, \; i = 1,2,3 \\
\Delta P_{tot} z_i - \Delta p_i N s_i &= 0, \; i = 1,2,3 \\
\omega_i - \omega_{max} z_i &\leq 0, \; i = 1,2,3 \\
P_i - P_{max,i} z_i &\leq 0, \; i = 1,2,3 \\
\Delta p_i - \Delta P_{tot} z_i &\leq 0, \; i = 1,2,3 \\
\dot{v}_i - V_{tot} z_i &\leq 0, \; i = 1,2,3 \\
x_i - z_i &\leq 0, \; i = 1,2,3 \\
N s_i - 3 z_i &\leq 0, \; i = 1,2,3 \\
N p_i - 3 z_i &\leq 0, \; i = 1,2,3
\end{aligned}$$

Variable bounds

$$\begin{aligned}
0 \leq x_i \leq 1, &\quad i = 1,2,3 \\
0 \leq \dot{v}_i \leq V_{tot}, &\quad i = 1,2,3 \\
0 \leq \omega_i \leq \omega_{max}, &\quad i = 1,2,3 \\
0 \leq P_i \leq P_i^{max}, &\quad i = 1,2,3 \\
0 \leq \Delta p_i \leq \Delta P_{tot}, &\quad i = 1,2,3 \\
N p_i \in \{0,1,2,3\}, &\quad i = 1,2,3 \\
N s_i \in \{0,1,2,3\}, &\quad i = 1,2,3 \\
z_i \in \{0,1\}, &\quad i = 1,2,3
\end{aligned}$$

Variable definitions

The parameters are V_{tot}, the total volumetric flowrate through the network, ΔP_{tot}, the prescribed pressure rise, ω_{max}, the maximum rotation speed of a pump, and P_i^{max}, $i = 1, \ldots, 3$, the maximum power requirement for a pump on level i.

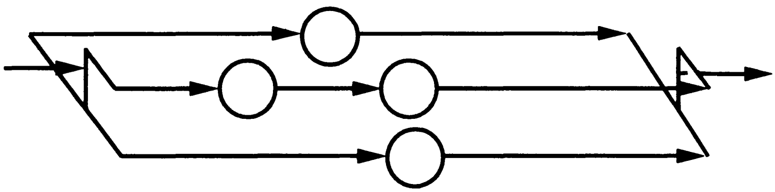


Figure 12.8: Global optimal configuration for pump network synthesis problem

The binary variables z_i, $i = 1, \ldots, 3$, denote the existence of level i. The integer variables Np_i, $i = 1, \ldots, 3$, denote the number of parallel lines at level i. The integer variables Ns_i, $i = 1, \ldots, 3$, denote the number of pumps in series at level i.

The continuous variables are the fraction of total flow going to level i, x_i, the flowrate on each line at level i, $\dot{v}_i$, the rotation speed of all pumps on level i, ω_i, the power requirements at level i, P_i and the pressure rise at level i, Δp_i.

Data

V_{tot}	$= 350$ m^3/h	ΔP_{tot}	$= 400$ kPa	ω_{max}	$= 2950$ rpm
P_1^{max}	$= 80$ kW	P_2^{max}	$= 25$ kW	P_3^{max}	$= 35$ kW

	Pump 1	Pump 2	Pump 3
Fixed cost (FIM)	38,900	15,300	20,100
C_i (FIM)	6,329.03	2,489.31	3,270.27
$C_{i'}$ (FIM/kW)	1,800	1,800	1,800

The capital costs are annualized by multiplying the fixed pump costs by a factor of 0.1627 which corresponds to a 10% interest rate and a 10 year life. The operating costs are based on 6000 hours per year and an electricity cost of 0.3 FIM/kWh. Here FIM denotes Finmark.

Problem Statistics

No. of continuous variables	15
No. of binary variables	3
No. of integer variables	6
No. of linear equalities	1
No. of nonlinear equalities	12
No. of known solutions	37

Global Solution

Figure 12.8 shows the lowest cost network (see Adjiman et al. (1998d)), which involves two levels and four pumps.

- Objective function: 128894 FIM/yr.
- Continuous variables

$x_1 = 0.914$	$x_2 = 0.086$	$x_3 = 0.000$
$\dot{v}_1 = 160\ \mathrm{m}^3/\mathrm{h}$	$\dot{v}_2 = 30\ \mathrm{m}^3/\mathrm{h}$	$\dot{v}_3 = 0$
$\omega_1 = 2855.10$ rpm	$\omega_2 = 2950.00$ rpm	$\omega_3 = 0$
$P_1 = 28.27$ kW	$P_2 = 2.63$ kW	$P_3 = 0$ kW
$\Delta p_1 = 400$ kPa	$\Delta p_2 = 200$ kPa	$\Delta p_3 = 0$

- Binary variables

$z_1 = 1$	$z_2 = 1$	$z_3 = 0$

- Integer variables

$Np_1 = 2$	$Np_2 = 1$	$Np_3 = 0$
$Ns_1 = 1$	$Ns_2 = 2$	$Ns_3 = 0$

12.6 Trim Loss Minimization

12.6.1 Introduction

Trim loss minimization problems arise in the paper cutting industry and have been studied in the context of integer nonconvex optimization by Westerlund et al. (1994) and Harjunkoski (1997). These problems involve only integer and binary variables, which appear in linear and bilinear functions. They have a very large number of solutions, many of which are redundant. The main task is to cut out some paper products of different sizes from a large raw paper roll, in order to meet a customer's order. Each product paper roll is characterized by its width b. All product rolls are assumed to be of equal length. The raw paper roll has a width B_{max}. In general, it is not possible to cut out an entire order without throwing away some of the raw paper. The optimum cutting scheme minimizes the waste paper or *trim loss*. In order to identify the best overall scheme, a maximum number of different cutting patterns P is postulated, where a pattern is defined by the position of the knives. Each cutting pattern may have to be repeated several times in the overall scheme to meet the demand. There are N different product sizes and n_i rolls of size b_i must be cut. The existence of each pattern is denoted by a binary variable z_j, $j = 1, \ldots, P$. The number of repeats of pattern j is denoted by the integer variable m_j. The number of products of size i in pattern j is given by the integer variable r_{ij}. A sample cut is shown in Figure 12.9 for

$$N = 3,\ n = \begin{pmatrix} 4 \\ 5 \\ 5 \end{pmatrix},\ m = \begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix} \text{ and } r = \begin{pmatrix} 0 & 2 & 3 \\ 4 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

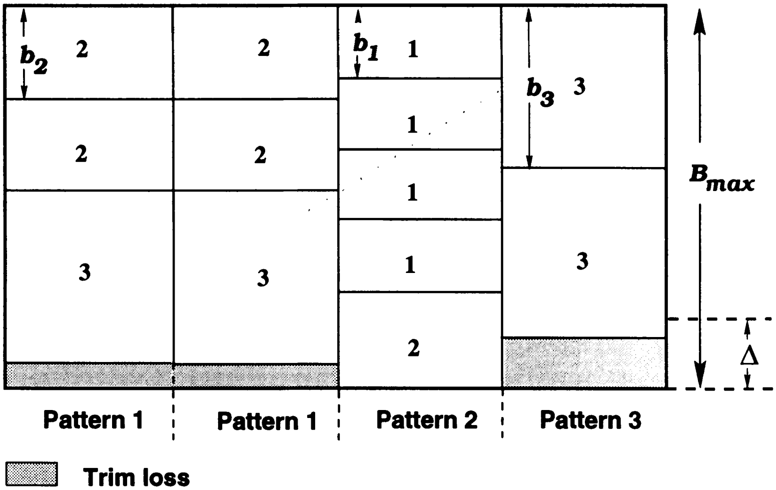


Figure 12.9: Trim loss minimization problem.

Some additional constraints are imposed on the cutting patterns. For instance, each pattern must have a minimum total width of $B_{max} - \Delta$. The number of knives is limited to Nk_{max}.

12.6.2 General Formulation

Objective function

$$\min_{\boldsymbol{m},\boldsymbol{y},\boldsymbol{r}} \sum_{j=1}^{P} m_j + 0.1\ j\ y_j$$

Constraints

$$
\begin{aligned}
\sum_j m_j \, r_{ij} &\geq n_i, \; i = 1, \ldots, N \\
(B_{max} - \Delta) \, y_j - \sum_i b_i \, r_{ij} &\leq 0, \; j = 1, \ldots, P \\
\sum_i b_i \, r_{ij} - B_{max} \, y_j &\leq 0, \; j = 1, \ldots, P \\
y_j - \sum_i r_{ij} &\leq 0, \; j = 1, \ldots, P \\
\sum_i r_{ij} - N k_{max} \, y_j &\leq 0, \; j = 1, \ldots, P \\
y_j - m_j &\leq 0, \; j = 1, \ldots, P \\
m_j - M_j y_j &\leq 0, \; j = 1, \ldots, P \\
\sum_j m_j &\geq \max \left\{ \left\lceil \frac{\sum_i n_i}{N k_{max}} \right\rceil, \left\lceil \frac{\sum_i b_i n_i}{B_{max}} \right\rceil \right\} \\
y_{k+1} - y_k &\leq 0, \; k = 1, \ldots, P-1 \\
m_{k+1} - m_k &\leq 0, \; k = 1, \ldots, P-1
\end{aligned}
$$

Variable bounds

$$
\begin{aligned}
y_j &\in \{0, 1\}, j = 1, \ldots, P \\
m_j &\in [0, M_j] \cap \mathcal{N}, j = 1, \ldots, P \\
r_{ij} &\in [0, N k_{max}] \cap \mathcal{N}, i = 1, \ldots, N, \; j = 1, \ldots, P
\end{aligned}
$$

The reported global solutions for the following four case studies are taken from Adjiman et al. (1998d).

12.6.3 Test Problem 1

Formulation

Objective function

$$
\min_{m, y, r} \; m_1 + m_2 + m_3 + m_4 + 0.1 y_1 + 0.2 y_2 + 0.3 y_3 + 0.4 y_4
$$

Constraints

$$\begin{aligned}
m_1 r_{11} + m_2 r_{12} + m_3 r_{13} + m_4 r_{14} &\geq 15 \\
m_2 r_{21} + m_2 r_{22} + m_3 r_{23} + m_4 r_{24} &\geq 28 \\
m_3 r_{31} + m_2 r_{32} + m_3 r_{33} + m_4 r_{34} &\geq 21 \\
m_4 r_{41} + m_2 r_{42} + m_3 r_{43} + m_4 r_{44} &\geq 30 \\
1750 y_1 - 290 r_{11} - 315 r_{21} - 350 r_{31} - 455 r_{41} &\leq 0 \\
1750 y_2 - 290 r_{12} - 315 r_{22} - 350 r_{32} - 455 r_{42} &\leq 0 \\
1750 y_3 - 290 r_{13} - 315 r_{23} - 350 r_{33} - 455 r_{43} &\leq 0 \\
1750 y_4 - 290 r_{14} - 315 r_{24} - 350 r_{34} - 455 r_{44} &\leq 0 \\
290 r_{11} + 315 r_{21} + 350 r_{31} + 455 r_{41} - 1850 y_1 &\leq 0 \\
290 r_{12} + 315 r_{22} + 350 r_{32} + 455 r_{42} - 1850 y_2 &\leq 0 \\
290 r_{13} + 315 r_{23} + 350 r_{33} + 455 r_{43} - 1850 y_3 &\leq 0 \\
290 r_{14} + 315 r_{24} + 350 r_{34} + 455 r_{44} - 1850 y_4 &\leq 0 \\
y_1 - r_{11} - r_{21} - r_{31} - r_{41} &\leq 0 \\
y_2 - r_{12} - r_{22} - r_{32} - r_{42} &\leq 0 \\
y_3 - r_{13} - r_{23} - r_{33} - r_{43} &\leq 0 \\
y_4 - r_{14} - r_{24} - r_{34} - r_{44} &\leq 0 \\
r_{11} + r_{21} + r_{31} + r_{41} - 5\, y_1 &\leq 0 \\
r_{12} + r_{22} + r_{32} + r_{42} - 5\, y_2 &\leq 0 \\
r_{13} + r_{23} + r_{33} + r_{43} - 5\, y_3 &\leq 0 \\
r_{14} + r_{24} + r_{34} + r_{44} - 5\, y_4 &\leq 0 \\
y_1 - m_1 &\leq 0 \\
y_2 - m_2 &\leq 0 \\
y_3 - m_3 &\leq 0 \\
y_4 - m_4 &\leq 0
\end{aligned}$$

$$
\begin{aligned}
m_1 - 30y_1 &\leq 0\\
m_2 - 30y_2 &\leq 0\\
m_3 - 30y_3 &\leq 0\\
m_4 - 30y_4 &\leq 0\\
m_1 + m_2 + m_3 + m_4 &\geq 19\\
y_1 - y_2 &\geq 0\\
y_2 - y_3 &\geq 0\\
y_3 - y_4 &\geq 0\\
m_1 - m_2 &\geq 0\\
m_2 - m_3 &\geq 0\\
m_3 - m_4 &\geq 0
\end{aligned}
$$

Variable bounds

$$
\begin{aligned}
(y_1, y_2, y_3, y_4) &\in \{0,1\}^4\\
(m_1, m_2, m_3, m_4) &\in [0,30]^4 \cap \mathcal{N}^4\\
r_{ij} &\in \{0,1,2,3,4,5\},\ i = 1,\ldots,4, j = 1,\ldots,4.
\end{aligned}
$$

Data

$$N = 4 \quad P = 4 \quad B_{max} = 1850 \text{ mm} \quad \Delta = 100 \text{ mm}$$

$$\boldsymbol{n} = (15, 28, 21, 30)^T$$

$$\boldsymbol{b} = (290, 315, 350, 455)^T$$

$$\boldsymbol{M} = (30, 30, 30, 30)^T$$

Problem Statistics

No. of binary variables	4
No. of integer variables	20
No. of convex inequalities	31
No. of nonconvex inequalities	4
No. of known solutions	more than 40

Global Solution

There exist several degenerate solutions to this problem. Only one is presented here.

- Objective function: 19.6.
- Binary variables: $\boldsymbol{y} = (1, 1, 1, 0)^T$.
- Integer variables

$$\boldsymbol{m} = (9, 7, 3, 0)^T$$

$$\boldsymbol{r} = \begin{pmatrix} 1 & 0 & 2 & 0 \\ 2 & 1 & 1 & 0 \\ 0 & 3 & 0 & 0 \\ 2 & 1 & 2 & 0 \end{pmatrix}$$

12.6.4 Test Problem 2

Formulation

Objective function

$$\min_{\boldsymbol{m},\boldsymbol{y},\boldsymbol{r}} \quad m_1 + m_2 + m_3 + m_4 + 0.1y_1 + 0.2y_2 + 0.3y_3 + 0.4y_4$$

Constraints

$$\begin{aligned}
m_1 r_{11} + m_2 r_{12} + m_3 r_{13} + m_4 r_{14} &\geq 9 \\
m_2 r_{21} + m_2 r_{22} + m_3 r_{23} + m_4 r_{24} &\geq 7 \\
m_3 r_{31} + m_2 r_{32} + m_3 r_{33} + m_4 r_{34} &\geq 12 \\
m_4 r_{41} + m_2 r_{42} + m_3 r_{43} + m_4 r_{44} &\geq 11 \\
1700y_1 - 330r_{11} - 360r_{21} - 385r_{31} - 415r_{41} &\leq 0 \\
1700y_2 - 330r_{12} - 360r_{22} - 385r_{32} - 415r_{42} &\leq 0 \\
1700y_3 - 330r_{13} - 360r_{23} - 385r_{33} - 415r_{43} &\leq 0 \\
1700y_4 - 330r_{14} - 360r_{24} - 385r_{34} - 415r_{44} &\leq 0 \\
330r_{11} + 360r_{21} + 385r_{31} + 415r_{41} - 1900y_1 &\leq 0 \\
330r_{12} + 360r_{22} + 385r_{32} + 415r_{42} - 1900y_2 &\leq 0 \\
330r_{13} + 360r_{23} + 385r_{33} + 415r_{43} - 1900y_3 &\leq 0 \\
330r_{14} + 360r_{24} + 385r_{34} + 415r_{44} - 1900y_4 &\leq 0
\end{aligned}$$

$$
\begin{aligned}
y_1 - r_{11} - r_{21} - r_{31} - r_{41} &\leq 0 \\
y_2 - r_{12} - r_{22} - r_{32} - r_{42} &\leq 0 \\
y_3 - r_{13} - r_{23} - r_{33} - r_{43} &\leq 0 \\
y_4 - r_{14} - r_{24} - r_{34} - r_{44} &\leq 0 \\
r_{11} + r_{21} + r_{31} + r_{41} - 5\, y_1 &\leq 0 \\
r_{12} + r_{22} + r_{32} + r_{42} - 5\, y_2 &\leq 0 \\
r_{13} + r_{23} + r_{33} + r_{43} - 5\, y_3 &\leq 0 \\
r_{14} + r_{24} + r_{34} + r_{44} - 5\, y_4 &\leq 0 \\
y_1 - m_1 &\leq 0 \\
y_2 - m_2 &\leq 0 \\
y_3 - m_3 &\leq 0 \\
y_4 - m_4 &\leq 0 \\
m_1 - 15y_1 &\leq 0 \\
m_2 - 12y_2 &\leq 0 \\
m_3 - 9y_3 &\leq 0 \\
m_4 - 6y_4 &\leq 0 \\
m_1 + m_2 + m_3 + m_4 &\geq 8 \\
y_1 - y_2 &\geq 0 \\
y_2 - y_3 &\geq 0 \\
y_3 - y_4 &\geq 0 \\
m_1 - m_2 &\geq 0 \\
m_2 - m_3 &\geq 0 \\
m_3 - m_4 &\geq 0
\end{aligned}
$$

Variable bounds

$$
\begin{aligned}
(y_1, y_2, y_3, y_4) &\in \{0,1\}^4 \\
m_1 &\in \{0,1,2,3,4,5,6,7,8,9,10,11,12,13,14,15\} \\
m_2 &\in \{0,1,2,3,4,5,6,7,8,9,10,11,12\} \\
m_3 &\in \{0,1,2,3,4,5,6,7,8,9\} \\
m_4 &\in \{0,1,2,3,4,5,6\} \\
r_{ij} &\in \{0,1,2,3,4,5\},\ i = 1,\ldots,4, j = 1,\ldots,4.
\end{aligned}
$$

Data

$$N = 4 \quad P = 4 \quad B_{max} = 1900 \text{ mm} \quad \Delta = 200 \text{ mm}$$

$$\boldsymbol{n} = (9, 7, 12, 11)^T$$

$$\boldsymbol{b} = (330, 360, 385, 415)^T$$

$$\boldsymbol{M} = (15, 12, 9, 6)^T$$

Problem Statistics

No. of binary variables	4
No. of integer variables	20
No. of convex inequalities	31
No. of nonconvex inequalities	4
No. of known solutions	more than 60

Global Solution

There exist several degenerate solutions to this problem. Only one is presented here.

- Objective function: 8.6.
- Binary variables: $\boldsymbol{y} = (1, 0, 0, 0)^T$.
- Integer variables

$$\boldsymbol{m} = (11, 0, 0, 0)^T$$

$$\boldsymbol{r} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

12.6.5 Test Problem 3

Formulation

Objective function

$$\min_{\boldsymbol{m},\boldsymbol{y},\boldsymbol{r}} \quad m_1 + m_2 + m_3 + m_4 + m_5 + 0.1y_1 + 0.2y_2 + 0.3y_3 + 0.4y_4 + 0.5y_5$$

<u>Constraints</u>

$$
\begin{aligned}
m_1r_{11} + m_2r_{12} + m_3r_{13} + m_4r_{14} + m_5r_{15} &\geq 12 \\
m_1r_{21} + m_2r_{22} + m_3r_{23} + m_4r_{24} + m_5r_{25} &\geq 6 \\
m_1r_{31} + m_2r_{32} + m_3r_{33} + m_4r_{34} + m_5r_{35} &\geq 15 \\
m_1r_{41} + m_2r_{42} + m_3r_{43} + m_4r_{44} + m_5r_{45} &\geq 6 \\
m_1r_{51} + m_2r_{52} + m_3r_{53} + m_4r_{54} + m_5r_{55} &\geq 9 \\
1800y_1 - 330r_{11} - 360r_{21} - 370r_{31} - 415r_{41} - 435r_{51} &\leq 0 \\
1800y_2 - 330r_{12} - 360r_{22} - 370r_{32} - 415r_{42} - 435r_{52} &\leq 0 \\
1800y_3 - 330r_{13} - 360r_{23} - 370r_{33} - 415r_{43} - 435r_{53} &\leq 0 \\
1800y_4 - 330r_{14} - 360r_{24} - 370r_{34} - 415r_{44} - 435r_{54} &\leq 0 \\
1800y_5 - 330r_{15} - 360r_{25} - 370r_{35} - 415r_{45} - 435r_{55} &\leq 0 \\
330r_{11} + 360r_{21} + 370r_{31} + 415r_{41} + 435r_{51} - 2000y_1 &\leq 0 \\
330r_{12} + 360r_{22} + 370r_{32} + 415r_{42} + 435r_{52} - 2000y_2 &\leq 0 \\
330r_{13} + 360r_{23} + 370r_{33} + 415r_{43} + 435r_{53} - 2000y_3 &\leq 0 \\
330r_{14} + 360r_{24} + 370r_{34} + 415r_{44} + 435r_{54} - 2000y_4 &\leq 0 \\
330r_{15} + 360r_{25} + 370r_{35} + 415r_{45} + 435r_{55} - 2000y_5 &\leq 0 \\
y_1 - r_{11} - r_{21} - r_{31} - r_{41} - r_{51} &\leq 0 \\
y_2 - r_{12} - r_{22} - r_{32} - r_{42} - r_{52} &\leq 0 \\
y_3 - r_{13} - r_{23} - r_{33} - r_{43} - r_{53} &\leq 0 \\
y_4 - r_{14} - r_{24} - r_{34} - r_{44} - r_{54} &\leq 0 \\
y_5 - r_{15} - r_{25} - r_{35} - r_{45} - r_{55} &\leq 0 \\
r_{11} + r_{21} + r_{31} + r_{41} + r_{51} - 5\ y_1 &\leq 0 \\
r_{12} + r_{22} + r_{32} + r_{42} + r_{52} - 5\ y_2 &\leq 0 \\
r_{13} + r_{23} + r_{33} + r_{43} + r_{53} - 5\ y_3 &\leq 0 \\
r_{14} + r_{24} + r_{34} + r_{44} + r_{54} - 5\ y_4 &\leq 0 \\
r_{15} + r_{25} + r_{35} + r_{45} + r_{55} - 5\ y_5 &\leq 0 \\
y_1 - m_1 &\leq 0 \\
y_2 - m_2 &\leq 0 \\
y_3 - m_3 &\leq 0 \\
y_4 - m_4 &\leq 0 \\
y_5 - m_5 &\leq 0 \\
m_1 - 15y_1 &\leq 0 \\
m_2 - 12y_2 &\leq 0 \\
m_3 - 9y_3 &\leq 0 \\
m_4 - 6y_4 &\leq 0 \\
m_5 - 6y_5 &\leq 0
\end{aligned}
$$

$$
\begin{aligned}
m_1 + m_2 + m_3 + m_4 + m_5 &\geq 10 \\
y_1 - y_2 &\geq 0 \\
y_2 - y_3 &\geq 0 \\
y_3 - y_4 &\geq 0 \\
y_4 - y_5 &\geq 0 \\
m_1 - m_2 &\geq 0 \\
m_2 - m_3 &\geq 0 \\
m_3 - m_4 &\geq 0 \\
m_4 - m_5 &\geq 0
\end{aligned}
$$

Variable bounds

$$
\begin{aligned}
(y_1, y_2, y_3, y_4, y_5) &\in \{0,1\}^5 \\
m_1 &\in \{0,1,2,3,4,5,6,7,8,9,10,11,12,13,14,15\} \\
m_2 &\in \{0,1,2,3,4,5,6,7,8,9,10,11,12\} \\
m_3 &\in \{0,1,2,3,4,5,6,7,8,9\}
\end{aligned}
$$

$$
\begin{aligned}
m_4 &\in \{0,1,2,3,4,5,6\} \\
m_5 &\in \{0,1,2,3,4,5,6\} \\
r_{ij} &\in \{0,1,2,3,4,5\}, \ i = 1, \ldots, 5, j = 1, \ldots, 5.
\end{aligned}
$$

Data

$$N = 5 \quad P = 5 \quad B_{max} = 2000 \text{ mm} \quad \Delta = 200 \text{ mm}$$

$$\boldsymbol{n} = (12, 6, 15, 6, 9)^T$$

$$\boldsymbol{b} = (330, 360, 370, 415, 435)^T$$

$$\boldsymbol{M} = (15, 12, 9, 6, 6)^T$$

Problem Statistics

No. of binary variables	5
No. of integer variables	30
No. of convex inequalities	39
No. of nonconvex inequalities	5
No. of known solutions	more than 40

Global Solution

There exist several degenerate solutions to this problem. Only one is presented here.

- Objective function: 10.3.
- Binary variables: $\boldsymbol{y} = (1, 0, 0, 0, 0)^T$.
- Integer variables

$$\boldsymbol{m} = (15, 0, 0, 0, 0)^T$$

$$\boldsymbol{r} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix}$$

12.6.6 Test Problem 4

Formulation

Objective function

$$\begin{aligned} \min_{\boldsymbol{m},\boldsymbol{y},\boldsymbol{r}} \quad & m_1 + m_2 + m_3 + m_4 + m_5 + m_6 \\ & + 0.1y_1 + 0.2y_2 + 0.3y_3 + 0.4y_4 + 0.5y_5 + 0.6y_6 \end{aligned}$$

Constraints

$$\begin{aligned} m_1 r_{11} + m_2 r_{12} + m_3 r_{13} + m_4 r_{14} + m_5 r_{15} + m_6 r_{16} &\geq 8 \\ m_1 r_{21} + m_2 r_{22} + m_3 r_{23} + m_4 r_{24} + m_5 r_{25} + m_6 r_{26} &\geq 16 \\ m_1 r_{31} + m_2 r_{32} + m_3 r_{33} + m_4 r_{34} + m_5 r_{35} + m_6 r_{36} &\geq 12 \\ m_1 r_{41} + m_2 r_{42} + m_3 r_{43} + m_4 r_{44} + m_5 r_{45} + m_6 r_{46} &\geq 7 \\ m_1 r_{51} + m_2 r_{52} + m_3 r_{53} + m_4 r_{54} + m_5 r_{55} + m_6 r_{56} &\geq 14 \\ m_1 r_{61} + m_2 r_{62} + m_3 r_{63} + m_4 r_{64} + m_5 r_{65} + m_6 r_{66} &\geq 16 \\ 2100y_1 - 330r_{11} - 360r_{21} - 380r_{31} - 430r_{41} - 490r_{51} - 530r_{61} &\leq 0 \\ 2100y_2 - 330r_{12} - 360r_{22} - 380r_{32} - 430r_{42} - 490r_{52} - 530r_{62} &\leq 0 \\ 2100y_3 - 330r_{13} - 360r_{23} - 380r_{33} - 430r_{43} - 490r_{53} - 530r_{63} &\leq 0 \end{aligned}$$

$$
\begin{aligned}
2100y_4 - 330r_{14} - 360r_{24} - 380r_{34} - 430r_{44} - 490r_{54} - 530r_{64} &\leq 0 \\
2100y_5 - 330r_{15} - 360r_{25} - 380r_{35} - 430r_{45} - 490r_{55} - 530r_{65} &\leq 0 \\
2100y_6 - 330r_{16} - 360r_{26} - 380r_{36} - 430r_{46} - 490r_{56} - 530r_{66} &\leq 0 \\
330r_{11} + 360r_{21} + 380r_{31} + 430r_{41} + 490r_{51} + 530r_{61} - 2200y_1 &\leq 0 \\
330r_{12} + 360r_{22} + 380r_{32} + 430r_{42} + 490r_{52} + 530r_{62} - 2200y_2 &\leq 0 \\
330r_{13} + 360r_{23} + 380r_{33} + 430r_{43} + 490r_{53} + 530r_{63} - 2200y_3 &\leq 0 \\
330r_{14} + 360r_{24} + 380r_{34} + 430r_{44} + 490r_{54} + 530r_{64} - 2200y_4 &\leq 0 \\
330r_{15} + 360r_{25} + 380r_{35} + 430r_{45} + 490r_{55} + 530r_{65} - 2200y_5 &\leq 0 \\
330r_{16} + 360r_{26} + 380r_{36} + 430r_{46} + 490r_{56} + 530r_{66} - 2200y_6 &\leq 0 \\
y_1 - r_{11} - r_{21} - r_{31} - r_{41} - r_{51} - r_{61} &\leq 0 \\
y_2 - r_{12} - r_{22} - r_{32} - r_{42} - r_{52} - r_{62} &\leq 0 \\
y_3 - r_{13} - r_{23} - r_{33} - r_{43} - r_{53} - r_{63} &\leq 0 \\
y_4 - r_{14} - r_{24} - r_{34} - r_{44} - r_{54} - r_{64} &\leq 0 \\
y_5 - r_{15} - r_{25} - r_{35} - r_{45} - r_{55} - r_{65} &\leq 0 \\
y_6 - r_{16} - r_{26} - r_{36} - r_{46} - r_{56} - r_{66} &\leq 0 \\
r_{11} + r_{21} + r_{31} + r_{41} + r_{51} + r_{61} - 5\ y_1 &\leq 0 \\
r_{12} + r_{22} + r_{32} + r_{42} + r_{52} + r_{62} - 5\ y_2 &\leq 0 \\
r_{13} + r_{23} + r_{33} + r_{43} + r_{53} + r_{63} - 5\ y_3 &\leq 0 \\
r_{14} + r_{24} + r_{34} + r_{44} + r_{54} + r_{64} - 5\ y_4 &\leq 0 \\
r_{15} + r_{25} + r_{35} + r_{45} + r_{55} + r_{65} - 5\ y_5 &\leq 0 \\
r_{16} + r_{26} + r_{36} + r_{46} + r_{56} + r_{66} - 5\ y_6 &\leq 0 \\
y_1 - m_1 &\leq 0 \\
y_2 - m_2 &\leq 0 \\
y_3 - m_3 &\leq 0 \\
y_4 - m_4 &\leq 0 \\
y_5 - m_5 &\leq 0 \\
y_6 - m_6 &\leq 0 \\
m_1 - 15y_1 &\leq 0 \\
m_2 - 12y_2 &\leq 0 \\
m_3 - 8y_3 &\leq 0 \\
m_4 - 7y_4 &\leq 0 \\
m_5 - 4y_5 &\leq 0 \\
m_6 - 2y_6 &\leq 0 \\
m_1 + m_2 + m_3 + m_4 + m_5 + m_6 &\geq 16
\end{aligned}
$$

$$
\begin{aligned}
y_1 - y_2 &\geq 0 \\
y_2 - y_3 &\geq 0 \\
y_3 - y_4 &\geq 0 \\
y_4 - y_5 &\geq 0 \\
y_5 - y_6 &\geq 0 \\
m_1 - m_2 &\geq 0 \\
m_2 - m_3 &\geq 0 \\
m_3 - m_4 &\geq 0 \\
m_4 - m_5 &\geq 0 \\
m_5 - m_6 &\geq 0
\end{aligned}
$$

Variable bounds

$$
\begin{aligned}
(y_1, y_2, y_3, y_4, y_5, y_6) &\in \{0,1\}^6 \\
m_1 &\in \{0,1,2,3,4,5,6,7,8,9,10,11,12,13,14,15\} \\
m_2 &\in \{0,1,2,3,4,5,6,7,8,9,10,11,12\} \\
m_3 &\in \{0,1,2,3,4,5,6,7,8\} \\
m_4 &\in \{0,1,2,3,4,5,6,7\} \\
m_5 &\in \{0,1,2,3,4\} \\
m_6 &\in \{0,1,2\} \\
r_{ij} &\in \{0,1,2,3,4,5\}, \; i = 1,\ldots,6, j = 1,\ldots,6.
\end{aligned}
$$

Data

$$N = 6 \quad P = 6 \quad B_{max} = 2200 \text{ mm} \quad \Delta = 100 \text{ mm}$$

$$\boldsymbol{n} = (8, 16, 15, 7, 14, 16)^T$$

$$\boldsymbol{b} = (330, 360, 380, 430, 490, 530)^T$$

$$\boldsymbol{M} = (15, 12, 8, 7, 4, 2)^T$$

Problem Statistics

No. of binary variables	6
No. of integer variables	42
No. of convex inequalities	47
No. of nonconvex inequalities	6
No. of known solutions	more than 25

Global Solution

There exist several degenerate solutions to this problem. Only one is presented here.

- Objective function: 15.3.
- Binary variables: $\boldsymbol{y} = (1,1,0,0,0,0)^T$.
- Integer variables

$$\boldsymbol{m} = (8,7,0,0,0,0)^T$$

$$\boldsymbol{r} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Chapter 13

Combinatorial Optimization Problems

13.1 Modeling with Integer Programming

Combinatorial optimization problems possess a discrete special structure, such that it is very difficult to develop general purpose test problems, as well as general purpose software for solving them. For the exact solution of these problems, usually an equivalent integer programming formulation is provided to an IP solver, that uses branch and bound to solve it. For a suboptimal solution, many heuristic procedures have been refined over the years, and there exist procedures designed to provide suboptimal solutions to general combinatorial optimization problems, given that the problem has been put into some prespecified format.

The general discrete (or combinatorial) optimization problem has the form:

$$\min_{\boldsymbol{x} \in F \subset D} f(\boldsymbol{x})$$

where F is a set of constraints, typically in the form of inequalities, and D is the set of n-dimensional *integral* vectors Z^n. Discrete optimization problems are classified according to the form that f, F and D have. For example the $0-1$ linear programming problem can be stated as

$$\begin{array}{ll} \min & \boldsymbol{c}^T \boldsymbol{x} \\ \text{s.t.} & \boldsymbol{A}\boldsymbol{x} \le \boldsymbol{b} \\ & \boldsymbol{x} \in \boldsymbol{B}^n := \{0, 1\}^n \end{array}$$

The set of n-dimensional *binary* vectors B^n is used frequently to model problems where the decision variables x are constrained to take *true* or *false* values. An immediate observation for the above $0-1$ linear program, is that the feasible set is *finite*, and one may conclude that the solution to the problem can be

C. A. Floudas et al., *Handbook of Test Problems in Local and Global Optimization*

found trivially by examining all solutions. From the algorithmic point of view however, this is an impossibility, since the number of feasible solutions usually grows exponentially with respect to the problem data (A, c and b).

Using the simple fact that $z \in \{0,1\} \Leftrightarrow z + w = 1, z \geq 0, w \geq 0, zw = 0$ it is clear that integer constraints are equivalent to continuous nonconvex (complementarity) constraints Pardalos (1996).

Many problems arising from diverse areas can be formulated as integer programming problems. One can argue that *combinatorial optimization* and *integer programming* are synonymous terms (Du and Pardalos (1998)). This is because the majority (if not all) of the combinatorial optimization problems are integer programming problems, usually involving binary variables.

13.1.1 Test problems in the Internet

In recent years many collections of test problems are available at the internet (Beasley (1996)). For example, the OR-Library, is a collection of several combinatorial optimization test problems (including integer programming, scheduling problems, set covering problems, and graph planarization). Information on the OR-Library can be obtained by email at

`o.library@ic.ac.uk,`

or at the web address:

`http://mscmga.ms.ic.ac.uk/.`

13.2 Quadratic Integer Programming

Many combinatorial optimization problems (including maximum clique and graph coloring) can be formulated as quadratic integer programming problems. The general $0-1$ quadratic programming is defined below:

$$\begin{array}{ll} \min\limits_{\boldsymbol{x}} & \boldsymbol{c}^T\boldsymbol{x} + \frac{1}{2}\boldsymbol{x}^T\boldsymbol{Q}\boldsymbol{x} \\ \text{s.t.} & \boldsymbol{A}\boldsymbol{x} \leq \boldsymbol{b} \\ & \boldsymbol{x} \in \boldsymbol{B}^n \end{array}$$

where $\boldsymbol{Q}$ in an rational $n \times n$ symmetric matrix. When only the constraint $\boldsymbol{x} \in \boldsymbol{B}^n$ is present, we have a pure (or unconstrained) $0-1$ integer program. It is clear that any bivalent problem is equivalent to the $0-1$ problem by a simple linear transformation.

13.2.1 Quadratic 0-1 Test problems

A test problem generator for constrained $0-1$ quadratic problems has been proposed by Pardalos (1991) (see also Pardalos (1987)). For any selected feasible $0-1$ point of a given domain, the method generates quadratic functions whose global minimum over the given domain occurs at the selected point.

QIP1 Test Problem - nonlinear constraints:

$$\begin{array}{ll} \min\limits_{\boldsymbol{x}} & \boldsymbol{c}^T\boldsymbol{x} + \frac{1}{2}\boldsymbol{x}^T\boldsymbol{Q}\boldsymbol{x} \\ \text{s.t.} & -1 \le x_1x_2 + x_3x_4 \le 1 \\ & -3 \le x_1 + x_2 + x_3 + x_4 \le 2 \\ & \boldsymbol{x} \in \{-1,1\}^4 \end{array}$$

where $\boldsymbol{c} = (6, 8, 4, -2)$ and

$$\boldsymbol{Q} = \begin{bmatrix} -1 & 2 & 0 & 0 \\ 2 & -1 & 2 & 0 \\ 0 & 2 & -1 & 2 \\ 0 & 0 & 2 & -1 \end{bmatrix}$$

The global solution is the point $\boldsymbol{x}^* = (-1, -1, -1, 1)$ with $f(\boldsymbol{x}^*) = -20$.

In Pardalos (1991) a standardized random test problem generator is also given for unconstrained $0-1$ programming.

QIP2 Test Problem - unconstrained:

$$\begin{array}{ll} \min\limits_{\boldsymbol{x}} & \boldsymbol{x}^T\boldsymbol{Q}\boldsymbol{x} \\ \text{s.t.} & \boldsymbol{x} \in \{0,1\}^{10} \end{array}$$

and

$$\boldsymbol{Q} = \begin{bmatrix} -1 & -2 & 2 & 8 & -5 & 1 & -4 & 0 & 0 & 8 \\ -2 & 2 & 0 & -5 & 4 & -4 & -4 & -5 & 0 & -5 \\ 2 & 0 & 2 & -3 & 7 & 0 & -3 & 7 & 5 & 0 \\ 8 & -5 & -3 & -1 & -3 & -1 & 7 & 1 & 7 & 2 \\ -5 & 4 & 7 & -3 & 1 & 0 & -4 & 2 & 4 & -2 \\ 1 & -4 & 0 & -1 & 0 & 1 & 9 & 5 & 2 & 0 \\ -4 & -4 & -3 & 7 & -4 & 9 & 3 & 1 & 2 & 0 \\ 0 & -5 & 7 & 1 & 2 & 5 & 1 & 0 & -3 & -2 \\ 0 & 0 & 5 & 7 & 4 & 2 & 2 & -3 & 2 & 3 \\ 8 & -5 & 0 & 2 & -2 & 0 & 0 & -2 & 3 & 3 \end{bmatrix}$$

The global solution is the point $\boldsymbol{x}^* = (1, 1, 0, 0, 1, 0, 1, 1, 0, 0)$ with $f(\boldsymbol{x}^*) = -29$.

At the present time there exist efficient algorithms for solving pure $0-1$ quadratic integer problems. **Q01SUBS** solves unconstrained quadratic $0-1$ problems both for dense and sparse matrices, including concave quadratic minimization problems with box constraints. **Q01SUBS** is available at the NEOS Server which can be accessed via the web:

http://www.mcs.anl.gov/home/otc/Server.

The code **Q01SUBS** can be used to provide large size test instances of quadratic $0-1$ problems of certain difficulty by controlling the diagonal dominance of the input data matrix.

13.3 Satisfiability Problems

Many propositional calculus problems can be formulated as integer programs (Cavalier et al. (1990); Du et al. (1997); Williams (1987)). Consider a *boolean* variable l_i which can take the values of either *True* of *False*, and a binary variable x_i where

$$x_i = \begin{cases} 1 & \text{if } l_i \text{ is True,} \\ 0 & \text{if } l_i \text{ is False.} \end{cases}$$

Then the logical expression $l_1 \wedge l_2$ is equivalent to the algebraic expression $x_1 x_2$, and $l_1 \vee l_2$ equivalent to $x_1 + x_2 - x_1 x_2$. Furthermore, $\bar{l}_i$ the *negation* of the boolean variable l_i can be represented as $1 - x_i$. Applying the just mentioned relationships recursively one can transform any propositional calculus problem into an equivalent $0-1$ polynomial programming problem. Furthermore, any product of binary variables can be replaced by a single binary variable, and two additional constraints. Specifically, the product $\prod_{i\in I} x_i$ can be replaced by the binary variable $y \in \{0,1\}$ and the two linear $0-1$ equations:

$$-\sum_{i\in I} x_i + y + |I| \geq 1$$

and

$$\sum_{i\in I} x_i - y|I| \geq 0,$$

where $|I|$ stands for the cardinality of the set I. The *Satisfiability* problem (SAT) is probably the most significant problem in propositional logic. It has many applications in the areas of artificial intelligence, mathematical logic, computer vision, and it was the first problem shown to be NP-complete Cook (1971). Assume that we have boolean variables l_i, $i = 1, \ldots, m$, and define a *clause* C_j as

$$C_j := \bigvee_{i\in I_j^+} l_i \vee \left(\bigvee_{i\in I_j^-} \bar{l}_i \right),$$

where I_j^+, I_j^- are index sets of the unnegated and negated boolean variables in clause j respectively. In SAT we are given a set n of clauses, and the problem is to find whether or not there is a truth assignment of the variables such that all clauses are satisfied (i.e. have a truth value). SAT can be transformed into an equivalent integer programming feasibility problem as follows. A truth assignment of the boolean variables l_i satisfies

$$\bigwedge_{j=1}^{n} C_j$$

if and only if the binary variables x_i as defined in (13.3) satisfy the following system of inequalities

$$\sum_{i \in I_j^+} x_i - \sum_{i \in I_j^-} x_i \geq 1 - |I_j^-|, \quad i = 1, \ldots, n.$$

Resolving feasibility for the above system of integral inequalities, will solve the SAT problem. A related problem which is equally important, is the weighted *Maximum Satisfiability* problem (MAX-SAT), where we are given a set of n clauses with weights w_j, and we have to find a truth assignment of the boolean variables such that the sum of the weights of the satisfied clauses is maximized. It is clear that SAT is a special case of MAX-SAT. Setting $w_j = 1, \forall j$ if the solution of the MAX-SAT is n then the set of clauses is satisfiable with the truth assignment indicated by the solution. MAX-SAT also admits a integer programming formulation. Define m binary variables x_i as in (13.3), and also define a continuous variable $y_j = 1$ if clause C_j is satisfied and $y_j = 0$ otherwise. Then the MAX-SAT is equivalent to the following mixed linear-integer programming formulation:

$$\begin{array}{ll} \max & \displaystyle\sum_{i=1}^{m} w_i y_i \\ \text{subject to:} & \displaystyle\sum_{i \in I_j^+} x_i + \sum_{i \in I_j^-} (1 - x_i) \geq y_j, \;\; j = 1, \ldots, n, \\ & x_i \in \{0, 1\}, \;\; i = 1, \ldots, m, \\ & 0 \leq y_i \leq 1, \;\; i = 1, \ldots, n, \end{array}$$

where I_j^+ and I_j^- denotes the set of boolean variables appearing unnegated (resp. negated) in clause C_j.

13.3.1 SAT Test Problems

During the second DIMACS Implementation Challenge a set of instances were chosen to provide the satisfiability benchmarks. These problems can be found in the web address:

`http://dimacs.rutgers.du/Challenges/index.html`

The most complete information on test problems and algorithms for all versions of the satisfiability problem can be found in the book by Du et al. (1997).

13.4 The Traveling Salesman Problem

Consider a *complete graph* $G := (V, E)$, where $V = \{v_1, v_2, \dots, v_n\}$ is the set of vertices and $E := \{(v_i, v_j) | v_i, v_j \in V, i, j = 1, 2 \dots, n\}$ is the set of edges. A *simple cycle* of the graph G is a sequence of vertices $(v_{i_1}, v_{i_2}, \dots, v_{i_k}, v_{i_1})$, such that the vertices $v_{i_1}, v_{i_2}, \dots, v_{i_k}$ are distinct, while a *Hamiltonian cycle*, or a *tour* of G is a simple cycle wich contains every vertex of V. Assume that each node in the graph represents a city, while $R^{n \times n} \ni D := (d_{ij})$ contains the Euclidean distances between any two nodes i and j. The traveling salesman problem (TSP) is to find a tour that visits every city once with the minimum total distance. Given that S_n is the set of all permutations of the integers $\{1, 2, \dots, n\}$ the TSP formulated as a combinatorial optimization problem is

$$\begin{array}{ll} \min & \sum_{i=1}^{n-1} d_{p(i)p(i+1)} + d_{p(n)p(1)} \\ \text{s.t.} & p \in \Pi_N. \end{array}$$

The TSP is a well known NP-Complete combinatorial optimization problem which has been studied extensively (Lawler et al. (1995)). Despite its compactness, little can be done in terms of solving the TSP by using the above formulation however. An integer programming formulation of the TSP is the following

$$\begin{array}{ll} \min & \sum_{i,j=1}^{n} d_{ij} x_{ij} \\ \text{s.t.} & \sum_{i=1}^{n} x_{ij} = 1, \quad j = 1, 2, \dots, n, \\ & \sum_{j=1}^{n} x_{ij} = 1, \quad i = 1, 2, \dots, n, \\ & \sum_{i,j \in S} x_{ij} \leq |S| - 1, \quad \forall\, S \subset V, S \neq V, \\ & x_{ij} \in \{0, 1\}, \quad i, j = 1, 2, \dots, n, \end{array}$$

where S represents a subtour or a disjoint cycle. The decision variables x_{ij} in the above formulation take the following values

$$x_{ij} = \begin{cases} 1 & \text{if node } j \text{ immediately follows } i \text{ in the tour,} \\ 0 & \text{otherwise.} \end{cases}$$

The first set of constraints are called the *assignment constraints* and ensure that in the tour each node is entered and left only once. The assignment constraints are used frequently in formulating particularly location problems. The third set of constraints eliminates any subtours in the solution. The above formulation of the TSP is considered very large in terms of the number of constraints, mainly because the number of the subtour elimination constraints is nearly 2^n. In a more compact formulation one replaces the last constraint with

$$u_i - u_j + nx_{ij} \leq n - 1, \quad 1 \leq i, j \leq n \text{ and } i \neq j,$$

where the u_i are real variables unrestricted in sign.

13.4.1 TSP test Problems

There is a large collection of TSP test problem instances available in the internet. TSPLIB is such a collection of TSP instances. The web address of TSPLIB is:

http://www.iwr.uni-heidelberg.de/iwr/comopt/soft/TSPLIB95/TSPLIB.html.

13.5 Assignment Problems

There is a large number of assignment problems arising mainly from location theory, that can be formulated as integer programs. Probably the simplest of all assignment problems is the *Linear Assignment Problem* (LAP). Consider that we are given n facilities and locations, and a matrix $R^{n\times n} \ni C := (c_{ij})$ where c_{ij} represents the cost of placing facility i to location j. Our objective is to find the optimal assignment of facilities to locations such that the total placement cost is minimized. Using the decision variables $x_{ij} \in \{0,1\}$ as

$$x_{ij} = \begin{cases} 1 & \text{if facility } i \text{ is assigned to location } j, \\ 0 & \text{otherwise,} \end{cases}$$

we can formulate the LAP as an integer $0-1$ program

$$\begin{aligned} \min \quad & \sum_{i,j=1}^{n} c_{ij}x_{ij} \\ \text{s.t.} \quad & \sum_{i=1}^{n} x_{ij} = 1, \quad j = 1, 2, \ldots, n, \\ & \sum_{j=1}^{n} x_{ij} = 1, \quad i = 1, 2, \ldots, n, \\ & x_{ij} \in \{0,1\}, \quad i, j = 1, 2, \ldots, n. \end{aligned}$$

In contrast with the TSP the LAP can be solved efficiently in $O(n^3)$ time. Consider now that we have the same set of facilities to place, and we are given a flow matrix $F := (f_{ij})$ where f_{ij} is the flow of material or information between facilities i and j, and a distance matrix $D := (d_{ij})$ where d_{ij} is the distance between facilities i and j. The Quadratic Assignment Problem (QAP) is to find the assignment of facilities to locations, such that the total cost associated with the distance and flow between any two locations, plus the cost of placement of facilities to locations is minimized. Formulated as an integer $0-1$ program the QAP can be stated as follows

$$
\begin{array}{ll}
\min & \displaystyle\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{l=1}^{n} f_{ij}d_{kl}x_{ik}x_{jl} + \sum_{i,j=1}^{n} c_{ij}x_{ij} \\
\text{s.t.} & \displaystyle\sum_{i=1}^{n} x_{ij} = 1, \quad j = 1,2,\dots,n, \\
& \displaystyle\sum_{j=1}^{n} x_{ij} = 1, \quad i = 1,2,\dots,n, \\
& x_{ij} \in \{0,1\}, \quad i,j = 1,2,\dots,n.
\end{array}
$$

Although extensive research has been done for more than three decades, the QAP, in contrast with its linear counterpart the linear assignment problem (LAP), remains one of the hardest optimization problems and no exact algorithm can solve problems of size $n > 20$, in reasonable computational time (Pardalos and Wolkowicz (1994)). Note that the TSP is a special case of the QAP, where the distance matrix D is the corresponding distance matrix of the TSP, the flow matrix F is the adjacency matrix of a complete cycle of length n, while there is no fixed cost matrix C.

13.5.1 QAP Test Problems

Test Problem Generators

A QAP test problem generator with a known optimal solution has been presented in Li and Pardalos (1992). The Fortran code of this generator can be obtained by sending an e-mail message to "coap@math.ufl.edu", and in the body of the message put "send 92006". Using this generator we present next two small instances of QAP.

QAP1 Test Problem - Symmetric matrices:

Flow matrix:

$$\begin{bmatrix} 0 & 5 & 3 & 7 & 9 & 3 & 9 & 2 & 9 & 0 \\ 5 & 0 & 7 & 8 & 3 & 2 & 3 & 3 & 5 & 7 \\ 3 & 7 & 0 & 9 & 3 & 5 & 3 & 3 & 9 & 3 \\ 7 & 8 & 9 & 0 & 8 & 4 & 1 & 8 & 0 & 4 \\ 9 & 2 & 2 & 8 & 0 & 8 & 8 & 7 & 5 & 9 \\ 3 & 2 & 4 & 4 & 9 & 0 & 4 & 8 & 0 & 3 \\ 8 & 4 & 1 & 1 & 8 & 4 & 0 & 7 & 9 & 5 \\ 3 & 2 & 2 & 8 & 6 & 8 & 6 & 0 & 5 & 5 \\ 9 & 6 & 9 & 0 & 7 & 0 & 9 & 5 & 0 & 5 \\ 0 & 7 & 2 & 4 & 9 & 1 & 4 & 7 & 4 & 0 \end{bmatrix}$$

Distance matrix:

$$\begin{bmatrix} 0 & 7 & 4 & 6 & 8 & 8 & 8 & 6 & 6 & 5 \\ 7 & 0 & 8 & 2 & 6 & 5 & 6 & 8 & 3 & 6 \\ 4 & 8 & 0 & 10 & 4 & 4 & 7 & 2 & 6 & 7 \\ 6 & 2 & 10 & 0 & 6 & 6 & 9 & 3 & 2 & 6 \\ 8 & 6 & 4 & 6 & 0 & 6 & 4 & 8 & 8 & 6 \\ 8 & 5 & 4 & 6 & 6 & 0 & 3 & 8 & 3 & 2 \\ 8 & 6 & 7 & 9 & 4 & 3 & 0 & 6 & 7 & 8 \\ 6 & 8 & 2 & 3 & 8 & 8 & 6 & 0 & 8 & 8 \\ 6 & 3 & 6 & 2 & 8 & 3 & 7 & 8 & 0 & 9 \\ 5 & 6 & 7 & 6 & 6 & 2 & 8 & 8 & 9 & 0 \end{bmatrix}$$

An optimal permutation is (9 1 8 3 6 7 2 5 4 10). The optimal objective function value is 2227.

QAP2 Test Problem - Asymmetric matrices:

Flow matrix:

$$\begin{bmatrix} 0 & 9 & 4 & 2 & 2 & 9 & 7 & 4 & 4 & 3 \\ 8 & 0 & 6 & 9 & 0 & 9 & 7 & 2 & 5 & 8 \\ 1 & 7 & 0 & 1 & 9 & 9 & 7 & 9 & 3 & 5 \\ 0 & 0 & 9 & 0 & 4 & 8 & 8 & 8 & 8 & 2 \\ 5 & 4 & 6 & 2 & 0 & 8 & 8 & 7 & 2 & 7 \\ 7 & 8 & 0 & 4 & 4 & 0 & 9 & 3 & 4 & 3 \\ 8 & 5 & 5 & 9 & 8 & 3 & 0 & 9 & 5 & 2 \\ 7 & 1 & 5 & 0 & 3 & 5 & 4 & 0 & 9 & 9 \\ 7 & 5 & 3 & 2 & 6 & 3 & 3 & 4 & 0 & 0 \\ 3 & 7 & 1 & 3 & 3 & 3 & 5 & 8 & 9 & 0 \end{bmatrix}$$

Distance matrix:

$$
\begin{bmatrix}
0 & 8 & 7 & 6 & 8 & 8 & 6 & 10 & 5 & 9 \\
7 & 0 & 8 & 2 & 10 & 2 & 8 & 8 & 4 & 7 \\
1 & 7 & 0 & 10 & 7 & 7 & 8 & 1 & 5 & 10 \\
7 & 1 & 9 & 0 & 6 & 6 & 10 & 3 & 3 & 2 \\
8 & 2 & 1 & 5 & 0 & 5 & 1 & 7 & 10 & 10 \\
7 & 8 & 1 & 7 & 6 & 0 & 4 & 9 & 3 & 1 \\
9 & 4 & 6 & 8 & 6 & 2 & 0 & 4 & 6 & 9 \\
2 & 8 & 3 & 4 & 9 & 6 & 8 & 0 & 8 & 8 \\
7 & 2 & 7 & 2 & 7 & 4 & 9 & 8 & 0 & 9 \\
2 & 4 & 3 & 10 & 1 & 3 & 7 & 9 & 10 & 0
\end{bmatrix}
$$

An optimal permutation is (9 4 5 10 7 2 6 3 1 8). The optimal objective function value is 2025.

QAPLIB Test Problems

There is a large collection QAPLIB of electronically available data instances for QAP (Burkard et al. (1997)). The data (and the updated best known solution) are available in the following web page:

`http://www.diku.dk/ $\sim$ karisch/qaplib`

The QAPLIB contains a large collection of instances including the first benchmark set of problems called Nugent. Next we provide the one such instance of size 15:

QAP3 Test Problem - nug15:

Flow matrix:

$$
\begin{bmatrix}
0 & 1 & 2 & 3 & 4 & 1 & 2 & 3 & 4 & 5 & 2 & 3 & 4 & 5 & 6 \\
1 & 0 & 1 & 2 & 3 & 2 & 1 & 2 & 3 & 4 & 3 & 2 & 3 & 4 & 5 \\
2 & 1 & 0 & 1 & 2 & 3 & 2 & 1 & 2 & 3 & 4 & 3 & 2 & 3 & 4 \\
3 & 2 & 1 & 0 & 1 & 4 & 3 & 2 & 1 & 2 & 5 & 4 & 3 & 2 & 3 \\
4 & 3 & 2 & 1 & 0 & 5 & 4 & 3 & 2 & 1 & 6 & 5 & 4 & 3 & 2 \\
1 & 2 & 3 & 4 & 5 & 0 & 1 & 2 & 3 & 4 & 1 & 2 & 3 & 4 & 5 \\
2 & 1 & 2 & 3 & 4 & 1 & 0 & 1 & 2 & 3 & 2 & 1 & 2 & 3 & 4 \\
3 & 2 & 1 & 2 & 3 & 2 & 1 & 0 & 1 & 2 & 3 & 2 & 1 & 2 & 3 \\
4 & 3 & 2 & 1 & 2 & 3 & 2 & 1 & 0 & 1 & 4 & 3 & 2 & 1 & 2 \\
5 & 4 & 3 & 2 & 1 & 4 & 3 & 2 & 1 & 0 & 5 & 4 & 3 & 2 & 1 \\
2 & 3 & 4 & 5 & 6 & 1 & 2 & 3 & 4 & 5 & 0 & 1 & 2 & 3 & 4 \\
3 & 2 & 3 & 4 & 5 & 2 & 1 & 2 & 3 & 4 & 1 & 0 & 1 & 2 & 3 \\
4 & 3 & 2 & 3 & 4 & 3 & 2 & 1 & 2 & 3 & 2 & 1 & 0 & 1 & 2 \\
5 & 4 & 3 & 2 & 3 & 4 & 3 & 2 & 1 & 2 & 3 & 2 & 1 & 0 & 1 \\
6 & 5 & 4 & 3 & 2 & 5 & 4 & 3 & 2 & 1 & 4 & 3 & 2 & 1 & 0
\end{bmatrix}
$$

Distance matrix:

$$\begin{bmatrix}
0 & 10 & 0 & 5 & 1 & 0 & 1 & 2 & 2 & 2 & 2 & 0 & 4 & 0 & 0 \\
10 & 0 & 1 & 3 & 2 & 2 & 2 & 3 & 2 & 0 & 2 & 0 & 10 & 5 & 0 \\
0 & 1 & 0 & 10 & 2 & 0 & 2 & 5 & 4 & 5 & 2 & 2 & 5 & 5 & 5 \\
5 & 3 & 10 & 0 & 1 & 1 & 5 & 0 & 0 & 2 & 1 & 0 & 2 & 5 & 0 \\
1 & 2 & 2 & 1 & 0 & 3 & 5 & 5 & 5 & 1 & 0 & 3 & 0 & 5 & 5 \\
0 & 2 & 0 & 1 & 3 & 0 & 2 & 2 & 1 & 5 & 0 & 0 & 2 & 5 & 10 \\
1 & 2 & 2 & 5 & 5 & 2 & 0 & 6 & 0 & 1 & 5 & 5 & 5 & 1 & 0 \\
2 & 3 & 5 & 0 & 5 & 2 & 6 & 0 & 5 & 2 & 10 & 0 & 5 & 0 & 0 \\
2 & 2 & 4 & 0 & 5 & 1 & 0 & 5 & 0 & 0 & 10 & 5 & 10 & 0 & 2 \\
2 & 0 & 5 & 2 & 1 & 5 & 1 & 2 & 0 & 0 & 0 & 4 & 0 & 0 & 5 \\
2 & 2 & 2 & 1 & 0 & 0 & 5 & 10 & 10 & 0 & 0 & 5 & 0 & 5 & 0 \\
0 & 0 & 2 & 0 & 3 & 0 & 5 & 0 & 5 & 4 & 5 & 0 & 3 & 3 & 0 \\
4 & 10 & 5 & 2 & 0 & 2 & 5 & 5 & 10 & 0 & 0 & 3 & 0 & 10 & 2 \\
0 & 5 & 5 & 5 & 5 & 5 & 1 & 0 & 0 & 0 & 5 & 3 & 10 & 0 & 4 \\
0 & 0 & 5 & 0 & 5 & 10 & 0 & 0 & 2 & 5 & 0 & 0 & 2 & 4 & 0
\end{bmatrix}$$

An optimal solution is (1 2 13 8 9 4 3 14 7 11 10 15 6 5 12). The optimal objective function value is 1150.

13.6 Graph Coloring

Let $G = (V, E)$, with vertex set $V = \{1, 2, \dots, n\}$ and edge set E, be an undirected graph with no loops or multiple edges. Vertices i and j are said to be *adjacent* if the edge, denoted by (i, j), is an element of E. A *proper coloring* of G is defined to be an assignment of colors to the vertices so that no pair of adjacent vertices share the same color. Equivalently, a proper coloring is a mapping f of V into $\{1, 2, \dots, n\}$ such that for any $(i, j) \in E$, $f(i) \neq f(j)$. A coloring naturally induces a partition of V such that the members of each set in the partition are pairwise non-adjacent; these sets are precisely the subsets of vertices assigned the same color. If there exists a coloring of G that utilizes no more than k colors, we say that G admits a *k-coloring*, or that G is *k-colorable.* The *chromatic number,* $\chi(G)$, of G is the smallest k for which G admits a k-coloring. Given a graph and an integer k, the *graph coloring problem* refers to the problem of determining whether $\chi(G) \leq k$.

There exist several mathematical programming formulations for *finding the chromatic number* of a graph. The graph coloring problem associated with G can be formulated as the following linear mixed 0-1 integer program **P**:

$$\min \sum_{k=1}^{n} y_k$$

$$
\begin{aligned}
\text{s.t.} \quad \textstyle\sum_{k=1}^{n} x_{ik} = 1 & \quad \forall\, i \in V \\
x_{ik} + x_{jk} \leq 1 & \quad \forall\, (i,j) \in E \\
y_k \geq x_{ik} & \quad \forall\, i \in V,\ k = 1, \ldots, n \\
x_{ik} \in \{0,1\} & \quad \forall\, i \in V,\ k = 1, \ldots, n.
\end{aligned}
$$

In the above model a binary variable is associated with each vertex of a graph $G = (V, E)$, where $|V| = n$. The first set of constraints ensure that exactly one color is assigned to each vertex. The second set of constraints ensure that adjacent vertices are assigned different colors. The optimal objective function value to the above program is the chromatic number of the graph. In the solution, x_{ik} equals 1 if vertex i is colored k, and is zero, otherwise. Moreover, the sets

$$S_k = \{i : x_{ik} = 1\},$$

for all k with $y_k > 0$ comprise an optimal partition of the vertices.

Another integer programming model is:

$$\min \gamma$$

$$
\begin{aligned}
\text{s.t.} \quad x_i \leq \gamma & \\
x_i - x_j - 1 \geq -n\delta_{ij} & \quad \forall\, (i,j) \in E \\
x_j - x_i - 1 \geq -n(1 - \delta_{ij}) & \quad \forall\, (i,j) \in E \\
\delta_{ij} \in \{0,1\} & \\
x_i \in Z^{+} & \quad \forall\, i \in V.
\end{aligned}
$$

The second and third set of constraints ensure that adjacent vertices are not assigned the same color. This can be seen by noting that if $x_i = x_j$ then no feasible assignment of δ_{ij} leads to simultaneous satisfaction of the constraints. The optimal objective function yields the chromatic number of the graph under consideration.

13.6.1 Test Problems

During the second DIMACS Implementation Challenge a set of 32 graph instances were chosen to provide the coloring benchmarks. These problems can be found in the web address:

http://dimacs.rutgers.du/Challenges/index.html.

13.7 Maximum Clique Problem

Let $G = (V, E)$, with vertex set $V = \{1, 2, \ldots, n\}$ and edge set $E \subseteq V \times V$, be an arbitrary undirected and weighted graph. For each vertex $i \in V$, a positive weight w_i is associated with i. $A_G = (a_{ij})_{n \times n}$ is the adjacency matrix of G, where $a_{ij} = 1$ if $(i,j) \in E$ is an edge of G, and $a_{ij} = 0$ if $(i,j) \notin E$. The *complement graph of* $G = (V,E)$ is the graph $\overline{G} = (V, \overline{E})$, where $\overline{E} = \{(i,j) \mid i,j \in V,\ i \neq j \text{ and } (i,j) \notin E\}$. For a subset $S \subseteq V$, we define the weight of S to be $W(S) = \sum_{i \in S} w_i$. We call $G(S) = (S, E \cap S \times S)$ *the subgraph induced by* S. Graph G is *complete* if all its vertices are pairwise adjacent, i.e. $\forall i,\ j \in V,\ (i,j) \in E$. A *clique* C is a subset of V such that $G(C)$ is complete. The maximum clique problem asks for a clique of maximum cardinality. The *maximum weight clique problem* asks for a clique of maximum weight. These problems are NP-complete on arbitrary graphs.

The maximum clique problem has many equivalent formulations as an integer programming problem, or as a continuous nonconvex optimization problem Pardalos (1996). The simplest one is the following *edge formulation*:

$$\max \sum_{i=1}^{n} w_i x_i$$

$$\text{s.t. } x_i + x_j \leq 1,\ \forall\ (i,j) \in \overline{E},$$

$$x_i \in \{0,1\},\ i = 1, \ldots, n.$$

This simple formulation of the Maximum Clique Problem and a linear $0-1$ problem, has not been useful in practice.

Recently, new efficient algorithms and heuristics have been developed using nontrival nonlinear integer formulations of the Maximum Clique Problem. Next we discuss quadratic zero-one formulations of the Maximum Clique Problem. To facilitate our discussion, define a transformation T from $\{0,1\}^n$ to 2^V,

$$T(x) = \{i \mid x_i = 1,\ i \in V\},\ \forall\, x \in \{0,1\}^n.$$

Denote the inverse of T by T^{-1}. If $x = T^{-1}(S)$ for some $S \in 2^V$ then $x_i = 1$ if $i \in S$ and $x_i = 0$ if $i \notin S$, $i = 1, \ldots, n$. We can rewrite the maximum problem (13.7) as a minimization problem (when $w_i = 1$) with $f(x) = -\sum_{i=1}^{n} x_i$. Using the fact that $x_i x_j = 0$ for all $(i,j) \in \overline{E}$ since for $x_i, x_j \in \{0,1\}$ $x_i + x_j \leq 1$ if and only if $x_i x_j = 0$, the constraints in (13.7) can be removed by adding two times the quadratic terms to the objective function, which is now

$$f(x) = -\sum_{i=1}^{n} x_i + 2 \sum_{(i,j) \in \overline{E},\, i>j} x_i x_j = x^T (A_{\overline{G}} - I) x.$$

The quadratic terms represent penalties for violations of $x_i x_j = 0$. This leads to the following *global quadratic zero-one* formulation:

$$\text{global} \min_{\boldsymbol{x}} f(\boldsymbol{x}) = \boldsymbol{x}^T \boldsymbol{A} \boldsymbol{x},$$

$$\text{s.t. } \boldsymbol{x} \in \{0,1\}^n, \text{ where } A = A_{\overline{G}} - I.$$

If $\boldsymbol{x}^*$ solves this problem, then the set C defined by $C = T(x^*)$ is a maximum clique of G with $|C| = -z = -f(x^*)$.

An *independent set* (*stable set, vertex packing*) is a subset of V whose elements are pairwise nonadjacent. The maximum independent set problem asks for an independent set of maximum cardinality. The size of a maximum independent set is the *stability number* of G (denoted by $\alpha(G)$). The maximum weight independent set problem asks for an independent set of maximum weight. Following the equivalence of the maximum clique problem with the maximum independent set problem, we have that the maximum independent set problem is equivalent to the following global quadratic zero-one problem:

$$\text{global } \min f(\boldsymbol{x}) = \boldsymbol{x}^T A \boldsymbol{x}$$

$$\text{s.t. } \boldsymbol{x} \in \{0,1\}^n, \text{ where } A = A_G - I.$$

If $\boldsymbol{x}^*$ solves this problem, then the set S defined by $S = T(\boldsymbol{x}^*)$ is a maximum independent set of G with $|S| = -z = -f(\boldsymbol{x}^*)$.

The above formulations for the maximum clique problem and the maximum independent set problem can be regarded as a special case by taking $w_i = 1, i = 1, 2, \dots, n$. The maximum weight independent set problem is equivalent to the following global quadratic zero-one problem:

$$\text{global } \min f(\boldsymbol{x}) = \boldsymbol{x}^T A \boldsymbol{x},$$

$$\text{s.t. } \boldsymbol{x} \in \{0,1\}^n,$$

where $a_{ii} = -w_i$, $i = 1, ..., n$, $a_{ij} = \frac{1}{2}(w_i + w_j)$, $\forall\ (i,j) \in E$, and $a_{ij} = 0$, $\forall\ (i,j) \in \overline{E}$. Let $\boldsymbol{x}^*$ solve this problem, then the set S defined by $S = T(\boldsymbol{x}^*)$ is a maximum independent set of G with weight $W(S) = -z = -f(\boldsymbol{x}^*)$.

The *Motzkin-Strauss* formulation of the Maximum Clique Problem is the quadratic program:

$$\max \boldsymbol{x}^T A_G \boldsymbol{x}$$

$$\text{s.t. } \boldsymbol{x}^T e = 1,$$

$$\boldsymbol{x} \geq 0 .$$

It is well known (Pardalos (1996)) that the global optimum value of this QP is $(1 - 1/\omega(G))$, where $\omega(G)$ is the clique number of G.

13.7.1 Maximum Clique: Coding Theory Test Problems

In Coding Theory, one wishes to find a binary code as large as possible that can correct a certain number of errors for a given size of the binary words (vectors), see Hasselberg et al. (1993). In order to correct errors, the code must consist of binary words among which any two differ in a certain number of positions so that a misspelled word can be detected and corrected. A misspelled word is corrected by replacing it with the word from the code that differs the least from the misspelled one.

The Hamming distance between the binary vectors $u = (u_1, u_2, \dots, u_n)$ and $v = (v_1, v_2, \dots, v_n)$ is the number of indices i such that $1 \le i \le n$ and $u_i \neq v_i$. We denote the Hamming distance by $dist(u, v)$.

It is well known that a binary code consisting of a set of binary vectors any two of which have Hamming distance greater or equal to d can correct $\lfloor \frac{d-1}{2} \rfloor$ errors (see Hasselberg et al. (1993)). Thus, what a coding theorist would like to find is the maximum number of binary vectors of size n with Hamming distance d. We denote this number by $A(n, d)$.

Another problem arising from coding theory, closely related to the one mentioned above, is to find a weighted binary code, that is, to find the maximum number of binary vectors of size n that have precisely w 1's and the Hamming distance of any two of these vectors is d. This number is denoted by $A(n, w, d)$. A binary code consisting of vectors of size n, weight w and distance d, can correct $w - \frac{d}{2}$ errors.

We define the Hamming graph $H(n, d)$, of size n and distance d, as the graph with vertex set the binary vectors of size n in which two vertices are adjacent if their Hamming distance is *at least* d. Then, $A(n, d)$ is the size of a maximum clique in $H(n, d)$. The graph $H(n, d)$ has 2^n vertices, $2^{n-1} \sum_{i=d}^{n} \binom{n}{i}$ edges and the degree of each vertex is $\sum_{i=d}^{n} \binom{n}{i}$.

We define the Johnson graph, $J(n, w, d)$, with parameters n, w and d, as the graph with vertex set the binary vectors of size n and weight w, where two vertices are adjacent if their Hamming distance is *at least* d. Then, similar to Hamming graph, the size of the weighted code, $A(n, w, d)$, equals the size of the maximum clique in $J(n, w, d)$. The graph $J(n, w, d)$ has $\binom{n}{w}$ vertices, $\frac{1}{2} \binom{n}{w} \sum_{k=\lceil \frac{d}{2} \rceil}^{w} \binom{w}{k} \binom{n-w}{k}$ edges and the degree of each vertex is $\sum_{k=\lceil \frac{d}{2} \rceil}^{w} \binom{w}{k} \binom{n-w}{k}$.

13.7.2 Maximum Clique: Keller Graphs

A family of hypercubes with disjoint interiors whose union is the Euclidean space R^n is a *tiling*. A lattice tiling is a tiling for which the centers of the cubes form a lattice.

In the beginning of the century, Minkowski conjectured that in a lattice tiling of R^n by translates of a unit hypercube, there exist two cubes that share a $(n-1)$-dimensional face. About fifty years later, Hajös (Hasselberg et al. (1993)) proved Minkowski's conjecture.

At 1930, Keller suggested that Minkowski's conjecture holds even in the absence of the lattice assumption. Ten years later Perron (Hasselberg et al. (1993)) proved the correctness of Keller's conjecture for $n \leq 6$. Since then, many papers have been devoted to prove or disprove this conjecture and recently, Lagarias and Shor (Hasselberg et al. (1993)) proved that Keller's conjecture fails for $n \geq 10$. Thus, it is left to prove whether the conjecture holds for $n = 7, 8, 9$.

We define the graph Γ_n as a graph with vertex set $V_n = \{(d_1, d_2, \ldots, d_n) : d_i \in \{0, 1, 2, 3\},\ i = 1, 2, \ldots, n\}$ where two vertices $u = (d_1, d_2, \ldots, d_n)$ and $v = (d'_1, d'_2, \ldots, d'_n)$ in V_n are adjacent if and only if

$$\exists i,\ 1 \leq i \leq n : d_i - d'_i \equiv 2 \bmod 4$$

and

$$\exists j \neq i,\ 1 \leq j \leq n : d_j \neq d'_j.$$

Corrádi and Szabó presented a graph theoretic equivalent of Keller's conjecture. It is shown that, there is a counterexample to Keller's conjecture if and only if there exist a $n \in N^+$ such that Γ_n has a clique of size 2^n.

Γ_n has 4^n vertices, $\frac{1}{2}4^n(4^n - 3^n - n)$ edges and the degree of each node is $4^n - 3^n - n$. Γ_n is very dense and has at least $8^n n!$ different maximum cliques. It can be shown (see Hasselberg et al. (1993)) that the maximum clique size of Γ_n is less than or equal to 2^n.

13.8 Steiner Problems in Networks (SPN)

The Steiner problem in graphs (SPG) consists of connecting a subset of given nodes on a graph with the minimum cost tree.

Instance Formulation of the Steiner Problem in Undirected Graphs: Let $G = (\mathcal{N}, \mathcal{A}, \mathcal{C})$ be an undirected graph, where

$\mathcal{N} = \{1, \ldots, n\}$ is a set of nodes, and

$\mathcal{A}$ is a set of undirected arcs (i, j) with each arc incident to two nodes, and

$\mathcal{C}$ is a set of nonnegative costs c_{ij} associated with undirected arcs (i, j).

Then, the SPG is defined as follows.

Instance: A graph $G = (\mathcal{N}, \mathcal{A}, \mathcal{C})$, a node subset $\mathcal{R} \in \mathcal{N}$.

Question: Find the minimum cost tree, on G, that would connect all the vertices in $\mathcal{R}$.

Instance Formulation of the Steiner Problem in Directed Graphs: The SPDG is the directed graph version of the Steiner problem. Consider $G^d = (\mathcal{N}, \mathcal{A}^d, \mathcal{C}^d)$ where

$\mathcal{N} = \{1, \ldots, n\}$ is a set of nodes, and

$\mathcal{A}^d$ is a set of directed arcs (i, j) incident to nodes in $\mathcal{N}$.

$\mathcal{C}^d = \{c^d_{ij}\}$ is a set of costs associated with $\mathcal{A}^d$.

Furthermore, let $\mathcal{R}$ (a set of regular nodes) be a subset of $\mathcal{N}$, and let r (a root node) be an arbitrary node in $\mathcal{R}$. Also, define a directed Steiner tree T rooted at node r, with respect to $\mathcal{R}$ on G, to be a directed tree where all nodes in $\mathcal{R}\backslash\{r\}$ can be reached from r via directed paths in T, and all leaf nodes are in $\mathcal{R}$. Next, we define the SPDG.

Instance: A graph $G^d = (\mathcal{N}, \mathcal{A}^d, \mathcal{C}^d)$, a node subset $\mathcal{R}$ and a root node r in $\mathcal{R}$.

Question: Find the minimum cost directed Steiner tree, on G with respect to $\mathcal{R}$, that has node r as root node.

In the light of the SPG and SPDG definitions given above, it is not hard for one to see that the SPDG is a generalization of the SPG. In fact, the SPG can be transformed to a special case of the SPDG where the arc cost structure is symmetric. This transformation can be done as follows. Given a graph $G = (\mathcal{N}, \mathcal{A}, \mathcal{C})$, create the corresponding directed graph $G^d = (\mathcal{N}, \mathcal{A}^d, \mathcal{C}^d)$, where every undirected arc $(i, j) \in \mathcal{A}$ corresponds to two oppositely directed arcs (i, j) and $(j, i) \in \mathcal{A}^d$ associated with the same cost $(c^d_{ij} = c^d_{ji} = c_{ij})$.

There are several equivalent formulations for the Steiner problems in graphs. The different mathematical formulations can be divided into three categories: mixed integer formulations, integer formulations and continuous formulations. Therefore different algorithmic approaches can be tested by using the same test problems.

13.8.1 Test Problems

An automatic test problem generator for problems with a known optimal solution has been proposed by Khoury et al. (1993).

Using this generator, next we provide a set of test problems: The network is represented by a table where column 1 entries are arc numbers. Column 2 and column 3 give the two end nodes of an arc. Arc costs are represented in column 4.

Test problem spgtp1

\# of nodes: 20
\# of arcs: 40
$\mathcal{R} \equiv \{2, 3, 7, 8, 18\}$
Minimum Steiner tree set of arcs $\equiv \{8, 15, 22, 29, 31, 38\}$
Minimum Steiner tree cost: 986

Arc #	End1 #	End2 #	Arc Cost
1	11	10	289
2	2	6	275
3	1	15	347
4	11	13	109
5	3	5	110
6	15	12	161
7	11	9	275
8	8	11	252
9	12	19	354
10	13	17	241
11	19	20	180
12	2	14	228
13	19	16	202
14	10	4	116
15	8	1	188
16	1	17	314
17	12	18	190
18	9	10	159
19	5	4	227
20	18	19	190
21	10	8	319
22	11	7	123
23	16	12	234
24	17	6	222
25	15	3	168
26	13	6	211
27	9	17	134
28	10	5	160
29	1	2	101
30	14	10	179
31	1	3	215
32	18	16	238
33	13	2	313
34	15	8	336
35	6	19	124
36	9	3	175
37	7	16	176
38	3	18	107
39	5	6	238
40	9	18	260

Test problem spgtp2

of nodes: 20
# of arcs: 40
$\mathcal{R} \equiv \{2, 5, 6, 7, 16\}$
Minimum Steiner tree set of arcs $\equiv \{8, 15, 19, 24, 26, 32, 36, 38\}$
Minimum Steiner tree cost: 3562

Arc #	End1 #	End2 #	Arc Cost
1	6	14	576
2	6	18	897
3	2	10	720
4	2	8	495
5	16	15	947
6	7	13	348
7	12	19	547
8	16	11	442
9	2	1	612
10	17	20	553
11	11	4	1187
12	17	3	307
13	1	6	1211
14	2	12	1459
15	11	9	153
16	8	5	1244
17	16	5	790
18	8	17	1032
19	11	17	830
20	9	10	1238
21	5	15	509
22	8	4	760
23	1	18	213
24	11	12	103
25	13	4	336
26	9	6	223
27	11	14	512
28	9	3	763
29	15	17	644
30	14	9	534
31	8	6	1263
32	17	7	524
33	6	11	496
34	17	13	1438
35	20	4	740
36	12	5	442
37	10	8	752
38	6	2	845
39	1	17	770
40	9	4	1301

Test problem spgtp3

\# of nodes: 20
\# of arcs: 40
$\mathcal{R} \equiv \{3, 6, 10, 13, 14, 16, 18\}$
Minimum Steiner tree set of arcs $\equiv \{5, 11, 19, 22, 27, 31, 33, 34, 37, 40\}$
Minimum Steiner tree cost: 2213

Arc #	End1 #	End2 #	Arc Cost
1	6	15	417
2	6	1	427
3	13	7	181
4	10	4	476
5	16	11	252
6	15	8	248
7	11	5	580
8	8	2	170
9	2	19	293
10	16	20	326
11	11	9	424
12	5	2	325
13	9	7	522
14	4	16	560
15	6	8	488
16	16	8	482
17	9	4	248
18	15	9	376
19	11	17	101
20	3	1	448
21	18	11	620
22	11	12	154
23	5	13	167
24	14	8	279
25	3	15	439
26	16	14	637
27	11	6	215
28	9	8	394
29	4	6	549
30	9	18	660
31	9	14	107
32	13	20	316
33	17	3	105
34	12	13	450
35	4	12	534
36	9	1	123
37	6	10	223
38	17	9	589
39	4	7	435
40	14	18	182

Test problem spgtp4

\# of nodes: 20

\# of arcs: 40

$\mathcal{R} \equiv \{2, 8, 10, 13, 14, 15, 16, 18\}$

Minimum Steiner tree set of arcs $\equiv \{1, 4, 6, 8, 9, 13, 15, 20, 21, 23, 29, 35, 37\}$

Minimum Steiner tree cost: 2864

Arc #	End1 #	End2 #	Arc Cost
1	16	11	252
2	9	4	260
3	16	4	88
4	11	12	215
5	1	16	469
6	11	5	107
7	15	17	319
8	17	14	450
9	12	18	223
10	13	4	400
11	6	13	372
12	8	4	363
13	2	15	152
14	1	18	472
15	6	10	182
16	17	19	305
17	14	1	339
18	17	20	306
19	11	7	267
20	11	9	101
21	11	17	154
22	17	3	274
23	5	8	355
24	2	10	663
25	16	6	420
26	8	17	404
27	9	10	658
28	5	16	290
29	11	6	289
30	8	3	373
31	11	15	277
32	14	9	865
33	8	6	448
34	6	9	400
35	9	2	105
36	17	10	651
37	5	13	279
38	20	4	84
39	10	11	661
40	9	5	289

Test problem spgtp5

of nodes: 20

# of arcs: 40

$\mathcal{R} \equiv \{1, 3, 4, 5, 6, 10, 16, 17, 18, 19\}$

Minimum Steiner tree set of arcs $\equiv \{3, 8, 13, 22, 26, 27, 28, 32, 33, 35, 36, 37\}$

Minimum Steiner tree cost: 2776

Arc #	End1 #	End2 #	Arc Cost
1	19	12	274
2	6	11	167
3	4	2	252
4	16	15	430
5	1	7	348
6	11	9	335
7	2	20	252
8	4	13	123
9	17	14	130
10	7	17	239
11	2	9	433
12	7	11	354
13	4	8	101
14	16	3	569
15	15	8	468
16	18	2	260
17	14	13	411
18	14	16	342
19	15	4	492
20	16	8	385
21	12	14	403
22	2	19	154
23	14	19	392
24	17	11	476
25	13	19	266
26	2	5	289
27	2	16	252
28	13	6	431
29	15	19	524
30	15	12	286
31	15	10	113
32	13	18	135
33	8	10	351
34	7	8	416
35	19	17	223
36	10	3	147
37	17	1	318
38	9	7	151
39	16	7	463
40	2	14	380

Remark: Steiner tree problems can be used also to generate hard instances of MAX-SAT problems. The exact translation of Steiner problems into MAX-SAT is given in H.Kautz et al. (1997).

Chapter 14

Nonlinear Systems of Equations

The solution of nonlinear systems of equations is an important problem in engineering. Applications include identifying the multiple steady states of a reactor network (Folger, 1986; Schlosser and Feinberg, 1994), predicting the azeotropes formed in a nonideal mixture (Fidkowski et al., 1993; Maranas et al., 1996), finding the steady-states of a flowsheet or part of a flowsheet (Zhang, 1987; Bullard and Biegler, 1991; Wilhelm and Swaney, 1994; Bekiaris et al., 1993), identifying equilibrium points in multiphase systems (Heidemann and Mandhane, 1973; Seader et al., 1990).

Many techniques are available to find one of the solutions of a given system such as Newton and quasi-Newton methods (Powell, 1970; Chen and Stadtherr, 1984; Duff et al., 1987; More, 1987; Paloschi and Perkins, 1988), homotopy continuation techniques (Lahaye, 1934; Leray and Schauder, 1934; Davidenko, 1953; Klopfenstein, 1961; Garcia and Zangwill, 1981), interval-Newton methods (Kearfott and Novoa, 1990; Kearfott et al., 1994; Seader and Kumar, 1994) and optimization-based techniques (Horst and Tuy, 1993; Maranas and Floudas, 1995). The approaches based on interval arithmetic or global optimization are the only ones that can guarantee the enclosure of all solutions. For a presentation of global optimization approaches for enclosing all solutions of constrained systems of nonlinear equations, the reader is directed to the article of Maranas and Floudas (1995), and the book by Floudas (2000).

The general formulation of these problems is given below.

$$\begin{aligned} \boldsymbol{h}(\boldsymbol{x}) &= \mathbf{0} \\ \boldsymbol{g}(\boldsymbol{x}) &\leq \mathbf{0} \\ \boldsymbol{x} &\in [\boldsymbol{x}^L, \boldsymbol{x}^U]. \end{aligned}$$

This can be transformed into an optimization problem of the form:

$$
\begin{aligned}
\min_{s,\, \boldsymbol{x}} \quad & s \\
\text{s.t.} \quad \boldsymbol{h}(\boldsymbol{x}) - s &\le \mathbf{0} \\
-\boldsymbol{h}(\boldsymbol{x}) - s &\le \mathbf{0} \\
\boldsymbol{g}(\boldsymbol{x}) &\le \mathbf{0} \\
\boldsymbol{x} &\in [\boldsymbol{x}^L, \boldsymbol{x}^U]
\end{aligned}
$$

In this chapter, we focus on locating all solutions of nonlinearly constrained systems of equations and present (i) test problems that are taken from the literature and (ii) test problems that correspond to the enclosure of all homogeneous azeotropes.

14.1 Literature problems

In this section we present nine test problems taken from the literature. Test problems 6, 7, 8, and 9 are regarded as challenging problems.

14.1.1 Test Problem 1: Himmelblau function

The goal of this example is to find all stationary points of the Himmelblau function (Reklaitis and Ragsdell, 1983).

Formulation

Equalities

$$
\begin{aligned}
4x_1^3 + 4x_1x_2 + 2x_2^2 - 42x_1 &= 14 \\
4x_2^3 + 2x_1^2 + 4x_1x_2 - 26x_2 &= 22
\end{aligned}
$$

Variable bounds

$$-5 \le x_1, x_2 \le 5$$

Problem Statistics

No. of continuous variables	2
No. of linear equalities	–
No. of nonlinear equalities	2
No. of known solutions	9

Known Solutions

x_1	-3.7793	-3.0730	-2.8051	-0.2709	-0.1280
x_2	-3.2832	-0.0814	3.1313	-0.9230	-1.9537

x_1	0.0867	3.0	3.3852	3.5844
x_2	2.8843	2.0	0.0739	-1.8481

14.1.2 Test Problem 2: Equilibrium Combustion

This problem aims to identify the concentrations of the products of a hydrocarbon combustion process at equilibrium (Meintjes and Morgan, 1990).

Formulation

Equalities

$$
\begin{aligned}
x_1 x_2 + x_1 - 3x_5 &= 0 \\
2x_1x_2 + x_1 + 3R_{10}x_2^2 & \\
+x_2x_3^2 + R_7x_2x_3 + R_9x_2x_4 + R_8x_2 - Rx_5 &= 0 \\
2x_2x_3^2 + R_7x_2x_3 + 2R_5x_3^2 + R_6x_3 - 8x_5 &= 0 \\
R_9x_2x_4 + 2x_4^2 - 4Rx_5 &= 0 \\
x_1x_2 + x_1 + R_{10}x_2^2 + x_2x_3^2 + R_7x_2x_3 & \\
+R_9x_2x_4 + R_8x_2 + R_5x_3^2 + R_6x_3 + x_4^2 &= 1
\end{aligned}
$$

Variable bounds

$$0.0001 \leq x_i \leq 100, \ i = 1, \cdots, 5$$

Data

$R = 10$	$R_5 = 0.193$	$R_6 = 4.10622\ 10^{-4}$
$R_7 = 5.45177\ 10^{-4}$	$R_8 = 4.4975\ 10^{-7}$	$R_9 = 3.40735\ 10^{-5}$
$R_{10} = 9.615\ 10^{-7}$		

Problem Statistics

No. of continuous variables	5
No. of linear equalities	–
No. of nonlinear equalities	5
No. of known solutions	1

Known Solution

$$\boldsymbol{x} = (0.003431, 31.325636, 0.068352, 0.859530, 0.036963)^T$$

14.1.3 Test Problem 3

A two equation system taken from Bullard and Biegler (1991) is solved in this example.

Formulation

Equalities

$$\begin{aligned} 10^4 x_1 x_2 - 1 &= 0 \\ e^{-x_1} + e^{-x_2} - 1.001 &= 0 \end{aligned}$$

Variable bounds

$$\begin{aligned} 5.49 \times 10^{-6} &\leq x_1 \leq 4.553 \\ 2.196 \times 10^{-3} &\leq x_2 \leq 18.21 \end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of linear equalities	–
No. of nonlinear equalities	2
No. of known solutions	1

Known Solution

$$\boldsymbol{x} = (1.450 \times 10^{-5}, 6.8933353)^T$$

14.1.4 Test Problem 4

A system of two nonlinear equations taken from Ferraris and Tronconi (1986) is solved here.

Formulation

Equalities

$$\begin{aligned} 0.5\sin(x_1 x_2) - 0.25 x_2/\pi - 0.5 x_1 &= 0 \\ (1 - 0.25/\pi)(\exp(2x_1) - e) + e x_2/\pi - 2e x_1 &= 0 \end{aligned}$$

Variable bounds

$$\begin{aligned} 0.25 &\leq x_1 \leq 1 \\ 1.5 &\leq x_2 \leq 2\pi \end{aligned}$$

Problem Statistics

No. of continuous variables	2
No. of linear equalities	–
No. of nonlinear equalities	2
No. of known solutions	2

Known Solutions

- Solution 1: $\boldsymbol{x} = (0.29945, 2.83693)^T$.
- Solution 2: $\boldsymbol{x} = (0.5, 3.14159)^T$.

14.1.5 Test Problem 5

This example is Brown's almost linear system (Kearfott and Novoa, 1990).

Formulation

Equalities

$$\begin{aligned} 2x_1 + x_2 + x_3 + x_4 + x_5 &= 6 \\ x_1 + 2x_2 + x_3 + x_4 + x_5 &= 6 \\ x_1 + x_2 + 2x_3 + x_4 + x_5 &= 6 \\ x_1 + x_2 + x_3 + 2x_4 + x_5 &= 6 \\ x_1 x_2 x_3 x_4 x_5 &= 1 \end{aligned}$$

Variable bounds

$$-2 \le x_i \le 2, \ i = 1, \ldots, 5$$

Problem Statistics

No. of continuous variables	5
No. of linear equalities	4
No. of nonlinear equalities	1
No. of known solutions	2

Known Solutions

- Solution 1: $\boldsymbol{x} = (1, 1, 1, 1, 1)^T$
- Solution 2: $\boldsymbol{x} = (0.916, 0.916, 0.916, 0.916, 1.418)^T$.

14.1.6 Test Problem 6

This is a robot kinematics problem taken from Kearfott and Novoa (1990).

Formulation

Equalities

$$\begin{aligned}
4.731\ 10^{-3}x_1x_3 - 0.3578x_2x_3 - 0.1238x_1 & \\
+x_7 - 1.637\ 10^{-3}x_2 - 0.9338x_4 - 0.3571 &= 0 \\
0.2238x_1x_3 + 0.7623x_2x_3 + 0.2638x_1 & \\
-x_7 - 0.07745x_2 - 0.6734x_4 - 0.6022 &= 0 \\
x_6x_8 + 0.3578x_1 + 4.731\ 10^{-3}x{+}_2 &= 0 \\
-0.7623x_1 + 0.2238x_2 + 0.3461 &= 0 \\
x_1^2 + x_2^2 - 1 &= 0 \\
x_3^2 + x_4^2 - 1 &= 0 \\
x_5^2 + x_6^2 - 1 &= 0 \\
x_7^2 + x_8^2 - 1 &= 0
\end{aligned}$$

Variable bounds

$$-1 \leq x_i \leq 1,\ i = 1, \ldots, 8$$

Problem Statistics

No. of continuous variables	8
No. of linear equalities	1
No. of nonlinear equalities	7
No. of known solutions	16

Known Solutions

x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
0.1644	-0.9864	-0.9471	-0.3210	-0.9982	-0.0594	0.4110	0.9116
0.1644	-0.9864	-0.9471	-0.3210	-0.9982	0.0594	0.4110	-0.9116
0.1644	-0.9864	-0.9471	-0.3210	0.9982	-0.0594	0.4110	0.9116
0.1644	-0.9864	-0.9471	-0.3210	0.9982	0.0594	0.4110	-0.9116
0.1644	-0.9864	0.7185	-0.6956	-0.9980	-0.0638	-0.5278	0.8494
0.1644	-0.9864	0.7185	-0.6956	-0.9980	0.0638	-0.5278	-0.8494
0.1644	-0.9864	0.7185	-0.6956	0.9980	-0.0638	-0.5278	0.8494
0.1644	-0.9864	0.7185	-0.6956	0.9980	0.0638	-0.5278	-0.8494
0.6716	0.7410	-0.6516	-0.7586	-0.9625	-0.2711	-0.4376	0.8992
0.6716	0.7410	-0.6516	-0.7586	-0.9625	0.2711	-0.4376	-0.8992
0.6716	0.7410	-0.6516	-0.7586	0.9625	-0.2711	-0.4376	0.8992

x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
0.6716	0.7410	-0.6516	-0.7586	0.9625	0.2711	-0.4376	-0.8992
0.6716	0.7410	0.9519	-0.3064	-0.9638	-0.2666	0.4046	0.9145
0.6716	0.7410	0.9519	-0.3064	-0.9638	0.2666	0.4046	-0.9145
0.6716	0.7410	0.9519	-0.3064	0.9638	0.2666	0.4046	-0.9145
0.6716	0.7410	0.9519	-0.3064	0.9638	-0.2666	0.4046	0.9145

14.1.7 Test Problem 7

This example represents a circuit design problem (Ratschek and Rokne, 1993).

Formulation

Equalities

$$\begin{aligned}
(1 - x_1x_2)x_3 \left\{\exp\left[x_5\left(g_{1k} - g_{3k}x_7\ 10^{-3} - g_{5k}x_8\ 10^{-3}\right)\right] - 1\right\}& \\
- g_{5k} + g_{4k}x_2 &= 0, \quad k = 1,\dots,4 \\
(1 - x_1x_2)x_4 \left\{\exp\left[x_6\left(g_{1k} - g_{2k} - g_{3k}x_7\ 10^{-3} - g_{4k}x_9\ 10^{-3}\right)\right] - 1\right\}& \\
- g_{5k}x_1 + g_{4k} &= 0, \quad k = 1,\dots,4 \\
x_1x_3 - x_2x_4 &= 0
\end{aligned}$$

Variable bounds

$$0 \leq x_i \leq 10, \; i = 1,\dots,9$$

Data

$$\boldsymbol{g} = \begin{pmatrix} 0.4850 & 0.7520 & 0.8690 & 0.9820 \\ 0.3690 & 1.2540 & 0.7030 & 1.4550 \\ 5.2095 & 10.0677 & 22.9274 & 20.2153 \\ 23.3037 & 101.7790 & 111.4610 & 191.2670 \\ 28.5132 & 111.8467 & 134.3884 & 211.4823 \end{pmatrix}$$

Problem Statistics

No. of continuous variables	9
No. of linear equalities	–
No. of nonlinear equalities	9
No. of known solutions	1

Known Solution

$$\boldsymbol{x} = (0.89999, 0.44999, 1.00001, 2.00007, 7.99997, \\ 7.99969, 5.00003, 0.99999, 2.00005)^T$$

14.1.8 Test Problem 8

The steady state of a series of CSTRs with recycle must be identified in this example (Kubicek et al., 1980).

Formulation

Equalities

$$
\begin{aligned}
(1-R)\left(\frac{D}{10(1+\beta_1)}-\phi_1\right)\exp\left(\frac{10\phi_1}{1+10\phi_1/\gamma}\right)-\phi_1 &= 0\\
\phi_1-(1+\beta_2)\,\phi_2 & \\
+(1-R)\left(D/10-\beta_1\phi_1-(1+\beta_2)\phi_2\right)\exp\left(\frac{10\phi_2}{1+10\phi_2/\gamma}\right) &= 0
\end{aligned}
$$

Variable bounds

$$0 \le \phi_1, \phi_2 \le 1$$

Data

$\gamma = 1000$	$D = 22$	$\beta_1 = 2$	$\beta_2 = 2$

The parameter R is varied between 0 and 1.

Problem Statistics

No. of continuous variables	2
No. of linear equalities	–
No. of nonlinear equalities	2

The number of known solutions varies between 1 and 7 for 13 different values of R.

Known Solutions

R	ϕ_1	ϕ_2
0.935	0.724987	0.245241
0.940	0.724234	0.245134
0.945	0.079754	0.664390
	0.172234	0.591344
	0.723330	0.244990
0.950	0.062799	0.103831
	0.062799	0.195656
	0.062799	0.675510
	0.206004	0.557881
	0.722227	0.244797
0.955	0.051212	0.078028
	0.051212	0.235148
	0.051212	0.682347
	0.236330	0.520375
	0.720847	0.244533
0.960	0.042125	0.061755
	0.042125	0.268726
	0.042125	0.686930
	0.266590	0.178424
	0.266590	0.327276
	0.266590	0.461132
	0.719074	0.244164

R	ϕ_1	ϕ_2
0.965	0.298523	0.168212
	0.034546	0.049423
	0.034546	0.302260
	0.034546	0.689784
	0.716707	0.243634
0.970	0.027994	0.039357
	0.027994	0.338384
	0.027994	0.690874
	0.333780	0.165215
	0.713383	0.242837
0.975	0.022196	0.030790
	0.022196	0.379801
	0.022196	0.689588
	0.374632	0.166725
	0.708353	0.241556
0.980	0.016978	0.023300
	0.016978	0.431009
	0.016978	0.683991
	0.425213	0.172848
	0.699758	0.239253
0.985	0.012223	0.016625
	0.012223	0.504131
	0.012223	0.666204
	0.496354	0.186263
	0.680842	0.233986
0.990	0.007848	0.010593
0.995	0.003789	0.005081

14.1.9 Test Problem 9

The goal of this example taken from Smith (1985) is to find all steady state temperatures of a nonisothermal CSTR.

Formulation

Equalities

$$\frac{b}{T_o} T \exp\left\{\frac{c}{T}\right\} - \frac{b(1+aT_0)}{aT_0} \exp\left\{\frac{c}{T}\right\} + \frac{T}{T_0} - 1 = 0$$

Variable bounds

$$100 \leq T \leq 1000$$

Data

$$a = \frac{-1000}{3\Delta H} \quad b = 1.344 \times 10^9 \quad c = -7548.1193 \quad T_0 = 298$$

Three different values of the reaction enthalpy ΔH are used.

Problem Statistics

No. of continuous variables	1
No. of linear equalities	–
No. of nonlinear equalities	1

The number of known solutions varies between 1 and 3 for three different values of ΔH.

Known Solutions

ΔH	T
-50,000	300.42
	347.41
	445.49
-35,958	299.63
	380.46
	380.51
-35,510.3	299.61

14.2 Enclosing All Homogeneous Azeotropes

14.2.1 Introduction

The ability to predict the presence and composition of all azeotropes in a mixture is essential for the design of nonideal separation processes. In addition, when some experimental data about the azeotropes in a system is available, a technique for finding all azeotropes can be very useful for determining which thermodynamic equation models the system most accurately.

The thermodynamic conditions for azeotropy can be written as a nonlinear system of equations. The number of solutions to the system is not known *a priori*, and there may be no solution at all. Recently, several methods for enclosing all homogeneous azeotropes have been presented in the literature. Harding et al. (1997) developed a deterministic global optimization approach for finding all azeotropes and illustrated the method through several examples using the Wilson, NRTL, UNIQUAC and UNIFAC activity coefficient equations. Fidkowski et al. (1993) developed a homotopy continuation approach for solving the system of nonlinear equations. They applied this method for the Wilson and modified Wilson equations. Chapman and Goodwin (1993) presented a local search method for finding homogeneous azeotropes. Their method employs a Levenberg-Marquardt algorithm.

The test problems for this section are taken from Harding et al. (1997). They cover a wide range of activity coefficient equations and contain up to five components. Global optimization-based approaches for enclosing all homogeneous azeotropes are described in detail in Harding et al. (1997) and the book by Floudas (2000).

14.2.2 General Formulation - Activity Coefficient Equations

The necessary and sufficient conditions for homogeneous azeotropy are:

- the vapor phase and liquid phase must be in equilibrium,
- the composition of the vapor phase must equal the composition of the liquid phase, and
- the material balance must be satisfied.

These conditions form a system of nonlinear equations:

$$\begin{aligned}
\ln y_i - \ln x_i - \ln P_i^{sat} + \ln P - \ln \gamma_i &= 0 \quad \forall\, i \in N \\
y_i - x_i &= 0 \quad \forall\, i \in N \\
\sum_{i \in N} x_i &= 1 \\
\sum_{i \in N} y_i &= 1
\end{aligned}$$

In order to locate all homogeneous azeotropes, all solutions to this system of nonlinear equations must be located. Maranas and Floudas (1995) proposed a method for finding all solutions to systems of nonlinear equations. In their approach, the nonlinear equations are allowed to be violated. This is done by writing each nonlinear equality as two inequalities and introducing a nonnegative slack variable for the amount of violation. An optimization problem can be formulated where the objective is to minimize the violation of the nonlinear equalities. There is a one-to-one correspondence between global minima of the optimization problem, $s^* = 0$, and solutions to the original system of nonlinear equations.

The goal is to enclose all homogeneous azeotropes in an N component mixture. This corresponds to finding all global minima where $s^* = 0$ for the following nonconvex NLP.

Objective function

The objective is to minimize the maximum violation of the nonlinear equality constraints.

$$\min_{x,T,s} s$$

Constraints

Equilibrium Expressions

This formulation is derived from the equivalence of chemical potentials of each component in the liquid and vapor phases. An activity coefficient equation is used to model the nonideal behavior in the liquid phase, and the vapor phase is considered to be ideal. Each nonlinear equality is split into two inequalities and a slack variable is subtracted from the left-hand side of each. When the slack variable is equal to zero then the original equality is satisfied.

$$\begin{aligned} -\ln P_i^{sat} - \ln \gamma_i - s &\leq -\ln P \qquad \forall\, i \in N \\ \ln P_i^{sat} + \ln \gamma_i - s &\leq \ln P \qquad \forall\, i \in N \end{aligned}$$

Mole Balance

$$\sum_{i \in N} x_i = 1$$

Variable bounds

$$0 \leq \boldsymbol{x} \leq 1$$

Variable definition

- s is a slack variable corresponding to the violation of the nonlinear equality constraints.
- P_i^{sat} denotes the saturated vapor pressure, and is a function of temperature. For the examples below, the Antoine Equation is used,

$$\ln P_i^{sat} = a_i - \frac{b_i}{T + c_i}$$

- $\ln \gamma_i$ is the liquid phase activity coefficient of component i.
- x_i is the liquid mole fraction of component i.
- T is temperature.

14.2.3 Wilson Equation

Wilson (1964) developed an activity coefficient equation that is often used to model solutions containing both polar and nonpolar components. The equation contains a single nonsymmetric binary interaction parameter.

$$\ln \gamma_i = 1 - \ln \left(\sum_{j \in N} x_j \Lambda_{ij} \right) - \sum_{j \in N} \frac{x_j \Lambda_{ji}}{\sum_{k \in N} x_k \Lambda_{jk}}$$

14.2.4 Test Problem 1

The ternary system (Acetone(1) - Methyl Acetate(2) - Methanol(3)) is commonly used in the literature of phase equilibria. Experimental data show that this system contains three binary and one ternary azeotrope. This is a difficult example due to the number of solutions that must be located.

Explicit Formulation

$$\begin{array}{ll}
\min & s \\
\text{subject to} & -a_1 + \frac{b_1}{T+c_1} + \ln(x_1\Lambda_{11} + x_2\Lambda_{22}) \\
& + \frac{x_1\Lambda_{11}}{x_1\Lambda_{11}+x_2\Lambda_{12}} + \frac{x_2\Lambda_{21}}{x_1\Lambda_{21}+x_2\Lambda_{22}} - s \leq 1 - \ln P \\
& a_1 - \frac{b_1}{T+c_1} - \ln(x_1\Lambda_{11} + x_2\Lambda_{22}) \\
& - \frac{x_1\Lambda_{11}}{x_1\Lambda_{11}+x_2\Lambda_{12}} - \frac{x_2\Lambda_{21}}{x_1\Lambda_{21}+x_2\Lambda_{22}} - s \leq -1 + \ln P \\
& -a_2 + \frac{b_2}{T+c_2} + \ln(x_1\Lambda_{21} + x_2\Lambda_{22}) \\
& + \frac{x_1\Lambda_{12}}{x_1\Lambda_{11}+x_2\Lambda_{12}} + \frac{x_2\Lambda_{22}}{x_1\Lambda_{21}+x_2\Lambda_{22}} - s \leq 1 - \ln P \\
& a_2 - \frac{b_2}{T+c_2} - \ln(x_1\Lambda_{21} + x_2\Lambda_{22}) \\
& - \frac{x_1\Lambda_{12}}{x_1\Lambda_{11}+x_2\Lambda_{12}} - \frac{x_2\Lambda_{22}}{x_1\Lambda_{21}+x_2\Lambda_{22}} - s \leq -1 + \ln P \\
& x_1 + x_2 = 1 \\
& x_1, x_2 \geq 0
\end{array}$$

Data

$$
\begin{aligned}
P &= 760 \text{ mmHg} \\
R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\
\boldsymbol{a} &= (16.388, 16.268, 18.607)^T \\
\boldsymbol{b} &= (2787.50, 2665.54, 3643.31)^T \\
\boldsymbol{c} &= (229.66, 219.73, 239.73)^T \\
\boldsymbol{\Lambda} &= \begin{pmatrix} 1.0 & 0.48 & 0.768 \\ 1.55 & 1.0 & 0.544 \\ 0.566 & 0.65 & 1.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	1
No. of nonconvex inequalities	6
No. of known solutions	4

Known Solutions

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

x_1	x_2	x_3	T
0.532	0.468	0.000	55.675
0.747	0.000	0.253	54.505
0.000	0.677	0.323	54.356
0.272	0.465	0.253	54.254

14.2.5 Test Problem 2

This example is for the quaternary system (Methanol(1) - Benzene(2) - i-Propanol(3) - n-Propanol(4)). Physical experiments have located three binary azeotropes.

Data

$$
\begin{aligned}
P &= 760 \text{ mmHg} \\
R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\
\boldsymbol{a} &= (18.607, 15.841, 20.443, 19.293)^T \\
\boldsymbol{b} &= (3643.31, 2755.64, 4628.96, 4117.07)^T \\
\boldsymbol{c} &= (239.73, 219.16, 252.64, 227.44)^T \\
\boldsymbol{\Lambda} &= \begin{pmatrix} 1.0 & 0.192 & 2.169 & 1.611 \\ 0.316 & 1.0 & 0.477 & 0.524 \\ 0.377 & 0.360 & 1.0 & 0.296 \\ 0.524 & 0.282 & 2.065 & 1.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	5
No. of linear equalities	1
No. of nonconvex inequalities	8
No. of known solutions	3

Known Solutions

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

x_1	x_2	x_3	x_4	T
0.624	0.376	0.000	0.000	58.129
0.000	0.586	0.414	0.000	71.951
0.000	0.780	0.000	0.220	76.946

14.2.6 Test Problem 3

This example is a five-component system (Acetone(1) - Chloroform(2) - Methanol(3) - Ethanol(4) - Benzene(5)). From experiments, the system has been found to contain six binary azeotropes, three ternary azeotrope and one quaternary azeotrope. This is an especially challenging example due to its size, and to the number of solutions that exist.

Data

$$
\begin{aligned}
P &= 760 \text{ mmHg} \\
R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\
\boldsymbol{a} &= (16.388, 16.014, 18.607, 18.679, 15.841)^T \\
\boldsymbol{b} &= (2787.50, 2696.25, 3643.31, 3667.70, 2755.64)^T \\
\boldsymbol{c} &= (229.66, 226.23, 239.73, 226.18, 219.16)^T \\
\boldsymbol{\Lambda} &= \begin{pmatrix} 1.0 & 1.269 & 0.696 & 0.636 & 0.590 \\ 1.552 & 1.0 & 0.697 & 1.005 & 1.273 \\ 0.767 & 0.176 & 1.0 & 1.676 & 0.188 \\ 0.826 & 0.188 & 0.531 & 1.0 & 0.198 \\ 0.990 & 0.928 & 0.308 & 0.461 & 1.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	6
No. of linear equalities	1
No. of nonconvex inequalities	10
No. of known solutions	9

Known Solutions

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

x_1	x_2	x_3	x_4	x_5	T
0.371	0.629	0.000	0.000	0.000	64.656
0.802	0.000	0.198	0.000	0.000	55.457
0.000	0.631	0.369	0.000	0.000	53.070
0.000	0.842	0.000	0.158	0.000	59.250
0.000	0.000	0.624	0.000	0.376	58.015
0.000	0.000	0.000	0.454	0.546	67.700
0.375	0.189	0.436	0.000	0.000	57.218
0.374	0.438	0.000	0.188	0.000	63.180
0.295	0.148	0.463	0.000	0.094	57.154

14.2.7 NRTL Equation

The non-random two-liquid (NRTL) equation was developed by Renon and Prausnitz (1968). This equation contains two binary interaction parameters.

$$
\ln \gamma_i = \frac{\sum\limits_{j \in N} \tau_{ji} G_{ji} x_j}{\sum\limits_{j \in N} G_{ji} x_j} + \sum_{j \in N} \frac{G_{ij} x_j}{\sum\limits_{k \in N} G_{kj} x_k} (\tau_{ij} - \frac{\sum\limits_{k \in N} \tau_{kj} G_{kj} x_k}{\sum\limits_{k \in N} G_{kj} x_k})
$$

14.2.8 Test Problem 4

The ternary system (Ethanol(1) - Methyl Ethyl Ketone(2) - Water(3)) contains three binary azeotropes and a ternary azeotrope.

Data

$$
\begin{aligned}
P &= 760 \text{ mmHg} \\
R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\
\boldsymbol{a} &= (18.679, 16.264, 18.585)^T \\
\boldsymbol{b} &= (3667.70, 2904.34, 3984.92)^T \\
\boldsymbol{c} &= (226.18, 221.97, 233.43)^T \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 0.094 & -0.254 \\ 0.673 & 0.0 & 0.979 \\ 2.092 & 2.628 & 0.0 \end{pmatrix} \\
\boldsymbol{G} &= \begin{pmatrix} 1.0 & 0.972 & 1.078 \\ 0.817 & 1.0 & 0.707 \\ 0.539 & 0.395 & 1.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	1
No. of nonconvex inequalities	6
No. of known solutions	4

Known Solutions

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

x_1	x_2	x_3	T
0.486	0.514	0.000	74.076
0.952	0.000	0.048	78.275
0.000	0.657	0.343	73.388
0.187	0.560	0.253	72.957

14.2.9 Test Problem 5

This example is for the quaternary system (Methanol(1) - Benzene(2) - i-Propanol(3) - n-Propanol(4)). Physical experiments have located three binary azeotropes. The NRTL equation predicts a composition for the methanol-benzene azeotrope that is quite different from the Wilson equation (test problem 2).

Data

$$
\begin{aligned}
P &= 760 \text{ mmHg} \\
R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\
\boldsymbol{a} &= (18.607, 15.841, 20.443, 19.293)^T \\
\boldsymbol{b} &= (3643.31, 2755.64, 4628.96, 4117.07)^T \\
\boldsymbol{c} &= (239.73, 219.16, 252.64, 227.44)^T \\
\boldsymbol{\tau} &= \begin{pmatrix} 0.0 & 0.040 & -0.191 & 0.035 \\ -0.671 & 0.0 & 1.010 & 1.212 \\ 0.093 & 0.508 & 0.0 & -0.934 \\ 0.013 & 0.396 & 1.375 & 0.0 \end{pmatrix} \\
\boldsymbol{G} &= \begin{pmatrix} 1.0 & 0.988 & 1.060 & 0.990 \\ 1.223 & 1.0 & 0.745 & 0.704 \\ 0.972 & 0.863 & 1.0 & 1.321 \\ 0.996 & 0.892 & 0.664 & 1.0 \end{pmatrix}
\end{aligned}
$$

Problem Statistics

No. of continuous variables	5
No. of linear equalities	1
No. of nonconvex inequalities	8
No. of known solutions	3

Known Solutions

x_1	x_2	x_3	x_4	T
0.063	0.937	0.000	0.000	80.166
0.000	0.588	0.412	0.000	71.832
0.000	0.776	0.000	0.224	77.131

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

14.2.10 UNIQUAC Equation

The UNIQUAC equation, Abrams and Prausnitz (1975), is based on two effects, a combinatorial effect due to differences in the shapes of the components and a residual effect from the energetic interactions between the components. This equation contains one binary interaction parameter, three pure component parameters, and one additional parameter.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

where,

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j \in N} l_j x_j$$

and,

$$\ln \gamma_i^R = q_i'(1 - \ln(\sum_{j \in N} \tau_{ji} \theta_j') - \sum_{j \in N} \frac{\tau_{ij} \theta_j'}{\sum_{k \in N} \theta_k' \tau_{kj}})$$

where,

$$\begin{aligned} \theta_i &= \frac{q_i x_i}{\sum_{j \in N} q_j x_j} \quad \forall\, i \in N \\ \theta_i' &= \frac{q_i' x_i}{\sum_{j \in N} q_j' x_j} \quad \forall\, i \in N \\ \phi_i &= \frac{r_i x_i}{\sum_{j \in N} r_j x_j} \quad \forall\, i \in N \end{aligned}$$

14.2.11 Test Problem 6

The ternary system (Ethanol(1) - Benzene(2) - Water(3)) has been widely studied due to the importance of the azeotropic distillation process used to separate ethanol and water using benzene as an entrainer. The system contains three binary homogeneous azeotropes. A fourth solution to this system of equations exists, however it does not correspond to a stable homogeneous azeotrope.

Data

$$\begin{aligned} P &= 760 \text{ mmHg} \\ R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\ z &= 10 \\ \boldsymbol{a} &= (18.912, 15.901, 18.304)^T \\ \boldsymbol{b} &= (3803.98, 2788.51, 3816.44)^T \\ \boldsymbol{c} &= (231.47, 220.79, 227.02)^T \\ \boldsymbol{\tau} &= \begin{pmatrix} 1.0 & 1.472 & 1.214 \\ 0.050 & 1.0 & 0.002 \\ 0.319 & 0.708 & 1.0 \end{pmatrix} \\ \boldsymbol{q} &= (1.970, 2.400, 1.400)^T \\ \boldsymbol{q}' &= (0.920, 2.400, 1.000)^T \\ \boldsymbol{r} &= (2.110, 3.190, 0.920)^T \\ \boldsymbol{l} &= (-0.410, 1.760, -2.320)^T \end{aligned}$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	1
No. of nonconvex inequalities	6
No. of known solutions	4

Known Solutions

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

x_1	x_2	x_3	T
0.428	0.572	0.000	67.331
0.000	0.608	0.392	61.317
0.886	0.000	0.114	78.153
0.013	0.604	0.383	61.583

14.2.12 Test Problem 7

There is experimental data for five binary azeotropes in the four-component system (Ethanol(1) - Methylcyclopentane(2) - Benzene(3) - Hexane(4)). The UNIQUAC equation predicts six binary, four ternary and one quaternary azeotrope. This is a difficult example because eleven solutions to the system of equations must be located.

Data

$$
\begin{aligned}
P &= 760 \text{ mmHg} \\
R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\
z &= 10 \\
\boldsymbol{a} &= (18.912, 15.810, 15.901, 15.912)^T \\
\boldsymbol{b} &= (3803.98, 2735.59, 2788.51, 2739.25)^T \\
\boldsymbol{c} &= (231.47, 226.28, 220.79, 226.28)^T \\
\boldsymbol{\tau} &= \begin{pmatrix} 1.0 & 1.804 & 1.472 & 1.536 \\ 0.025 & 1.0 & 0.618 & 1.946 \\ 0.050 & 1.217 & 1.0 & 1.082 \\ 0.042 & 0.441 & 0.687 & 1.0 \end{pmatrix} \\
\boldsymbol{q} &= (1.970, 3.010, 2.400, 3.860)^T \\
\boldsymbol{q'} &= (0.920, 3.010, 2.400, 3.860)^T \\
\boldsymbol{r} &= (2.110, 3.970, 3.190, 4.500)^T \\
\boldsymbol{l} &= (-0.410, 1.830, 1.760, -0.300)^T
\end{aligned}
$$

Problem Statistics

No. of continuous variables	5
No. of linear equalities	1
No. of nonconvex inequalities	8
No. of known solutions	11

Known Solutions

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

x_1	x_2	x_3	x_4	T
0.316	0.684	0.000	0.000	63.489
0.441	0.000	0.559	0.000	67.292
0.334	0.000	0.000	0.666	61.265
0.000	0.738	0.262	0.000	70.367
0.000	0.654	0.000	0.346	72.892
0.000	0.000	0.307	0.693	66.919
0.301	0.545	0.154	0.000	63.029
0.344	0.418	0.000	0.238	64.401
0.300	0.000	0.172	0.528	60.669
0.000	0.458	0.333	0.209	71.235
0.322	0.322	0.222	0.133	63.558

14.2.13 UNIFAC Equation

The UNIFAC equation is a group-contribution method developed by Fredenslund et al. (1975) for systems where insufficient data is available to obtain accurate binary interaction parameters. In this method, molecules are considered to be collections of groups of elements (e.g., CH_3) with a total of G groups. Interactions between groups are obtained from a standard table, Gmehling et al. (1990). The UNIFAC equation contains two group parameters, one group binary interaction parameter, and one additional parameter.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

where,

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j \in N} l_j x_j$$

and,

$$
\begin{aligned}
\ln \gamma_i^R = \sum_{g \in G} Q_g v_{gi} \quad \Bigg\{ & - \sum_{m \in G} \frac{\Psi_{gm} \sum_{j \in N} Q_m v_{mj} x_j}{\sum_{l \in G} \Psi_{lm} \sum_{k \in N} Q_l v_{lk} x_k} \\
& - \ln \left(\sum_{m \in G} \Psi_{mg} \sum_{j \in N} Q_m v_{mj} x_j \right) \\
& + \ln \left(\sum_{j \in N} q_j x_j \right) \\
& + \ln \left(\sum_{m \in G} \Psi_{mg} Q_m v_{mi} \right) \\
& - \ln q_i \\
& + \sum_{m \in G} \frac{\Psi_{gm} Q_m v_{mi}}{\sum_{l \in G} \Psi_{lm} Q_l v_{li}} \Bigg\}
\end{aligned}
$$

where,

$$
\begin{aligned}
\theta_i &= \frac{q_i x_i}{\sum_{j \in N} q_j x_j} \quad \forall\, i \in N \\
\phi_i &= \frac{r_i x_i}{\sum_{j \in N} r_j x_j} \quad \forall\, i \in N
\end{aligned}
$$

14.2.14 Test Problem 8

The ternary system (Acetone(1) - Methyl Ethyl Ketone(2) - Cyclohexane(3)) contains two binary azeotropes.

Data

$$
\begin{aligned}
P &= 760 \text{ mmHg} \\
R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\
z &= 10 \\
\boldsymbol{a} &= (16.388, 16.264, 15.753)^T \\
\boldsymbol{b} &= (2787.50, 2904.34, 2766.63)^T \\
\boldsymbol{c} &= (229.66, 221.97, 222.65)^T \\
\boldsymbol{v} &= \begin{pmatrix} 2 & 0 & 1 \\ 2 & 1 & 1 \\ 0 & 6 & 0 \end{pmatrix} \\
\boldsymbol{\Psi} &= \begin{pmatrix} 1.0 & 1.0 & 0.0105 \\ 1.0 & 1.0 & 0.0105 \\ 0.0002 & 0.0002 & 1.0 \end{pmatrix} \\
\boldsymbol{q} &= (2.336, 2.876, 3.240)^T \\
\boldsymbol{r} &= (2.5735, 3.2479, 4.0464)^T \\
\boldsymbol{l} &= (-0.386, -0.3884, 0.9856)^T \\
\boldsymbol{Q} &= (0.848, 0.540, 0.640)^T \\
\boldsymbol{R} &= (0.9011, 0.6744, 0.7713)^T
\end{aligned}
$$

Problem Statistics

No. of continuous variables	4
No. of linear equalities	1
No. of nonconvex inequalities	6
No. of known solutions	2

Known Solutions

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

x_1	x_2	x_3	T
0.878	0.000	0.122	55.726
0.000	0.424	0.576	71.822

14.2.15 Test Problem 9

This is the same four-component system as in test problem 5, (Ethanol(1) - Methylcyclopentane(2) - Benzene(3) - Hexane(4)). However, in this case the UNIFAC equation predicts only the five binary azeotropes which have been reported experimentally. The presence of five solutions to the system of nonlinear equations and the complexity of the UNIFAC equation makes this example especially challenging.

Data

$$
\begin{aligned}
P &= 760 \text{ mmHg} \\
R &= 1.98721 \text{ (cal)mol}^{-1}\text{K}^{-1} \\
z &= 10 \\
\boldsymbol{a} &= (18.912, 15.810, 15.901, 15.912)^T \\
\boldsymbol{b} &= (3803.98, 2735.59, 2788.51, 2739.25)^T \\
\boldsymbol{c} &= (231.47, 226.28, 220.79, 226.28)^T \\
\boldsymbol{v} &= \begin{pmatrix} 1 & 0 & 0 & 1 & 0 \\ 1 & 4 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 6 \\ 2 & 4 & 0 & 0 & 0 \end{pmatrix} \\
\boldsymbol{\Psi} &= \begin{pmatrix} 1.0 & 1.0 & 1.0 & 0.0611 & 0.9082 \\ 1.0 & 1.0 & 1.0 & 0.0611 & 0.9082 \\ 1.0 & 1.0 & 1.0 & 0.0611 & 0.9082 \\ 0.6009 & 0.6009 & 0.6009 & 1.0 & 0.7783 \\ 0.9552 & 0.9552 & 0.9552 & 0.1202 & 1.0 \end{pmatrix} \\
\boldsymbol{q} &= (1.970, 3.010, 2.400, 3.860)^T \\
\boldsymbol{r} &= (2.110, 3.970, 3.190, 4.500)^T \\
\boldsymbol{l} &= (-0.410, 1.830, 1.760, -0.300)^T \\
\boldsymbol{Q} &= (0.848, 0.540, 0.228, 1.124, 0.400)^T \\
\boldsymbol{R} &= (0.9011, 0.6744, 0.4469, 1.2044, 0.5313)^T
\end{aligned}
$$

Problem Statistics

No. of continuous variables	5
No. of linear equalities	1
No. of nonconvex inequalities	8
No. of known solutions	5

Known Solutions

- Objective function: $s = 0$ corresponding to a valid solution of the original system of nonlinear equations.

x_1	x_2	x_3	x_4	T
0.371	0.629	0.000	0.000	60.632
0.450	0.000	0.550	0.000	67.841
0.357	0.000	0.000	0.643	59.054
0.000	0.865	0.135	0.000	71.651
0.000	0.000	0.065	0.935	68.900

Chapter 15

Dynamic Optimization Problems

15.1 Introduction

A class of problems for which there has been a scarcity of work in the area of global optimization are the dynamic optimization problems. These problems involve dynamic variables whose values change in time. Such problems exist in the areas of optimal control, parameter estimation for dynamic models, reactor network synthesis where the dynamic models arise from the differential modeling of the tubular reactors (plug flow reactors), and for dynamic simulation and optimization.

15.1.1 General Formulation

The problems that are considered here conform to the following general formulation:

$$\begin{array}{lrcl}
\min & J(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{u}(t_i), \boldsymbol{x}) & & \\
\text{s.t.} & \boldsymbol{f}(\dot{\boldsymbol{z}}(t), \boldsymbol{z}(t), \boldsymbol{u}(t), \boldsymbol{x}, t) & = & \mathbf{0} \\
& \boldsymbol{c}(\boldsymbol{z}(t_0), \boldsymbol{x}) & = & \mathbf{0} \\
& \boldsymbol{h}'(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{u}(t_i), \boldsymbol{x}) & = & \mathbf{0} \\
& \boldsymbol{g}'(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{u}(t_i), \boldsymbol{x}) & \leq & \mathbf{0} \\
& \boldsymbol{h}''(\boldsymbol{x}) & = & \mathbf{0} \\
& \boldsymbol{g}''(\boldsymbol{x}) & \leq & \mathbf{0} \\
& \boldsymbol{x} & \in & \mathcal{X} \subseteq \mathcal{R}^p \\
& t_i & \in & [t_0, t_N]
\end{array}$$

where J is the objective function, $\boldsymbol{f}$ is the set of dynamic state equations, $\boldsymbol{c}$ are the initial conditions, $\boldsymbol{g}'$ and $\boldsymbol{h}'$ are the point constraints, and $\boldsymbol{g}''$ and $\boldsymbol{h}''$ are the general algebraic constraints. The variables in the problem are $\boldsymbol{x}$, the vector of time invariant continuous variables, $\boldsymbol{z}$, the vector of dynamic state variables, and $\boldsymbol{u}$, the vector of control variables. The independent variable is t.

15.1.2 Solution Techniques (Local)

There are several ways to solve the optimal control problem. These methods are (a) the solution of the necessary conditions, (b) dynamic programming, (c) complete discretization, and (d) control parameterization. The solution of the necessary conditions and the application of Pontryagin's maximum principle as described in Bryson and Ho (1988) leads to the solution of two-point boundary value problems. Dynamic programming approaches employing grids for both the state and control variables have been proposed and applications are reported in Luus (1990b,a); Luus and Rosen (1991); Luus (1993). Complete discretization methods discretize all the dynamic equations with respect to all dynamic variables. The DAEs are thus transformed into algebraic equations, and the problem can be solved using nonlinear programming techniques. Finite element collocation techniques were proposed by Cuthrell and Biegler (1987) for the full discretization of DAE problems. The collocation methods were extended in Logsdon and Biegler (1989) and Vasantharajan and Biegler (1990) to include appropriate error constraints. The control parameterization techniques apply discretization only to the control variables. These methods are described in Sargent and Sullivan (1977) and in Vassiliadis et al. (1994a,b). The problem is formulated as an NLP where the control parameters are determined through the optimization procedure and the DAE system is solved through an integration technique. The use of the control parameterization techniques for solving optimization problems in process synthesis are described by Schweiger and Floudas (1997, 1998b).

Since the methods used for solving the dynamic optimization problems often involve the use of approximations, the best solution that can be obtained is closely related to the solution algorithm. In other words, the same problem may have different solutions and a different global solution when different solution techniques are used.

The examples presented in this chapter have all been solved using the control parameterization approach. Because of this, a brief description of the control parameterization is provided.

15.1.3 Control Parameterization

The basic idea behind the control parameterization approach is to express the control variables $\boldsymbol{u}(t)$ as functions of time invariant parameters. This parameterization can be done in terms of the independent variable t (open loop):

$$\boldsymbol{u}(t) = \phi(\boldsymbol{w}, t)$$

or in terms of the state variables $\boldsymbol{z}(t)$ (closed loop):

$$\boldsymbol{u}(t) = \psi(\boldsymbol{w}, \boldsymbol{z}(t))$$

For the following example problems, open loop parameterization will be considered.

A convenient choice for the control parameterization function $\phi(\boldsymbol{w}, t)$ is a polynomial expression such as Lagrange polynomials. The time horizon is divided into intervals with the controls defined as polynomials over each interval. The Lagrange polynomial expression of order M in interval i has the form

$$\begin{array}{llr} \phi_i(\boldsymbol{w}, t) = & \sum_{j=1}^{n} \boldsymbol{w}_{ij} & \text{for} \quad N = 1 \\ \phi_i(\boldsymbol{w}, t) = & \sum_{j=1}^{n} \boldsymbol{w}_{ik} \prod_{k=1, k \neq j}^{M} \frac{\bar{t} - \bar{t}_k}{t_j - t_k} & \text{for} \quad N \geq 2 \end{array}$$

where $\bar{t}$ is the normalized time over the interval i

$$\bar{t} = \frac{t - t_{i-1}}{t_i - t_{i-1}}$$

This parameterization allows for polynomial expressions of various order to be used. For example, a piecewise linear expression with continuity between the intervals is expressed as

$$\phi_i = \boldsymbol{w}_i \frac{\bar{t} - \bar{t}_{i+1}}{\bar{t}_i - \bar{t}_{i+1}} + \boldsymbol{w}_{i+1} \frac{\bar{t} - \bar{t}_i}{\bar{t}_{i+1} - \bar{t}_i}$$

Since the control parameters change from one interval to the next discontinuities arise in the DAE system.

The set of time invariant parameters $\boldsymbol{x}$ is now expanded to include the control parameters:

$$\boldsymbol{x} = \{\boldsymbol{x}, \boldsymbol{w}\}$$

The set of DAEs $(\boldsymbol{f})$ is expanded to include parameterization functions

$$\boldsymbol{f}(\cdot) = \{\boldsymbol{f}(\cdot), \phi(\cdot)\}$$

and the control variables are converted to dynamic state variables:

$$\boldsymbol{z} = \{\boldsymbol{z}, \boldsymbol{u}\}$$

Through the application of the control parameterization, the control variables are effectively removed from the problem and the following NLP/DAE results:

$$\begin{array}{lrcl} \min & J(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{x}) & & \\ \text{s.t.} & \boldsymbol{f}(\dot{\boldsymbol{z}}(t), \boldsymbol{z}(t), \boldsymbol{x}, t) & = & \mathbf{0} \\ & \boldsymbol{c}(\boldsymbol{z}(t_0), \boldsymbol{x}) & = & \mathbf{0} \\ & \boldsymbol{h}'(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{x}) & = & \mathbf{0} \\ & \boldsymbol{g}'(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{x}) & \leq & \mathbf{0} \\ & \boldsymbol{h}''(\boldsymbol{x}) & = & \mathbf{0} \\ & \boldsymbol{g}''(\boldsymbol{x}) & \leq & \mathbf{0} \\ & \boldsymbol{x} & \in & \mathcal{X} \subseteq \mathcal{R}^p \\ & t_i & \in & [t_0, t_N] \end{array}$$

This problem is an optimization in the space of the $\boldsymbol{x}$ variables where J, $\boldsymbol{g}'$, and $\boldsymbol{h}'$, are implicit functions of $\boldsymbol{x}$ variables through the solution of the DAE system.

15.1.4 Solution of NLP/DAE

Standard gradient based methods for solving NLPs locally such as reduced gradient methods, conjugate gradient methods, and sequential quadratic programming methods, require function evaluations along with the gradient evaluations. For this problem, the function evaluations and gradients with respect to $\boldsymbol{x}$ are required for J, $\boldsymbol{h}'$, $\boldsymbol{g}'$, $\boldsymbol{h}''$, and $\boldsymbol{g}''$. For $\boldsymbol{h}''$, and $\boldsymbol{g}''$, analytical expressions can be obtained. However, for J, $\boldsymbol{h}'$, $\boldsymbol{g}'$ the function evaluations and gradients are determined as implicit functions of $\boldsymbol{x}$ through the solution of the DAE system. Integrating the DAE system along with the variational equations provides the values of the state variables at the time instances, $\boldsymbol{z}(t_i)$, as well as the gradients $\frac{d\boldsymbol{h}'}{d\boldsymbol{x}}$. With this information known, the functions J, $\boldsymbol{g}'$, and $\boldsymbol{h}'$ are evaluated directly, and the gradients are determined by applying the chain rule:

$$
\begin{aligned}
\frac{dJ}{d\boldsymbol{x}} &= \left(\frac{\partial J}{\partial \boldsymbol{z}}\right)\left(\frac{\partial \boldsymbol{z}}{\partial \boldsymbol{x}}\right) + \left(\frac{\partial J}{\partial \boldsymbol{x}}\right) \\
\frac{d\boldsymbol{h}'}{d\boldsymbol{x}} &= \left(\frac{\partial \boldsymbol{h}'}{\partial \boldsymbol{z}}\right)\left(\frac{\partial \boldsymbol{z}}{\partial \boldsymbol{x}}\right) + \left(\frac{\partial \boldsymbol{h}'}{\partial \boldsymbol{x}}\right) \\
\frac{d\boldsymbol{g}'}{d\boldsymbol{x}} &= \left(\frac{\partial \boldsymbol{g}'}{\partial \boldsymbol{z}}\right)\left(\frac{\partial \boldsymbol{z}}{\partial \boldsymbol{x}}\right) + \left(\frac{\partial \boldsymbol{g}'}{\partial \boldsymbol{x}}\right)
\end{aligned}
$$

In problems where the time horizon needs to be optimized, the independent variable is scaled and the integration is performed over this scaled variable. The scaling factor becomes a variable which can be optimized.

15.2 Chemical Reactor Network Problems

15.2.1 Introduction

Reactor network synthesis has been a widely studied problem in the area of process synthesis. It deals with determining the types, sizes, and interconnections of reactors which optimize a desired performance objective. The reactor network synthesis problem has been discussed previously in Section 8.4 of Chapter 8.

<u>Problem Statement</u>

In reactor network synthesis, the goal is to determine the reactor network that transforms the given raw materials into the desired products. The following information is assumed to be given in the problem definition:

- the reaction mechanism and stoichiometry
- the chemical kinetic data
- the rate laws
- the energetic data
- the inlet stream(s) conditions
- the performance objective (output).

The synthesis problem is to determine:

- the type, size, and interconnection of reactor units
- the stream flowrates, compositions, and temperatures
- the composition and temperatures within the reactors
- the heating and cooling requirements
- the optimal performance objective.

The two reactor types that are often encountered in reactor network synthesis are the Continuous Stirred Tank Reactor (CSTR) and the Plug Flow Reactor (PFR). The CSTR is assumed to be perfectly mixed such that there are no spatial variations in concentration, temperature, and reaction rate within the reactor. The PFR is a tubular reactor where there are no radial variations in concentration, temperature, and reaction rate. Other types of reactors used in the synthesis problem are the Maximum Mixed Reactor (MMR), Segregated Flow Reactor (SFR), and the Cross Flow Reactor (CFR). The CFR is a generalization of the PFR, MMR, and SFR.

Since the mathematical modeling of the tubular reactors results in differential equations, the resulting problem is formulated as a dynamic optimization problem.

The reactor network consists of mixers, splitters, CSTRs and CFRs. Splitters are used to split the feed and the outlet of each reactor. Mixers are situated at the inlet to each reactor to mix the streams which come from the feed splitter and the splitters after each reactor. A final mixer is used to mix the streams which go from the splitter after each reactor unit to the product stream. A flowsheet which has two CSTRs is shown in Figure 15.1

15.2.2 General Formulation

In the general formulation, two assumptions will be made: constant density and, for nonisothermal systems, constant heat capacity which is the same for all components.

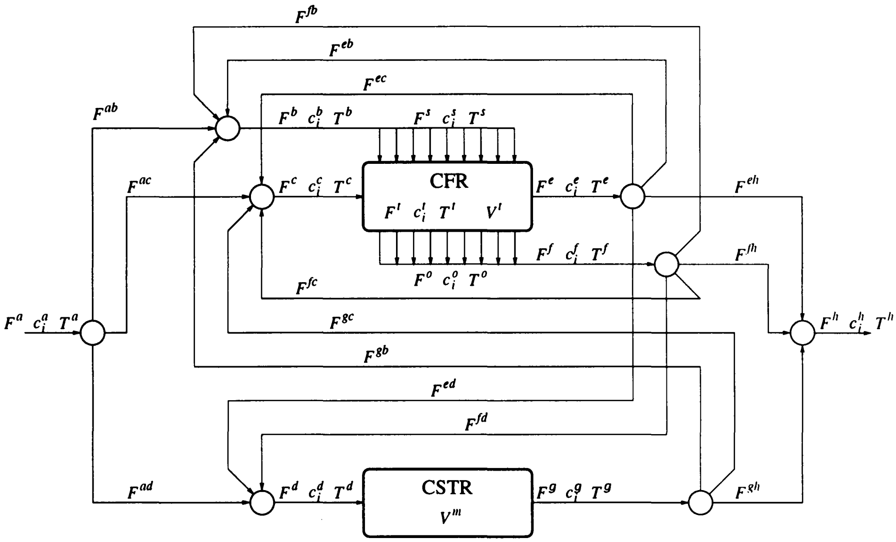


Figure 15.1: Example of a reactor network superstructure consisting of one CSTR and one CFR

The general formulation has been derived for any number of CSTRs and CFRs, any number of reaction components, any number of reaction paths, any number of feed streams, and any number of product streams.

In the general formulation, the following sets will be used:

Set	description
I	Components
J	Reactions
K	CFR reactor units
L	CSTR reactor units
R	Feeds
P	Products

Constraints

Feed splitter

$$F_r^a = \sum_{k\in K} F_{r,k}^{ab} + F_{r,k}^{ac} + \sum_{l\in L} F_{r,l}^{ad} \quad \forall r \in R$$

CFR sidestream mixer total balance

$$F_k^b = \sum_{r\in R} F_{r,k}^{ab} + \sum_{k'\in K} F_{k',k}^{eb} + F_{k',k}^{fb} + \sum_{l\in L} F_{l,k}^{gb} \quad \forall k \in K$$

CFR sidestream mixer component balance

$$c_{k,i}^b F_k^b = \sum_{r\in R} c_{r,i}^a F_{r,k}^{ab} + \sum_{k'\in K} c_{k',i}^e F_{k',k}^{eb} + c_{k',i}^f F_{k',k}^{fb} + \sum_{l\in L} c_{l,i}^g F_{l,k}^{gb} \quad \forall i \in I \quad \forall k \in K$$

CFR main mixer total balance

$$F_k^c = \sum_{r \in R} F_{r,k}^{ac} + \sum_{k' \in K} F_{k',k}^{ec} + F_{k',k}^{fc} + \sum_{l \in L} F_{l,k}^{gc} \quad \forall k \in K$$

CFR main mixer component balance

$$c_{k,i}^c F_k^c = \sum_{r \in R} c_{r,i}^a F_{r,k}^{ac} + \sum_{k' \in K} c_{k',i}^e F_{k',k}^{ec} + c_{k',i}^f F_{k',k}^{fc} + \sum_{l \in L} c_{l,i}^g F_{l,k}^{gc} \quad \forall i \in I \quad \forall k \in K$$

CSTR feed mixer total balance

$$F_l^d = \sum_{r \in R} F_{r,l}^{ad} + \sum_{k \in K} F_{k,l}^{ed} + F_{k,l}^{fd} + \sum_{l' \in L} F_{l',l}^{gd} \quad \forall l \in L$$

CSTR feed mixer component balance

$$c_{l,i}^d F_l^d = \sum_{r \in R} c_{r,i}^a F_{r,l}^{ad} + \sum_{k \in K} c_{k,i}^e F_{k,l}^{ed} + c_{k,i}^f F_{k,l}^{fd} + \sum_{l' \in L} c_{l',i}^g F_{l',l}^{gb} \quad \forall i \in I \quad \forall l \in L$$

CSTR total balance

$$F_l^g = F_l^d \quad \forall l \in L$$

CSTR component balances

$$F_l^g c_{l,i}^g = F_l^d c_{l,i}^d + V_l^m \sum_{j \in J} \nu_{i,j} r_{l,j}^m \quad \forall i \in I \quad \forall l \in L$$

CSTR reaction rates

$$r_{l,j}^m = f_j^r(c_{l,i}^m, T_l^m) \quad \forall j \in J \quad \forall l \in L$$

CFR total balance

$$\frac{dF_k^t}{d\bar{V}} = -\frac{dF_k^s}{d\bar{V}} - \frac{dF_k^o}{d\bar{V}} \quad \forall k \in K$$

CFR component balance

$$F_k^t \frac{dc_{k,i}^t}{d\bar{V}} = -(c_{k,i}^s - c_{k,i}^t)\frac{dF_k^s}{d\bar{V}} + V_k^t \sum_{j \in J} \nu_{i,j} r_{k,j}^t \quad \forall i \in I \quad \forall k \in K$$

Leaving sidestream

$$F_k^o \frac{dc_{k,i}^o}{d\bar{V}} = (c_{k,i}^t - c_{k,i}^o)\frac{dF_k^o}{\bar{V}} \quad \forall i \in I \quad \forall k \in K$$

Initial conditions ($\bar{V} = 0$)

$$F_k^s = F_k^b \quad \forall k \in K$$

$$c^s_{k,i} = c^b_{k,i} \quad \forall i \in I \quad \forall k \in K$$

$$F^t_k = F^c_k \quad \forall k \in K$$

$$c^t_{k,i} = c^c_{k,i} \quad \forall i \in I \quad \forall k \in K$$

Point constraints ($\bar{V} = 1$)

$$F^e_k = F^t_k \quad \forall k \in K$$

$$c^e_{k,i} = c^t_{k,i} \quad \forall i \in I \quad \forall k \in K$$

$$F^f_k = F^o_k \quad \forall k \in K$$

$$c^f_{k,i} = c^o_{k,i} \quad \forall i \in I \quad \forall k \in K$$

CFR reaction rates

$$r^t_{k,j} = f^r_j(c^t_{k,i}, T^t_k) \quad \forall j \in J \quad \forall k \in K$$

CFR main splitters

$$F^e_k = \sum_{k' \in K} F^{eb}_{k,k'} + F^{ec}_{k,k'} + \sum_{l \in L} F^{ed}_{k,l} + \sum_{p \in P} F^{eh}_{k,p} \quad \forall k \in K$$

CFR side exit splitters

$$F^f_k = \sum_{k' \in K} F^{fb}_{k,k'} + F^{fc}_{k,k'} + \sum_{l \in L} F^{fd}_{k,l} + \sum_{p \in P} F^{fh}_{k,p} \quad \forall k \in K$$

CSTR product splitters

$$F^g_l = \sum_{k \in K} F^{gb}_{l,k} + F^{gc}_{l,k} + \sum_{l' \in L} F^{gd}_{l,l'} + \sum_{p \in P} F^{gh}_{l,p} \quad \forall l \in L$$

Product mixer total balance

$$F^h_p = \sum_{k \in K} F^{eh}_{k,p} + F^{fh}_{k,p} + \sum_{l \in L} F^{gh}_{l,p} \quad \forall p \in P$$

Product mixer component balance

$$F^h_p c^h_{p,i} = \sum_{k \in K} F^{eh}_{k,p} c^e_{k,i} + F^{fh}_{k,p} c^f_{k,i} + \sum_{l \in L} F^{gh}_{l,p} c^g_{l,i} \quad \forall i \in I \quad \forall p \in P$$

Control Parameterization

The control parameterization requires the selection of the control variables. For these problems, the sidestream flowrates for the CFR and the temperature in the CFR are selected as the control variables. For the control parameterization, 10 equally spaced intervals are used and piecewise linear polynomials are used for the flowrates and a piecewise quadratic polynomial is used for the temperature. Since the derivatives are needed explicitly, they are calculated as well. Continuity in the first derivatives of the temperature is also enforced.

Control parameterization equations for the CFR side feed stream

$$F_k^s = \kappa_{k,i}^s \frac{t - \bar{t}_{i,2}}{\bar{t}_{i,0} - \bar{t}_{i,2}} + \kappa_{k,i+1}^s \frac{t - \bar{t}_{i,0}}{\bar{t}_{i,2} - \bar{t}_{i,0}} \quad \forall k \in K \quad \forall i \in CI$$

$$\frac{dF_k^s}{dv} = \frac{\kappa_{k,i}^s}{\bar{t}_{i,0} - \bar{t}_{i,2}} + \frac{\kappa_{k,i+1}^s}{\bar{t}_{i,2} - \bar{t}_{i,0}} \quad \forall k \in K \quad \forall i \in CI$$

Control parameterization equations for the CFR side exit stream

$$F_k^o = \kappa_{k,i}^o \frac{t - \bar{t}_{i,2}}{\bar{t}_{i,0} - \bar{t}_{i,2}} + \kappa_{k,i+1}^o \frac{t - \bar{t}_{i,0}}{\bar{t}_{i,2} - \bar{t}_{i,0}} \quad \forall k \in K \quad \forall i \in CI$$

$$\frac{dF_k^o}{dv} = \frac{\kappa_{k,i}^o}{\bar{t}_{i,0} - \bar{t}_{i,2}} + \frac{\kappa_{k,i+1}^o}{\bar{t}_{i,2} - \bar{t}_{i,0}} \quad \forall k \in K \quad \forall i \in CI$$

Control parameterization equations for the CFR temperature

$$\begin{aligned} T_k^t &= \kappa_{k,i,0}^t \frac{(t-\bar{t}_{i,1})(t-\bar{t}_{i,2})}{(\bar{t}_{i,0}-\bar{t}_{i,1})(\bar{t}_{i,0}-\bar{t}_{i,2})} \\ &+\kappa_{k,i,1}^t \frac{(t-\bar{t}_{i,0})(t-\bar{t}_{i,2})}{(\bar{t}_{i,1}-\bar{t}_{i,0})(\bar{t}_{i,1}-\bar{t}_{i,2})} \\ &+\kappa_{k,i+1,0}^t \frac{(t-\bar{t}_{i,0})(t-\bar{t}_{i,1})}{(\bar{t}_{i,2}-\bar{t}_{i,0})(\bar{t}_{i,2}-\bar{t}_{i,1})} \\ &\forall k \in K \quad \forall i \in CI \end{aligned}$$

$$\begin{aligned} \frac{dt_k^t}{dv} &= \kappa_{k,i,0}^t \frac{(t-\bar{t}_{i,1})+(t-\bar{t}_{i,2})}{(\bar{t}_{i,0}-\bar{t}_{i,1})(\bar{t}_{i,0}-\bar{t}_{i,2})} \\ &+\kappa_{k,i,1}^t \frac{(t-\bar{t}_{i,0})+(t-\bar{t}_{i,2})}{(\bar{t}_{i,1}-\bar{t}_{i,0})(\bar{t}_{i,1}-\bar{t}_{i,2})} \\ &+\kappa_{k,i+1,0}^t \frac{(t-\bar{t}_{i,0})+(t-\bar{t}_{i,1})}{(\bar{t}_{i,2}-\bar{t}_{i,0})(\bar{t}_{i,2}-\bar{t}_{i,1})} \\ &\forall k \in K \quad \forall i \in CI \end{aligned}$$

Continuity in the first derivatives of the temperature

$$\kappa^t_{k,i-1,0}\frac{\bar{t}_{i-1,2}-\bar{t}_{i-1,1}}{(\bar{t}_{i-1,0}-\bar{t}_{i-1,1})(\bar{t}_{i-1,0}-\bar{t}_{i-1,2})}$$

$$+\kappa^t_{k,i-1,1}\frac{\bar{t}_{i-1,2}-\bar{t}_{i-1,0}}{(\bar{t}_{i-1,1}-\bar{t}_{i-1,0})(\bar{t}_{i-1,1}-\bar{t}_{i-1,2})}$$

$$+\kappa^t_{k,i,0}\frac{(2\bar{t}_{i-1,2}-\bar{t}_{i-1,1}-\bar{t}_{i-1,0})}{(\bar{t}_{i-1,2}-\bar{t}_{i-1,0})(\bar{t}_{i-1,2}-\bar{t}_{i-1,1})}$$

$$=\kappa^t_{k,i,0}\frac{(2\bar{t}_{i,0}-\bar{t}_{i,2}-\bar{t}_{i,1})}{(\bar{t}_{i,0}-\bar{t}_{i,1})(\bar{t}_{i,0}-\bar{t}_{i,2})}$$

$$+\kappa^t_{k,i,1}\frac{(\bar{t}_{i,0}-\bar{t}_{i,2})}{(\bar{t}_{i,1}-\bar{t}_{i,0})(\bar{t}_{i,1}-\bar{t}_{i,2})}$$

$$+\kappa^t_{k,i+1,0}\frac{(\bar{t}_{i,0}-\bar{t}_{i,1})}{(\bar{t}_{i,2}-\bar{t}_{i,0})(\bar{t}_{i,2}-\bar{t}_{i,1})}$$

$$\forall k \in K \quad \forall i \in CI, i > 0$$

The array of collocation points is

$$\bar{t}_{ci,co} = \begin{pmatrix} 0.00 & 0.05 & 0.10 \\ 0.10 & 0.15 & 0.20 \\ 0.20 & 0.25 & 0.30 \\ 0.30 & 0.35 & 0.40 \\ 0.40 & 0.45 & 0.50 \\ 0.50 & 0.55 & 0.60 \\ 0.60 & 0.65 & 0.70 \\ 0.70 & 0.75 & 0.80 \\ 0.80 & 0.85 & 0.90 \\ 0.90 & 0.95 & 1.00 \end{pmatrix}$$

Note that there are other possible ways to handle the control parameterization. For example, the control parameterization could have been done for the derivatives and the integrator could have been used to calculate the flow rates and the temperature. This would require that the initial conditions for these variables be specified. Since they would depend on the parameters, they would need to be optimized.

Objective Function

The objective function varies from problem to problem. In many cases it is the maximization of the yield of the desired product. It may be based upon economic criteria reflecting the value of the products, cost of reactants, cost of the utilities, and the cost of the reactors.

Variables

Time Invariant Variables

Flowrates			
$F^{ab}_{r,k}$	$\forall r \in R$	$\forall k \in K$	Volumetric flowrates from feed splitters to CFR side mixers
$F^{ac}_{r,k}$	$\forall r \in R$	$\forall k \in K$	Volumetric flowrates from feed splitters to CFR main mixers
$F^{ad}_{r,l}$	$\forall r \in R$	$\forall l \in L$	Volumetric flowrates from feed splitters to CSTR mixers
F^{b}_{k}	$\forall k \in K$		Volumetric flowrates into CFR side inlets
F^{c}_{k}	$\forall k \in K$		Volumetric flowrates into CFR main inlets
F^{d}_{l}	$\forall l \in L$		Volumetric flowrates into CSTRs
F^{e}_{k}	$\forall k \in K$		Volumetric flowrates out of CFR main outlet
F^{f}_{k}	$\forall k \in K$		Volumetric flowrates into CFR side outlet
F^{g}_{l}	$\forall l \in L$		Volumetric flowrates out of CSTRs
$F^{eb}_{k,k'}$	$\forall k \in K$	$\forall k' \in K$	Volumetric flowrates from CFR main splitter to CFR side inlet mixers
$F^{ec}_{k,k'}$	$\forall k \in K$	$\forall k' \in K$	Volumetric flowrates from CFR main splitter to CFR main mixers
$F^{ed}_{k,l}$	$\forall k \in K$	$\forall l \in L$	Volumetric flowrates from CFR main splitters to CSTR mixers
$F^{fb}_{k,k'}$	$\forall k \in K$	$\forall k' \in K$	Volumetric flowrates from CFR side splitters to CFR side inlet mixers
$F^{fc}_{k,k'}$	$\forall k \in K$	$\forall k' \in K$	Volumetric flowrates from CFR side splitters to CFR main inlet mixers
$F^{fd}_{k,l}$	$\forall k \in K$	$\forall l \in L$	Volumetric flowrates from CFR side splitters to CSTR inlet mixers
$F^{gb}_{l,k}$	$\forall l \in L$	$\forall k \in K$	Volumetric flowrates from CSTR outlet splitters to CFR side inlets mixers
$F^{gc}_{l,k}$	$\forall l \in L$	$\forall k \in K$	Volumetric flowrates from CSTR outlet splitters to CFR main inlet mixers
$F^{gd}_{l,l'}$	$\forall l \in L$	$\forall l' \in L$	Volumetric flowrates from CSTR outlet splitters to CSTR inlet mixers
$F^{eh}_{k,p}$	$\forall k \in K$	$\forall p \in P$	Volumetric flowrates from CFR main outlet splitters to product mixer
$F^{fh}_{k,p}$	$\forall k \in K$	$\forall p \in P$	Volumetric flowrates from CFR side outlet splitters to product mixer
$F^{gh}_{l,p}$	$\forall l \in L$	$\forall p \in P$	Volumetric flowrates from CSTR outlet splitter to product mixer
F^{h}_{p}	$\forall p \in P$		Volumetric flowrates of the product streams

		Concentrations	
$c^b_{k,i}$	$\forall k \in K$	$\forall i \in I$	Concentrations of species in the CFR side streams
$c^c_{k,i}$	$\forall k \in K$	$\forall i \in I$	Concentrations of species in the CFR main inlet streams
$c^d_{l,i}$	$\forall l \in L$	$\forall i \in I$	Concentrations of species in the CSTR inlet streams
$c^e_{k,i}$	$\forall k \in K$	$\forall i \in I$	Concentrations of species in the CFR main outlet streams
$c^f_{k,i}$	$\forall k \in K$	$\forall i \in I$	Concentrations of species in the CFR side outlet streams
$c^g_{l,i}$	$\forall l \in L$	$\forall i \in I$	Concentrations of species in the CSTR outlet streams
$c^h_{p,i}$	$\forall p \in P$	$\forall i \in I$	Concentrations of species in the product streams
		Temperatures	
T^m_l	$\forall l \in L$		Temperatures in the CSTRs
		Reactor Volumes	
V^m_l	$\forall l \in L$		Volume of the CSTRs
V^t_k	$\forall k \in K$		Volume of the CFRs
		Reaction Rates	
$r^m_{l,j}$	$\forall l \in L$	$\forall j \in J$	Rate of reaction j in CSTR reactor l
		Control Parameters	
$\kappa^s_{k,i}$	$\forall k \in K$	$\forall i \in CI$	Control parameters for the side feed
$\kappa^o_{k,i}$	$\forall k \in K$	$\forall i \in CI$	Control parameters for the side exit
$\kappa^t_{k,i,j}$	$\forall k \in K$	$\forall i \in CI$	Control parameters for the temperature

Dynamic Variables

		Flowrates	
F^t_k	$\forall k \in K$		Volumetric flowrates within CFRs
F^s_k	$\forall k \in K$		Volumetric flowrates of CFR side inlets
F^o_k	$\forall k \in K$		Volumetric flowrates of CFR side outlets
		Concentrations	
$c^t_{k,i}$	$\forall k \in K$	$\forall i \in I$	Concentrations of species within CFRs
$c^o_{k,i}$	$\forall k \in K$	$\forall i \in I$	Concentrations of species within CFR side outlet
		Temperatures	
T^t_k	$\forall k \in K$		Temperature within the CFRs
		Reaction Rates	
$r^t_{k,j}$	$\forall k \in K$	$\forall j \in J$	Rate of reaction j in CSTR reactor l

Variable Bounds

The variable bounds vary from one problem to the next. The flowrates, concentrations, temperatures, volumes and reaction rates have a lower bound of zero due to physical restrictions. The upper bounds on the flow rates are set arbitrarily (generally 10 times the feed flowrate) to help the solution algorithm. The upper bounds on the concentrations are set to the maximum possible concentration that any species could achieve. The temperature ranges for the nonisothermal problems are usually specified for each problem. The upper bounds on the reactor volumes and reaction rates are set arbitrarily to help the solution algorithm.

Since the recycle around a CSTR unit is not necessary, the upper and lower bounds for these flowrates are set to zero.

15.2.3 Specific Information

Specific information needs to be provided for each problem. This information includes the reaction mechanism, the reaction paramters, the rate expressions, and any additional information required for the problem.

Reaction Mechanism

For each problem, a reaction mechanism indicating the species and reaction steps involved is provided.

Parameters

The parameters for the problems are the stoichiometric coefficient matrix, the kinetic constants, and the feed conditions. The stoichiometric coefficient matrix, $\nu_{i,j}$ indicates the relative number of moles of products and reactants that participate in a given reaction.

		Reaction constants	
$\nu_{i,j}$	$\forall i \in I$	$\forall j \in J$	Stoichiometric coefficient matrix
k_j	$\forall j \in J$		Kinetic rate constant
E_j	$\forall j \in J$		Activation Energy
ΔH_j	$\forall j \in J$		Heat of reaction
		Feed conditions	
F_r^a	$\forall r \in R$		Flowrate of feed streams
$c_{r,i}^a$	$\forall r \in R$	$\forall i \in I$	Concentrations of species in feed streams

Rate Expressions

The rate expressions ($f_j^r(c_i, T)$) are specified for each problem. These expressions often involve the products of the concentrations of the species. The rate expressions have the form

$$f_j^r(c_i, T) = k_j(T) \prod_{i \in I} c_i^{\nu_{i,j}^f}$$

where $\nu^f_{i,j}$ correspond to the positive coefficients in the stoichiometric matrix representing the forward reactions. (For equilibrium reactions, both the forward and reverse reactions must appear separately and the rate constants for both must be provided.)

For isothermal reactions, the values of k_j are fixed. For most nonisothermal problems, Arrhenius temperature dependence will be assumed:

$$k_j(T) = \hat{k}_j \exp\left(\frac{-E_j}{RT}\right)$$

Additional Information

For most problems, this is all of the information that will be required. Some problems will have additional restrictions on the sizes of the reactors, the amount of conversion, etc.

15.2.4 Problem Characteristics

This problem has bilinearities which result from the mass balances of the mixers. The rate expressions usually involve the products of the concentrations and thus lead to squared or bilinear terms for first order kinetics, trilinear terms for second order kinetics, and so on. For nonisothermal problems, the temperature dependence is an exponential which is multiplied by the product of the concentrations.

For each problem, the number of CSTRs and CFRs that can potentially exist in the network must be given. Existence of the CSTRs in the network could be handled with binary variables, however, this would lead to an MINLP. Existence of the reactors is handled through the volume of the reactors. Reactors with zero volume are mixers and do not exist.

15.2.5 Test Problems

Unless otherwise stated, all of the example problems use one CSTR and one CFR in the reactor network superstructure. The same set of test problems that were used in Section 8.4 of Chapter 8 are presented here. These problems have been formulated in the MINOPT modeling language and the solutions provided have been obtained using MINOPT (Schweiger and Floudas (1998c, 1997)). These problems have multiple local optima which have been found by using MINOPT to solve the problem with random starting points. The best known solution and simplest configuration are given for each problem.

15.2.6 Test Problem 1 : Nonisothermal Van de Vusse Reaction Case I

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$
$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:

Maximize the yield of **B**

$$\max c_{1,B}^h$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	5.4×10^9 h^{-1}	15.84 kcal/mol	-84 K L/mol
2	1.6×10^{12} h^{-1}	23.76 kcal/mol	-108 K L/mol
3	3.6×10^5 L/(mol h)	7.92 kcal/mol	-60 K L/mol
Feed Conditions			
F_r^a	100 L/s		
$c_{r,i}^a$	1.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**		

Rate Expressions

$$f_1^r = \hat{k}_1 e^{\frac{-E_1}{RT}} c_A$$
$$f_2^r = \hat{k}_2 e^{\frac{-E_2}{RT}} c_B$$
$$f_3^r = \hat{k}_3 e^{\frac{-E_3}{RT}} c_A^2$$

Additional Information

The temperatures in the reactors are bounded between 300 K and 810 K.

Explicit Formulation

$$
\begin{aligned}
F_1^a &= F_{1,1}^{ab} + F_{1,1}^{ac} + F_{1,1}^{ad} \\
F_k^b &= F_{1,1}^{ab} + F_{1,1}^{eb} + F_{1,1}^{fb} + F_{1,1}^{gb} \\
c_{1,A}^b F_1^b &= c_{1,A}^a F_{1,1}^{ab} + c_{1,A}^e F_{1,1}^{eb} + c_{1,A}^f F_{1,1}^{fb} + c_{1,A}^g F_{1,1}^{gb} \\
c_{1,B}^b F_1^b &= c_{1,B}^a F_{1,1}^{ab} + c_{1,B}^e F_{1,1}^{eb} + c_{1,B}^f F_{1,1}^{fb} + c_{1,B}^g F_{1,1}^{gb} \\
c_{1,C}^b F_1^b &= c_{1,C}^a F_{1,1}^{ab} + c_{1,C}^e F_{1,1}^{eb} + c_{1,C}^f F_{1,1}^{fb} + c_{1,C}^g F_{1,1}^{gb} \\
c_{1,D}^b F_1^b &= c_{1,D}^a F_{1,1}^{ab} + c_{1,D}^e F_{1,1}^{eb} + c_{1,D}^f F_{1,1}^{fb} + c_{1,D}^g F_{1,1}^{gb} \\
F_1^c &= F_{1,1}^{ac} + F_{1,1}^{ec} + F_{1,1}^{fc} + F_{1,1}^{gc} \\
c_{1,A}^c F_1^c &= c_{1,A}^a F_{1,1}^{ac} + c_{1,A}^e F_{1,1}^{ec} + c_{1,A}^f F_{1,1}^{fc} + c_{1,A}^g F_{1,1}^{gc} \\
c_{1,B}^c F_1^c &= c_{1,B}^a F_{1,1}^{ac} + c_{1,B}^e F_{1,1}^{ec} + c_{1,B}^f F_{1,1}^{fc} + c_{1,B}^g F_{1,1}^{gc} \\
c_{1,C}^c F_1^c &= c_{1,C}^a F_{1,1}^{ac} + c_{1,C}^e F_{1,1}^{ec} + c_{1,C}^f F_{1,1}^{fc} + c_{1,C}^g F_{1,1}^{gc} \\
c_{1,D}^c F_1^c &= c_{1,D}^a F_{1,1}^{ac} + c_{1,D}^e F_{1,1}^{ec} + c_{1,D}^f F_{1,1}^{fc} + c_{1,D}^g F_{1,1}^{gc} \\
F_1^d &= F_{1,1}^{ad} + F_{1,1}^{ed} + F_{1,1}^{fd} + F_{1,1}^{gd} \\
c_{1,A}^d F_1^d &= c_{1,A}^a F_{1,1}^{ad} + c_{1,A}^e F_{1,1}^{ed} + c_{1,A}^f F_{1,1}^{fd} + c_{1,A}^g F_{1,1}^{gb} \\
c_{1,B}^d F_1^d &= c_{1,B}^a F_{1,1}^{ad} + c_{1,B}^e F_{1,1}^{ed} + c_{1,B}^f F_{1,1}^{fd} + c_{1,B}^g F_{1,1}^{gb} \\
c_{1,C}^d F_1^d &= c_{1,C}^a F_{1,1}^{ad} + c_{1,C}^e F_{1,1}^{ed} + c_{1,C}^f F_{1,1}^{fd} + c_{1,C}^g F_{1,1}^{gb} \\
c_{1,D}^d F_1^d &= c_{1,D}^a F_{1,1}^{ad} + c_{1,D}^e F_{1,1}^{ed} + c_{1,D}^f F_{1,1}^{fd} + c_{1,D}^g F_{1,1}^{gb} \\
F_1^g &= F_1^d \\
F_1^g c_{1,A}^g &= F_1^d c_{1,A}^d + V_1^m (\nu_{A,1} r_{1,1}^m + \nu_{A,2} r_{1,2}^m + \nu_{A,3} r_{1,3}^m) \\
F_1^g c_{1,B}^g &= F_1^d c_{1,B}^d + V_1^m (\nu_{B,1} r_{1,1}^m + \nu_{B,2} r_{1,2}^m + \nu_{B,3} r_{1,3}^m) \\
F_1^g c_{1,C}^g &= F_1^d c_{1,C}^d + V_1^m (\nu_{C,1} r_{1,1}^m + \nu_{C,2} r_{1,2}^m + \nu_{C,3} r_{1,3}^m) \\
F_1^g c_{1,D}^g &= F_1^d c_{1,D}^d + V_1^m (\nu_{D,1} r_{1,1}^m + \nu_{D,2} r_{1,2}^m + \nu_{D,3} r_{1,3}^m) \\
r_{1,1}^m &= 5.4 \times 10^9 e^{-7971.82/T_1^m} c_{1,A}^g \\
r_{1,2}^m &= 1.6 \times 10^{12} e^{-11957.7/T_1^m} c_{1,B}^g \\
r_{1,3}^m &= 3.6 \times 10^5 e^{-3985.91/T_1^m} c_{1,A}^g c_{1,A}^g
\end{aligned}
$$

$$
\begin{aligned}
\frac{dF_1^t}{dV} &= -\frac{dF_1^s}{dV} - \frac{dF_1^o}{dV} \\
F_1^t \frac{dc_{1,A}^t}{dV} &= -(c_{1,A}^s - c_{1,A}^t)\frac{dF_1^s}{dV} + V_1^t (\nu_{A,1} r_{1,1}^t + \nu_{A,2} r_{1,2}^t + \nu_{A,3} r_{1,3}^t) \\
F_1^t \frac{dc_{1,B}^t}{dV} &= -(c_{1,B}^s - c_{1,B}^t)\frac{dF_1^s}{dV} + V_1^t (\nu_{B,1} r_{1,1}^t + \nu_{B,2} r_{1,2}^t + \nu_{B,3} r_{1,3}^t) \\
F_1^t \frac{dc_{1,C}^t}{dV} &= -(c_{1,C}^s - c_{1,C}^t)\frac{dF_1^s}{dV} + V_1^t (\nu_{C,1} r_{1,1}^t + \nu_{C,2} r_{1,2}^t + \nu_{C,3} r_{1,3}^t) \\
F_1^t \frac{dc_{1,D}^t}{dV} &= -(c_{1,D}^s - c_{1,D}^t)\frac{dF_1^s}{dV} + V_1^t (\nu_{D,1} r_{1,1}^t + \nu_{D,2} r_{1,2}^t + \nu_{D,3} r_{1,3}^t) \\
F_1^o \frac{dc_{1,A}^o}{dV} &= (c_{1,A}^t - c_{1,A}^o)\frac{dF_1^o}{V} \\
F_1^o \frac{dc_{1,B}^o}{dV} &= (c_{1,B}^t - c_{1,B}^o)\frac{dF_1^o}{V} \\
F_1^o \frac{dc_{1,C}^o}{dV} &= (c_{1,C}^t - c_{1,C}^o)\frac{dF_1^o}{V} \\
F_1^o \frac{dc_{1,D}^o}{dV} &= (c_{1,D}^t - c_{1,D}^o)\frac{dF_1^o}{V}
\end{aligned}
$$

$$
\begin{aligned}
F_1^s &= F_1^b & F_1^t &= F_1^c \\
c_{1,A}^s &= c_{1,A}^b & c_{1,A}^t &= c_{1,A}^c \\
c_{1,B}^s &= c_{1,B}^b & c_{1,B}^t &= c_{1,B}^c \\
c_{1,C}^s &= c_{1,C}^b & c_{1,C}^t &= c_{1,C}^c \\
c_{1,D}^s &= c_{1,D}^b & c_{1,D}^t &= c_{1,D}^c \\
F_1^e &= F_1^t & F_1^f &= F_1^o \\
c_{1,A}^e &= c_{1,A}^t & c_{1,A}^f &= c_{1,A}^o \\
c_{1,B}^e &= c_{1,B}^t & c_{1,B}^f &= c_{1,B}^o \\
c_{1,C}^e &= c_{1,C}^t & c_{1,C}^f &= c_{1,C}^o \\
c_{1,D}^e &= c_{1,D}^t & c_{1,D}^f &= c_{1,D}^o
\end{aligned}
$$

$$
\begin{aligned}
r_{1,1}^t &= 5.4 \times 10^9 e^{-7971.82/T_1^t} c_{1,A}^t \\
r_{1,2}^t &= 1.6 \times 10^{12} e^{-11957.7/T_1^t} c_{1,B}^t \\
r_{1,3}^t &= 3.6 \times 10^5 e^{-3985.91/T_1^t} c_{1,A}^t c_{1,A}^t \\
F_1^e &= F_{1,1}^{eb} + F_{1,1}^{ec} + F_{1,1}^{ed} + F_{1,1}^{eh} \\
F_1^f &= F_{1,1}^{fb} + F_{1,1}^{fc} + F_{1,1}^{fd} + F_{1,1}^{fh} \\
F_1^g &= F_{1,1}^{gb} + F_{1,1}^{gc} + F_{1,1}^{gd} + F_{1,1}^{gh} \\
F_1^h &= F_{1,1}^{eh} + F_{1,1}^{fh} + F_{1,1}^{gh} \\
F_1^h c_{1,A}^h &= F_{1,1}^{eh} c_{1,A}^e + F_{1,1}^{fh} c_{1,A}^f + F_{1,1}^{gh} c_{1,A}^g \\
F_1^h c_{1,B}^h &= F_{1,1}^{eh} c_{1,B}^e + F_{1,1}^{fh} c_{1,B}^f + F_{1,1}^{gh} c_{1,B}^g \\
F_1^h c_{1,C}^h &= F_{1,1}^{eh} c_{1,C}^e + F_{1,1}^{fh} c_{1,C}^f + F_{1,1}^{gh} c_{1,C}^g \\
F_1^h c_{1,D}^h &= F_{1,1}^{eh} c_{1,D}^e + F_{1,1}^{fh} c_{1,D}^f + F_{1,1}^{gh} c_{1,D}^g
\end{aligned}
$$

$$
\begin{aligned}
T_1^t &= \kappa_{1,i,0}^t (t-\tau_{i,1})(t-\tau_{i,2})/(\tau_{i,0}-\tau_{i,1})/(\tau_{i,0}-\tau_{i,2}) \\
&+\kappa_{1,i,1}^t (t-\tau_{i,0})(t-\tau_{i,2})/(\tau_{i,1}-\tau_{i,0})/(\tau_{i,1}-\tau_{i,2}) \\
&+\kappa_{1,i+1,0}^t (t-\tau_{i,0})/(t-\tau_{i,1})/(\tau_{i,2}-\tau_{i,0})/(\tau_{i,2}-\tau_{i,1})
\end{aligned}
$$

$$
\begin{aligned}
\frac{dT_1^t}{dV} &= \kappa_{1,i,0}^t ((t-\tau_{i,1})+(t-\tau_{i,2}))/(\tau_{i,0}-\tau_{i,1})/(\tau_{i,0}-\tau_{i,2}) \\
&+\kappa_{1,i,1}^t ((t-\tau_{i,0})+(t-\tau_{i,2}))/(\tau_{i,1}-\tau_{i,0})/(\tau_{i,1}-\tau_{i,2}) \\
&+\kappa_{1,i+1,0}^t ((t-\tau_{i,0})+(t-\tau_{i,1}))/(\tau_{i,2}-\tau_{i,0})/(\tau_{i,2}-\tau_{i,1})
\end{aligned}
$$

$$
\begin{aligned}
F_k^s &= \kappa_{1,i}^s (t-\tau_{i,2})/(\tau_{i,0}-\tau_{i,2}) + \kappa_{1,i+1}^s (t-\tau_{i,0})/(\tau_{i,2}-\tau_{i,0}) \\
\frac{dF_1^s}{dV} &= \kappa_{1,i}^s/(\tau_{i,0}-\tau_{i,2}) + \kappa_{1,i+1}^s/(\tau_{i,2}-\tau_{i,0}) \\
F_k^o &= \kappa_{1,i}^o (t-\tau_{i,2})/(\tau_{i,0}-\tau_{i,2}) + \kappa_{1,i+1}^o (t-\tau_{i,0})/(\tau_{i,2}-\tau_{i,0}) \\
\frac{dF_1^o}{dV} &= \kappa_{1,i}^o/(\tau_{i,0}-\tau_{i,2}) + \kappa_{1,i+1}^o/(\tau_{i,2}-\tau_{i,0})
\end{aligned}
$$

Problem Statistics

No. of continuous variables	100
No. of dynamic variables	18
No. of linear equalities	20
No. of linear inequalities	20
No. of nonlinear equalities	23
No. of point equalities	9
No. of dynamic equations	18

Best Known Solution

- Objective function: 0.8267309 mol/L

- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.00 & F^{ac}_{r,k} = 100.000 & F^{ad}_{r,l} = 0.00 \\
F^{b}_{k} = 0.00 & F^{c}_{k} = 100.000 & F^{d}_{l} = 100.000 \\
F^{e}_{k} = 100.000 & F^{f}_{k} = 0.00 & F^{g}_{l} = 100.000 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 100.00 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 0.00 & F^{gd}_{l,l'} = 0.00 \\
F^{eh}_{k,p} = 0.00 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 100.000 \\
F^{h}_{p} = 100.00 & &
\end{array}
$$

$$c^{b}_{k,i} = (1.000000, 0.000000, 0.0000000, 0.0000000)^T$$
$$c^{c}_{k,i} = (1.000000, 0.000000, 0.0000000, 0.0000000)^T$$
$$c^{d}_{l,i} = (0.110190, 0.748042, 0.0639591, 0.0389047)^T$$
$$c^{e}_{k,i} = (0.110190, 0.748042, 0.0639591, 0.0389047)^T$$
$$c^{f}_{k,i} = (1.000000, 0.000000, 0.0000000, 0.0000000)^T$$
$$c^{g}_{l,i} = (0.00819274, 0.826731, 0.0763064, 0.0443850)^T$$
$$c^{h}_{p,i} = (0.00819274, 0.826731, 0.0763064, 0.0443850)^T$$
$$V^{m}_{l} = 10000.0 \quad V^{t}_{k} = 2.45039 \quad T^{m}_{l} = 323.968$$
$$r^{m}_{l,j} = (0.000910363, 0.000123473, 0.000109607)^T$$
$$\kappa^{s}_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa^o_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa^t_{k,m,i} = \begin{pmatrix} 582.4623 & 300.0000 \\ 325.3572 & 451.5398 \\ 471.5539 & 447.4510 \\ 441.2828 & 441.4477 \\ 436.3444 & 430.4997 \\ 428.4403 & 427.5221 \\ 425.1011 & 422.8199 \\ 422.3212 & 421.5077 \\ 418.2821 & 416.9589 \\ 421.8527 & 395.3906 \\ 300.0000 & 400.0000 \end{pmatrix}$$

15.2.7 Test Problem 2 : Isothermal Van de Vusse Reaction Case I

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$

$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:
Maximize the yield of **B**:

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	10 s^{-1} (first order)
k_2	1 s^{-1} (first order)
k_3	0.5 L/(mol s) (second order)
	Feed Conditions
F^a_r	100 L/s
$c^a_{r,i}$	0.58 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f_1^r = k_1 c_A$$
$$f_2^r = k_2 c_B$$
$$f_3^r = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	77
No. of dynamic variables	16
No. of linear equalities	13
No. of linear inequalities	20
No. of nonlinear equalities	21
No. of point equalities	9
No. of dynamic equations	16

Best Known Solution

- Objective function: 0.4370782 mol/L
- Variables

$$\begin{array}{lll}
F_{r,k}^{ab} = 0.00 & F_{r,k}^{ac} = 100.000 & F_{r,l}^{ad} = 0.00 \\
F_k^{b} = 0.00 & F_k^{c} = 100.000 & F_l^{d} = 0.00 \\
F_k^{e} = 100.000 & F_k^{f} = 0.00 & F_l^{g} = 0.00 \\
F_{k,k'}^{eb} = 0.00 & F_{k,k'}^{ec} = 0.00 & F_{k,l}^{ed} = 0.00 \\
F_{k,k'}^{fb} = 0.00 & F_{k,k'}^{fc} = 0.00 & F_{k,l}^{fd} = 0.00 \\
F_{l,k}^{gb} = 0.00 & F_{l,k}^{gc} = 0.00 & F_{l,l'}^{gd} = 0.00 \\
F_{k,p}^{eh} = 100.00 & F_{k,p}^{fh} = 0.00 & F_{l,p}^{gh} = 0.00 \\
F_p^{h} = 100.00 & &
\end{array}$$

$$\begin{aligned}
c_{k,i}^b &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c_{k,i}^c &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c_{l,i}^d &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c_{k,i}^e &= (0.0437085, 0.437078, 0.0831118, 0.00805073)^T \\
c_{k,i}^f &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c_{l,i}^g &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c_{p,i}^h &= (0.0437085, 0.437078, 0.0831118, 0.00805073)^T
\end{aligned}$$

$$V_l^m = 0.00 \quad V_k^t = 25.3347$$

$$r_{l,j}^m = (0.00, 0.00, 0.00)^T$$

$$\kappa_{k,m}^s = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$
$$\kappa_{k,m}^o = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

15.2.8 Test Problem 3 : Isothermal Van de Vusse Reaction Case II

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$

$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:

Maximize the yield of **B**:

$$\max c_{1,B}^h$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -1 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	10 s^{-1} (first order)
k_2	1 s^{-1} (first order)
k_3	0.5 L/(mol s) (second order)
	Feed Conditions
F_r^a	100 L/s
$c_{r,i}^a$	0.58 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f_1^r = k_1 c_A$$
$$f_2^r = k_2 c_B$$
$$f_3^r = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	77
No. of dynamic variables	16
No. of linear equalities	13
No. of linear inequalities	20
No. of nonlinear equalities	21
No. of point equalities	9
No. of dynamic equations	16

Best Known Solution

- Objective function: 0.442966 mol/L
- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.00 & F^{ac}_{r,k} = 100.000 & F^{ad}_{r,l} = 0.00 \\
F^{b}_{k} = 0.00 & F^{c}_{k} = 100.000 & F^{d}_{l} = 0.00 \\
F^{e}_{k} = 100.000 & F^{f}_{k} = 0.00 & F^{g}_{l} = 0.00 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 0.00 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 0.00 & F^{gd}_{l,l'} = 0.00 \\
F^{eh}_{k,p} = 100.000 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 0.00 \\
F^{h}_{p} = 100.00 & &
\end{array}
$$

$$
\begin{aligned}
c^{b}_{k,i} &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c^{c}_{k,i} &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c^{d}_{l,i} &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c^{e}_{k,i} &= (0.0442974, 0.442966, 0.0845351, 0.00820189)^T \\
c^{f}_{k,i} &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c^{g}_{l,i} &= (0.580000, 0.000000, 0.000000, 0.000000)^T \\
c^{h}_{p,i} &= (0.0442974, 0.442966, 0.0845351, 0.00820189)^T
\end{aligned}
$$

$$V^m_l = 0.00 \quad V^t_k = 25.4573$$

$$r^m_{l,j} = (0.00, 0.00, 0.00)^T$$

$$
\begin{aligned}
\kappa^s_{k,m} &= (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T \\
\kappa^o_{k,m} &= (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T
\end{aligned}
$$

15.2.9 Test Problem 4 : Isothermal Van de Vusse Reaction Case III

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$

$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:

Maximize the yield of **B**:

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	10 s^{-1} (first order)
k_2	1 s^{-1} (first order)
k_3	0.5 L/(mol s) (second order)
	Feed Conditions
F_r^a	100 L/s
$c_{r,i}^a$	5.8 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f_1^r = k_1 c_A$$
$$f_2^r = k_2 c_B$$
$$f_3^r = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	77
No. of dynamic variables	16
No. of linear equalities	13
No. of linear inequalities	20
No. of nonlinear equalities	21
No. of point equalities	9
No. of dynamic equations	16

Best Known Solution

- Objective function: 3.68185 mol/L
- Variables

$$\begin{array}{lll}
F_{r,k}^{ab} = 0.00 & F_{r,k}^{ac} = 0.00 & F_{r,l}^{ad} = 100.000 \\
F_k^b = 0.00 & F_k^c = 100.000 & F_l^d = 100.000 \\
F_k^e = 100.000 & F_k^f = 0.00 & F_l^g = 100.000 \\
F_{k,k'}^{eb} = 0.00 & F_{k,k'}^{ec} = 0.00 & F_{k,l}^{ed} = 0.00 \\
F_{k,k'}^{fb} = 0.00 & F_{k,k'}^{fc} = 0.00 & F_{k,l}^{fd} = 0.00 \\
F_{l,k}^{gb} = 0.00 & F_{l,k}^{gc} = 100.00 & F_{l,l'}^{gd} = 0.00 \\
F_{k,p}^{eh} = 100.000 & F_{k,p}^{fh} = 0.00 & F_{l,p}^{gh} = 0.00 \\
F_p^h = 100.00 & &
\end{array}$$

$$
\begin{aligned}
c^b_{k,i} &= (5.80000, 0.00000, 0.000000, 0.000000)^T \\
c^c_{k,i} &= (2.40827, 2.45481, 0.278627, 0.329144)^T \\
c^d_{l,i} &= (5.80000, 0.00000, 0.000000, 0.000000)^T \\
c^e_{k,i} &= (0.368196, 3.68185, 0.847795, 0.451080)^T \\
c^f_{k,i} &= (5.80000, 0.00000, 0.000000, 0.000000)^T \\
c^g_{l,i} &= (2.40827, 2.45481, 0.278627, 0.329144)^T \\
c^h_{p,i} &= (0.368196, 3.68185, 0.847795, 0.451080)^T
\end{aligned}
$$

$$V^m_l = 11.3502 \quad V^t_k = 16.9843$$

$$r^m_{l,j} = (24.0827, 2.45481, 2.89989)^T$$

$$\kappa^s_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa^o_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

15.2.10 Test Problem 5 : Isothermal Van de Vusse Reaction Case IV

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$

$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:

Maximize the yield of **B**:

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Rate Constants	
k_1	1 s^{-1} (first order)
k_2	2 s^{-1} (first order)
k_3	10 L/(mol s) (second order)
Feed Conditions	
F^a_r	100 L/s
$c^a_{r,i}$	1 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$\begin{aligned} f_1^r &= k_1 c_A \\ f_2^r &= k_2 c_B \\ f_3^r &= k_3 c_A^2 \end{aligned}$$

Problem Statistics

No. of continuous variables	77
No. of dynamic variables	16
No. of linear equalities	13
No. of linear inequalities	20
No. of nonlinear equalities	21
No. of point equalities	9
No. of dynamic equations	16

Best Known Solution

- Objective function: 0.07026654 mol/L
- Variables

$$\begin{array}{lll} F_{r,k}^{ab} = 0.00 & F_{r,k}^{ac} = 0.00 & F_{r,l}^{ad} = 100.000 \\ F_k^b = 0.00 & F_k^c = 100.000 & F_l^d = 100.000 \\ F_k^e = 100.000 & F_k^f = 0.00 & F_l^g = 100.000 \\ F_{k,k'}^{eb} = 0.00 & F_{k,k'}^{ec} = 0.00 & F_{k,l}^{ed} = 0.00 \\ F_{k,k'}^{fb} = 0.00 & F_{k,k'}^{fc} = 0.00 & F_{k,l}^{fd} = 0.00 \\ F_{l,k}^{gb} = 0.00 & F_{l,k}^{gc} = 100.00 & F_{l,l'}^{gd} = 0.00 \\ F_{k,p}^{eh} = 100.000 & F_{k,p}^{fh} = 0.00 & F_{l,p}^{gh} = 0.00 \\ F_p^h = 100.00 & & \end{array}$$

$$\begin{aligned} c_{k,i}^b &= (1.00000, 0.000000, 0.000000, 0.000000)^T \\ c_{k,i}^c &= (0.316222, 0.0586978, 0.0346578, 0.295211)^T \\ c_{l,i}^d &= (1.00000, 0.000000, 0.000000, 0.000000)^T \\ c_{k,i}^e &= (0.140537, 0.0702665, 0.0557588, 0.366719)^T \\ c_{k,i}^f &= (1.00000, 0.000000, 0.000000, 0.000000)^T \\ c_{l,i}^g &= (0.316222, 0.0586979, 0.0346578, 0.295211)^T \\ c_{p,i}^h &= (0.140537, 0.0702665, 0.0557588, 0.366719)^T \end{aligned}$$

$$V_l^m = 29.5222 \quad V_k^t = 15.7581$$

$$r_{l,j}^m = (0.316222, 0.117396, 0.999964)^T$$

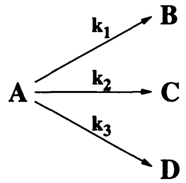
$$\kappa_{k,m}^s = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa_{k,m}^o = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

15.2.11 Test Problem 6 : Isothermal Trambouze Reaction

Problem Information

Reaction Mechanism



The first reaction is zero order, the second is first order, and the third is second order.

Objective:

Maximize the selectivity of **C** to **A**

$$\max \frac{c^h_{1,C}}{1 - c^h_{1,A}}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & -1 & -1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	0.025 gmol/(L min) (first order)
k_2	0.2 min^{-1} (first order)
k_3	0.4 L/(mol min) (second order)
	Feed Conditions
F^a_r	100 L/min pure **A**
$c^a_{r,i}$	1 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**

Rate Expressions

$$f^r_1 = k_1$$
$$f^r_2 = k_2 c_A$$
$$f^r_3 = k_3 c_A^2$$

Problem Statistics

No. of continuous variables	85
No. of dynamic variables	19
No. of linear equalities	13
No. of linear inequalities	20
No. of nonlinear equalities	27
No. of point equalities	11
No. of dynamic equations	19

Best Known Solution

- Objective function: 0.5

- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.00 & F^{ac}_{r,k} = 0.00 & F^{ad}_{r,l} = 100.000 \\
F^{b}_{k} = 0.00 & F^{c}_{k} = 0.00 & F^{d}_{l} = 100.000 \\
F^{e}_{k} = 0.00 & F^{f}_{k} = 0.00 & F^{g}_{l} = 100.000 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 0.00 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 0.00 & F^{gd}_{l,l'} = 0.00 \\
F^{eh}_{k,p} = 0.00 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 100.000 \\
F^{h}_{p} = 100.000 & &
\end{array}
$$

$$
\begin{array}{l}
c^{b}_{k,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T \\
c^{c}_{k,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T \\
c^{d}_{l,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T \\
c^{e}_{k,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T \\
c^{f}_{k,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T \\
c^{g}_{l,i} = (0.250000, 0.187500, 0.375000, 0.187500)^T \\
c^{h}_{p,i} = (0.250000, 0.187500, 0.375000, 0.187500)^T
\end{array}
$$

$$V^m_l = 750.00 \quad V^t_k = 0.00 \quad r^m_{l,j} = (0.0250000, 0.0450000, 0.0250000)^T$$

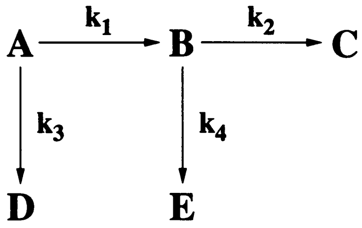
$$\kappa^s_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa^o_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

15.2.12 Test Problem 7 : Isothermal Denbigh Reaction Case I

Problem Information

<u>Reaction Mechanism</u>



Objective:

Maximize the selectivity of **B** to **D**:

$$\max \frac{c^h_{1,B}}{c^h_{1,D}}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -1 & 0 \\ 0.5 & -1 & 0 & -1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	1.0 L/(mol s) (second order)
k_2	0.6 s^{-1} (first order)
k_3	0.6 s^{-1} (first order)
k_4	0.1 L/(mol s) (second order)
	Feed Conditions
F^a_r	100 L/s
$c^a_{r,i}$	6.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0.6 mol/L **D**, 0 mol/L **E**

Rate Expressions

$$\begin{aligned} f^r_1 &= k_1 c_A^2 \\ f^r_2 &= k_2 c_B \\ f^r_3 &= k_3 c_A \\ f^r_4 &= k_4 c_B^2 \end{aligned}$$

Problem Statistics

No. of continuous variables	85
No. of dynamic variables	19
No. of linear equalities	13
No. of linear inequalities	20
No. of nonlinear equalities	27
No. of point equalities	11
No. of dynamic equations	19

Best Known Solution

- Objective function: 1.321759
- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.00 & F^{ac}_{r,k} = 100.000 & F^{ad}_{r,l} = 0.00 \\
F^{b}_{k} = 0.00 & F^{c}_{k} = 100.000 & F^{d}_{l} = 0.00 \\
F^{e}_{k} = 100.000 & F^{f}_{k} = 0.00 & F^{g}_{l} = 0.00 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 0.00 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 0.00 & F^{gd}_{l,l'} = 0.00 \\
F^{eh}_{k,p} = 100.00 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 0.00 \\
F^{h}_{p} = 100.00 & &
\end{array}
$$

$$
\begin{aligned}
c^{b}_{k,i} &= (6.00000, 0.00000, 0.000000, 0.60000, 0.0000000)^T \\
c^{c}_{k,i} &= (6.00000, 0.00000, 0.000000, 0.60000, 0.0000000)^T \\
c^{d}_{l,i} &= (6.00000, 0.00000, 0.000000, 0.60000, 0.0000000)^T \\
c^{e}_{k,i} &= (2.44063, 1.40768, 0.117826, 1.06500, 0.0216797)^T \\
c^{f}_{k,i} &= (6.00000, 0.00000, 0.000000, 0.60000, 0.0000000)^T \\
c^{g}_{l,i} &= (6.00000, 0.00000, 0.000000, 0.60000, 0.0000000)^T \\
c^{h}_{p,i} &= (2.44063, 1.40768, 0.117826, 1.06500, 0.0216797)^T
\end{aligned}
$$

$$V^m_l = 0.00 \quad V^t_k = 20.7497 \quad r^m_{l,j} = (0.00, 0.00, 0.00)^T$$

$$\kappa^s_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa^o_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

15.2.13 Test Problem 8 : Isothermal Denbigh Reaction Case II

Problem Information

Reaction Mechanism

$$
\begin{tikzcd}
\mathbf{A} \arrow[r, "\mathbf{k_1}"] \arrow[d, "\mathbf{k_3}"] & \mathbf{B} \arrow[r, "\mathbf{k_2}"] \arrow[d, "\mathbf{k_4}"] & \mathbf{C} \\
\mathbf{D} & \mathbf{E} &
\end{tikzcd}
$$

Objective:

Maximize the production of **C** subject to 95% conversion of **A**

$$\max c^h_{1,C}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -1 & 0 \\ 1 & -1 & 0 & -1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

	Rate Constants
k_1	1.0 L/(mol s) (second order)
k_2	0.6 s^{-1} (first order)
k_3	0.6 s^{-1} (first order)
k_4	0.1 L/(mol s) (second order)
	Feed Conditions
F_r^a	100 L/s pure **A**
$c_{r,i}^a$	6.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**, 0 mol/L **E**

Rate Expressions

$$\begin{aligned} f_1^r &= k_1 c_A^2 \\ f_2^r &= k_2 c_B \\ f_3^r &= k_3 c_A \\ f_4^r &= k_4 c_B^2 \end{aligned}$$

Additional Information

For this problem, two CSTRs and one CFR are considered. There is an additional constraint due to the requirement of 95% conversion of **A**:

$$c_{1,1}^h = 0.3\text{mol/L}$$

Problem Statistics

No. of continuous variables	111
No. of dynamic variables	19
No. of linear equalities	19
No. of linear inequalities	20
No. of nonlinear equalities	39
No. of point equalities	11
No. of dynamic equations	19

Best Known Solution

- Objective function: 3.539890 mol/L
- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.00 & F^{ac}_{r,k} = 13.4112 & F^{ad}_{r,l} = 86.5888, 0.00 \\
F^{b}_{k} = 0.00 & F^{c}_{k} = 95.0043 & F^{d}_{l} = 86.5888, 95.0043 \\
F^{e}_{k} = 95.0043 & F^{f}_{k} = 0.00 & F^{g}_{l} = 86.5888, 95.0043 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 0.00, 95.0043 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00, 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 81.5931, 0.00 & F^{gd}_{l,l'} = 0.00, 0.00 \\
F^{eh}_{k,p} = 0.00 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 4.99574, 95.0043 \\
F^{h}_{p} = 100.00 & &
\end{array}
$$

$$c^b_{k,i} = (6.00000, 0.000000, 0.000000, 0.000000, 0.000000)^T$$
$$c^c_{k,i} = (6.00000, 0.000000, 0.000000, 0.000000, 0.000000)^T$$

$$c^d_{l,i} = \begin{pmatrix} 6.00000 & 0.000000 & 0.000000 & 0.000000 & 0.0000 \\ 0.7994710 & 2.527592 & 1.199291 & 0.9305851 & 0.5430603 \end{pmatrix}$$

$$c^e_{k,i} = (0.799471, 2.52759, 1.19929, 0.930585, 0.543060)^T$$
$$c^f_{k,i} = (6.00000, 0.00000, 0.00000, 0.000000, 0.000000)^T$$
$$c^g_{l,i} = (6.00000, 0.00000, 0.00000, 0.000000, 0.000000)^T$$
$$c^g_{l,i} = (0.000269045, 0.000850987, 3.72603, 1.72943, 0.543419)^T$$
$$c^h_{p,i} = (0.300000, 0.000808474, 3.53989, 1.643031, 0.516271)^T$$
$$V^m_l = 0.00, 470143 \quad V^t_k = 73.5632$$

$$r^m_{l,j} = \begin{pmatrix} 36.000 & 0.0000 & 3.6000 & 0.0000 \\ 7.2385 \times 10^{-8} & 0.00051059 & 0.00016143 & 7.2418^{-8} \end{pmatrix}$$

$$\kappa^s_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$
$$\kappa^o_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

15.2.14 Test Problem 9 : Isothermal Levenspiel Reaction

Problem Information

Reaction Mechanism

$$\mathbf{A} + \mathbf{B} \xrightarrow{\mathbf{k}} \mathbf{2B}$$

Objective:

Maximize the production of **B**

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$$

Rate Constants	
k_1	1.0 L/(mol s) (second order)
Rate Constants	
F_r^a	100 L/s
$c_{r,i}^a$	0.45 mol/L **A**, 0.55 mol/L **B**

Rate Expression

$$f_1^r = k_1 c_A c_B$$

Additional Information

The reactor volume is bounded below 100 L.

Problem Statistics

No. of continuous variables	61
No. of dynamic variables	10
No. of linear equalities	12
No. of linear inequalities	20
No. of nonlinear equalities	11
No. of point equalities	5
No. of dynamic equations	10

Best Known Solution

- Objective function: 0.7686438 mol/L
- Variables

$$\begin{array}{lll}
F_{r,k}^{ab} = 0.00 & F_{r,k}^{ac} = 100.000 & F_{r,l}^{ad} = 0.00 \\
F_k^b = 0.00 & F_k^c = 100.000 & F_l^d = 0.00 \\
F_k^e = 100.000 & F_k^f = 0.00 & F_l^g = 0.00 \\
F_{k,k'}^{eb} = 0.00 & F_{k,k'}^{ec} = 0.00 & F_{k,l}^{ed} = 0.00 \\
F_{k,k'}^{fb} = 0.00 & F_{k,k'}^{fc} = 0.00 & F_{k,l}^{fd} = 0.00 \\
F_{l,k}^{gb} = 0.00 & F_{l,k}^{gc} = 0.00 & F_{l,l'}^{gd} = 0.00 \\
F_{k,p}^{eh} = 100.000 & F_{k,p}^{fh} = 0.00 & F_{l,p}^{gh} = 0.00 \\
F_p^h = 100.000 & &
\end{array}$$

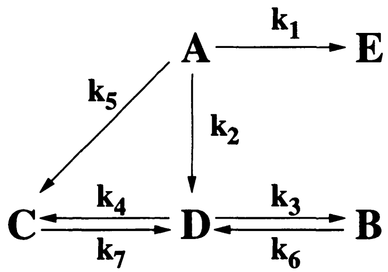
$$\begin{aligned}
c_{k,i}^b &= (0.450000, 0.550000)^T \\
c_{k,i}^c &= (0.450000, 0.550000)^T \\
c_{l,i}^d &= (0.450000, 0.550000)^T \\
c_{k,i}^e &= (0.231356, 0.768644)^T \\
c_{k,i}^f &= (0.450000, 0.550000)^T \\
c_{l,i}^g &= (0.450000, 0.550000)^T \\
c_{p,i}^h &= (0.231356, 0.768644)^T
\end{aligned}$$

$$V_l^m = 0.00 \quad V_k^t = 100.000 \quad r_{l,j}^m = (0.229493)^T$$
$$\kappa_{k,m}^s = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$
$$\kappa_{k,m}^o = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

15.2.15 Test Problem 10 : α-Pinene Reaction

Problem Information

Reaction Mechanism



Objective:

Maximize the selectivity of **C** to **D**

$$\max \frac{c_{1,C}^h}{c_{1,D}^h}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & -1 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & -1 \\ 0 & 1 & -1 & -2 & 0 & 1 & 2 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Rate Constants	
k_1	0.33384 s^{-1} (first order)
k_2	0.26687 s^{-1} (first order)
k_3	0.14940 s^{-1} (second order)
k_4	0.18957 L/(mol s) (second order)
k_5	0.009598 L/(mol s) (second order)
k_6	0.29425 s^{-1} (second order)
k_7	0.011932 s^{-1} (second order)
Feed Conditions	
F_r^a	100 L/s pure **A**
$c_{r,i}^a$	1.00 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**, 0 mol/L **D**, 0 mol/L **E**

Rate Expressions

$$
\begin{aligned}
f_1^r &= k_1 c_A \\
f_2^r &= k_2 c_A \\
f_3^r &= k_3 c_D \\
f_4^r &= k_4 c_D^2 \\
f_5^r &= k_5 c_A^2 \\
f_6^r &= k_6 c_B \\
f_7^r &= k_7 c_C
\end{aligned}
$$

Additional Information

The sum of the reactor volumes is bounded below 6000 L.

Problem Statistics

No. of continuous variables	88
No. of dynamic variables	22
No. of linear equalities	16
No. of linear inequalities	21
No. of nonlinear equalities	27
No. of point equalities	11
No. of dynamic equations	22

Best Known Solution

- Objective function: 1.557033
- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.00 & F^{ac}_{r,k} = 10.2219 & F^{ad}_{r,l} = 89.7781 \\
F^{b}_{k} = 0.00 & F^{c}_{k} = 10.2219 & F^{d}_{l} = 89.7781 \\
F^{e}_{k} = 10.2219 & F^{f}_{k} = 0.00 & F^{g}_{l} = 89.7781 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 0.00 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 0.00 & F^{gd}_{l,l'} = 0.00 \\
F^{eh}_{k,p} = 10.2219 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 89.7781 \\
F^{h}_{p} = 100.000 & &
\end{array}
$$

$$
\begin{aligned}
c^b_{k,i} &= (1.000000, 0.000000, 0.000000, 0.000000, 0.000000)^T \\
c^c_{k,i} &= (1.000000, 0.000000, 0.000000, 0.000000, 0.000000)^T \\
c^d_{l,i} &= (1.000000, 0.000000, 0.000000, 0.000000, 0.000000)^T \\
c^e_{k,i} &= (0.000000, 0.0497595, 0.152595, 0.0980035, 0.547048)^T \\
c^f_{k,i} &= (1.000000, 0.000000, 0.000000, 0.000000, 0.000000)^T \\
c^g_{l,i} &= (1.000000, 0.000000, 0.000000, 0.000000, 0.000000)^T \\
c^h_{p,i} &= (0.897781, 0.00508637, 0.0155981, 0.0100178, 0.0559187)^T
\end{aligned}
$$

$$V_l^m = 0.00 \quad V_k^t = 6000.00$$

$$r_{l,j}^m = (0.33384, 0.26687, 0.0000, 0.0000, 0.0095980, 0.0000, 0.0000)^T$$
$$\kappa_{k,m}^s = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$
$$\kappa_{k,m}^o = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

15.2.16 Test Problem 11 : Nonisothermal Van de Vusse Reaction Case II

Problem Information

Reaction Mechanism

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$

$$\mathbf{2A} \xrightarrow{\mathbf{k_3}} \mathbf{D}$$

Objective:

Maximize the yield of **B**

$$\max c_{1,B}^h$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	5.4×10^9 h^{-1}	15.84 kcal/mol	84 K L/mol
2	3.6×10^5 h^{-1}	7.92 kcal/mol	108 K L/mol
3	1.6×10^{12} L/(mol h)	23.76 kcal/mol	60 K L/mol
Feed Conditions			
F_r^a	100 L/s		
$c_{r,i}^a$	1.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**		

Rate Expressions

$$f_1^r = \hat{k}_1 e^{\frac{-E_1}{RT}} c_A$$
$$f_2^r = \hat{k}_2 e^{\frac{-E_2}{RT}} c_B$$
$$f_3^r = \hat{k}_3 e^{\frac{-E_3}{RT}} c_A^2$$

Additional Information

The temperatures in the reactors are bounded between 450 K and 810 K.

Problem Statistics

No. of continuous variables	100
No. of dynamic variables	18
No. of linear equalities	20
No. of linear inequalities	20
No. of nonlinear equalities	23
No. of point equalities	9
No. of dynamic equations	18

Best Known Solution

- Objective function: 0.8229079 mol/L

- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.00 & F^{ac}_{r,k} = 0.00 & F^{ad}_{r,l} = 100.000 \\
F^{b}_{k} = 0.00 & F^{c}_{k} = 100.000 & F^{d}_{l} = 100.000 \\
F^{e}_{k} = 100.000 & F^{f}_{k} = 0.00 & F^{g}_{l} = 100.000 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 0.00 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 100.00 & F^{gd}_{l,l'} = 0.00 \\
F^{eh}_{k,p} = 100.000 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 0.00 \\
F^{h}_{p} = 100.000 & &
\end{array}
$$

$$
\begin{aligned}
c^{b}_{k,i} &= (1.000000, 0.000000, 0.000000, 0.000000)^T \\
c^{c}_{k,i} &= (0.931253, 0.0640282, 0.00227142, 0.00122377)^T \\
c^{d}_{l,i} &= (1.000000, 0.000000, 0.000000, 0.000000)^T \\
c^{e}_{k,i} &= (0.00831126, 0.822908, 0.0794098, 0.0446855)^T \\
c^{f}_{k,i} &= (1.000000, 0.000000, 0.000000, 0.000000)^T \\
c^{g}_{l,i} &= (0.931253, 0.0640282, 0.00227142, 0.00122377)^T \\
c^{h}_{p,i} &= (0.00831126, 0.822908, 0.0794098, 0.0446855)^T
\end{aligned}
$$

$$V^{m}_{l} = 0.0736545 \quad V^{t}_{k} = 0.0807310$$

$$T^{m}_{l} = 446.889$$

$$r^{m}_{l,j} = (90.0143, 3.08389, 3.32300)^T$$

$$\kappa^{s}_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

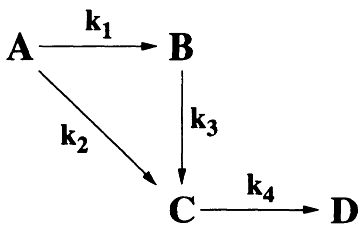
$$\kappa^o_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa^t_{k,m,i} = \begin{pmatrix} 479.235 & 481.342 \\ 483.339 & 485.439 \\ 487.856 & 490.382 \\ 492.812 & 495.611 \\ 499.249 & 502.868 \\ 505.612 & 509.531 \\ 516.674 & 523.016 \\ 524.534 & 530.571 \\ 550.471 & 565.379 \\ 556.442 & 609.401 \\ 810.000 & 800.000 \end{pmatrix}$$

15.2.17 Test Problem 12 : Nonisothermal Naphthalene Reaction

Problem Information

Reaction Mechanism



Objective:
Maximize the yield of **B**

$$\max c^h_{1,B}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 1 & -1 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	2.0×10^{13} h^{-1}	38.00 kcal/mol	364 K L/mol
2	2.0×10^{13} h^{-1}	38.00 kcal/mol	129 K L/mol
3	8.15×10^{17} h^{-1}	50.00 kcal/mol	108 K L/mol
4	2.1×10^{5} h^{-1}	20.00 kcal/mol	222 K L/mol
Feed Conditions			
F_r^a	100 L/h		
$c_{r,i}^a$	1.0 mol/L **A**, 0 mol/L **B**, 0 mol/L **C**		

Rate Expressions

$$f_1^r = \hat{k}_1 e^{\frac{-E_1}{RT}} c_A$$
$$f_2^r = \hat{k}_2 e^{\frac{-E_2}{RT}} c_A$$
$$f_3^r = \hat{k}_3 e^{\frac{-E_3}{RT}} c_B$$
$$f_4^r = \hat{k}_4 e^{\frac{-E_4}{RT}} c_C$$

Additional Information

The temperatures in the reactors are bounded between 900 K and 1500 K.

Problem Statistics

No. of continuous variables	101
No. of dynamic variables	19
No. of linear equalities	20
No. of linear inequalities	20
No. of nonlinear equalities	24
No. of point equalities	9
No. of dynamic equations	19

Best Known Solution

- Objective function: 0.9999585 mol/L
- Variables

$$F_{r,k}^{ab} = 0.00 \quad F_{r,k}^{ac} = 100.000 \quad F_{r,l}^{ad} = 0.00$$
$$F_k^{b} = 0.00 \quad F_k^{c} = 100.000 \quad F_l^{d} = 0.00$$
$$F_k^{e} = 100.000 \quad F_k^{f} = 0.00 \quad F_l^{g} = 0.00$$
$$F_{k,k'}^{eb} = 0.00 \quad F_{k,k'}^{ec} = 0.00 \quad F_{k,l}^{ed} = 0.00$$
$$F_{k,k'}^{fb} = 0.00 \quad F_{k,k'}^{fc} = 0.00 \quad F_{k,l}^{fd} = 0.00$$
$$F_{l,k}^{gb} = 0.00 \quad F_{l,k}^{gc} = 0.00 \quad F_{l,l'}^{gd} = 0.00$$
$$F_{k,p}^{eh} = 100.000 \quad F_{k,p}^{fh} = 0.00 \quad F_{l,p}^{gh} = 0.00$$
$$F_p^{h} = 100.00$$

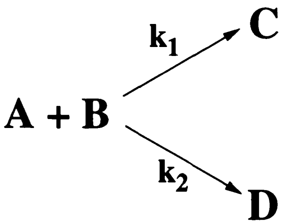
$$c^b_{k,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T$$
$$c^c_{k,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T$$
$$c^d_{l,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T$$
$$c^e_{k,i} = (3.22531 \times 10^{-6}, 4.96095 \times 10^{-8}, 0.999959, 3.82322 \times 10^{-5})^T$$
$$c^f_{k,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T$$
$$c^g_{l,i} = (1.000000, 0.000000, 0.000000, 0.000000)^T$$
$$c^h_{p,i} = (3.22531 \times 10^{-6}, 4.96095 \times 10^{-8}, 0.999959, 3.82322 \times 10^{-5})^T$$
$$V^m_l = 0.00 \quad V^t_k = 0.000189577 \quad T^m_l = 900.000$$
$$r^m_{l,j} = (0.00, 0.00, 0.00)^T$$
$$\kappa^s_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$
$$\kappa^o_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa^t_{k,m,i} = \begin{pmatrix} 900.000 & 900.000 \\ 1242.86 & 1500.00 \\ 1242.86 & 900.000 \\ 900.000 & 1008.96 \\ 992.983 & 930.514 \\ 900.000 & 900.000 \\ 929.074 & 952.697 \\ 936.343 & 909.086 \\ 900.000 & 900.000 \\ 900.000 & 900.000 \\ 900.000 & 900.000 \end{pmatrix}$$

15.2.18 Test Problem 13 : Nonisothermal Parallel Reactions

Problem Information

Reaction Mechanism



Objective:

Maximize the yield of **C** while minimizing the volume of the reactor

$$\max 100 c^h_{1,C} - \sum_{l \in L} v^m_l$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & -1 \\ -1 & -1 \\ 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	5.4×10^7	19.138 kcal/mol	10 K L/mol
2	3.6×10^5	9.569 kcal/mol	20 K L/mol
Feed Conditions			
F_1^a	50 L/s pure **A**		
F_2^a	50 L/s pure **B**		
$c_{1,i}^a$	1.0 mol/L **A**, 0 mol/L **B**		
$c_{2,i}^a$	0 mol/L **A**, 1.0 mol/L **B**		

Rate Expressions

$$f_1^r = \hat{k}_1 e^{\frac{-E_1}{RT}} c_A c_B^{0.3}$$
$$f_2^r = \hat{k}_2 e^{\frac{-E_2}{RT}} c_A^{0.5} c_B^{1.8}$$

Additional Information

The temperatures in the reactors are bounded between 450 K and 800 K.

Problem Statistics

No. of continuous variables	102
No. of dynamic variables	17
No. of linear equalities	21
No. of linear inequalities	20
No. of nonlinear equalities	22
No. of point equalities	9
No. of dynamic equations	17

Best Known Solution

- Objective function: 44.78686
- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.0, 49.0076 & F^{ac}_{r,k} = 50.0, 0.992433 & F^{ad}_{r,l} = 0.0, 0.0 \\
F^{b}_{k} = 49.0076 & F^{c}_{k} = 50.9924 & F^{d}_{l} = 0.00 \\
F^{e}_{k} = 100.000 & F^{f}_{k} = 0.00 & F^{g}_{l} = 0.00 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 0.00 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 0.00 & F^{gd}_{l,l'} = 0.00 \\
F^{eh}_{k,p} = 1000.00 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 0.00 \\
F^{h}_{p} = 1000.00 & &
\end{array}
$$

$$
\begin{aligned}
c^{b}_{k,i} &= (0.000000, 1.000000, 0.000000, 0.000000)^T \\
c^{c}_{k,i} &= (0.980538, 0.0194624, 0.000000, 0.000000)^T \\
c^{d}_{l,i} &= (0.500000, 0.500000, 0.000000, 0.000000)^T \\
c^{e}_{k,i} &= (0.0119436, 0.0119435, 0.481617, 0.00643913)^T \\
c^{f}_{k,i} &= (0.500000, 0.500000, 0.000000, 0.000000)^T \\
c^{g}_{l,i} &= (0.500000, 0.500000, 0.000000, 0.000000)^T \\
c^{h}_{p,i} &= (0.0119436, 0.0119435, 0.481617, 0.00643913)^T
\end{aligned}
$$

$$V^{m}_{l} = 0.00 \quad V^{t}_{k} = 3.37487$$

$$
\begin{aligned}
T^{m}_{l} &= 800.0 \\
r^{m}_{l,j} &= (0.000332841, 0.135224)^T \\
\kappa^{s}_{k,m} &= (49.0076, 30.8666, 20.3423, 13.4839, 8.72020, 5.25364 \\
&\quad 2.73586, 0.268785, 0.00, 0.00, 0.00)^T \\
\kappa^{o}_{k,m} &= (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T
\end{aligned}
$$

$$
\kappa^{t}_{k,m,i} = \begin{pmatrix}
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000 \\
800.000 & 800.000
\end{pmatrix}
$$

15.2.19 Test Problem 14 : Sulfur Dioxide Oxidation

Problem Information

Reaction Mechanism

$$SO_2 + \frac{1}{2} O_2 \rightleftharpoons SO_3$$

Species 1 is SO_2, species 2 is O_2, species 3 is SO_3, and species 4 is N_2.

Objective:
Maximize the yield of SO_3

$$\max c_{1,3}^{h}$$

Parameters

$$\nu_{i,j} = \begin{bmatrix} -1 & 1 \\ -0.5 & 0.5 \\ 1 & -1 \\ 0 & 0 \end{bmatrix}$$

Rate Constants			
reaction	$\hat{k}$	E	$\frac{\Delta H}{\rho C_p}$
1	6.284×10^{11} mol/(hr kgcat)	15.500 kcal/mol	96.5 K kg/mol
2	2.732×10^{16} mol/(hr kgcat)	26.7995 kcal/mol	96.5 K kg/mol
Feed Conditions			
F_r^a	7731 kg/h		
$c_{r,i}^a$	2.5 mol/kg $\mathbf{SO_2}$, 3.46 mol/kg $\mathbf{O_2}$, 0 mol/kg $\mathbf{SO_3}$, 26.05 mol/kg $\mathbf{N_2}$		

Rate Expressions
The rates are given in terms of kg mol SO_3 per kg catalyst.

$$r_1 = \hat{k}_1 e^{\frac{-E_1}{T}} \frac{(c_{l,1}^g)^{0.5} c_{l,2}^g}{\left(\sum_{i \in I} c_{l,i}^g\right)^{1.5}}$$

$$r_2 = \hat{k}_2 e^{\frac{-E_2}{T}} \frac{(c_{l,2}^g)^{0.5} c_{l,3}^g}{(c_{l,1}^g)^{0.5} \left(\sum_{i \in I} c_{l,i}^g\right)}$$

Additional Information
The temperatures in the reactors are bounded between 300 K and 1200 K and the size of the reactor bounded below 50000 kg of catalyst.

Problem Statistics

No. of continuous variables	99
No. of dynamic variables	17
No. of linear equalities	21
No. of linear inequalities	20
No. of nonlinear equalities	22
No. of point equalities	9
No. of dynamic equations	17

Best Known Solution

- Objective function: 2.497518 mol/kg
- Variables

$$
\begin{array}{lll}
F^{ab}_{r,k} = 0.000 & F^{ac}_{r,k} = 7731.00 & F^{ad}_{r,l} = 0.00 \\
F^{b}_{k} = 0.00 & F^{c}_{k} = 100.000 & F^{d}_{l} = 0.00 \\
F^{e}_{k} = 7731.00 & F^{f}_{k} = 0.0000 & F^{g}_{l} = 0.00 \\
F^{eb}_{k,k'} = 0.00 & F^{ec}_{k,k'} = 0.00 & F^{ed}_{k,l} = 0.00 \\
F^{fb}_{k,k'} = 0.00 & F^{fc}_{k,k'} = 0.00 & F^{fd}_{k,l} = 0.00 \\
F^{gb}_{l,k} = 0.00 & F^{gc}_{l,k} = 0.00 & F^{gd}_{l,l'} = 0.00 \\
F^{eh}_{k,p} = 7731.00 & F^{fh}_{k,p} = 0.00 & F^{gh}_{l,p} = 0.00 \\
F^{h}_{p} = 7731.00 & &
\end{array}
$$

$$
\begin{aligned}
c^{b}_{k,i} &= (2.50000, 3.46000, 0.00000, 26.0500)^T \\
c^{c}_{k,i} &= (2.50000, 3.46000, 0.00000, 26.0500)^T \\
c^{d}_{l,i} &= (2.50000, 3.46000, 0.00000, 26.0500)^T \\
c^{e}_{k,i} &= (0.00248248, 2.21124, 2.49752, 26.0500)^T \\
c^{f}_{k,i} &= (2.50000, 3.46000, 0.00000, 26.0500)^T \\
c^{g}_{l,i} &= (2.50000, 3.46000, 0.00000, 26.0500)^T \\
c^{h}_{p,i} &= (0.00248248, 2.21124, 2.49752, 26.0500)^T
\end{aligned}
$$

$$V^m_l = 0.00 \quad V^t_k = 50000.0 \quad T^m_l = 1200.0$$

$$r^m_{l,j} = (0.00, 0.00)^T$$

$$\kappa^s_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$\kappa^o_{k,m} = (0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00)^T$$

$$
\kappa^t_{k,m,i} = \begin{pmatrix}
791.584 & 713.502 \\
673.290 & 654.609 \\
641.118 & 631.775 \\
625.537 & 620.599 \\
615.160 & 609.744 \\
604.874 & 601.064 \\
598.823 & 596.981 \\
594.365 & 591.607 \\
589.340 & 586.898 \\
583.615 & 581.643 \\
583.131 & 1200.00
\end{pmatrix}
$$

15.3 Parameter Estimation Problems

15.3.1 Introduction

The problem of estimating parameters in dynamic models is as important and even more difficult than with algebraic models. The extra difficulty arises from the inclusion of differential-algebraic equations in the optimization problem. This type of problem arises most often in the estimation of kinetic constants from time series data. The statistical approach used is similar to that presented for the algebraic problems in section 8.5, with the exception that all the variables receive an equal weighting in the objective function.

A general formulation of the problem will be presented where the only difference between examples is in the definition of the model equations. Next a set of example problems will be given. The first two problems represent rather simple models of irreversible and reversible first order series reactions. The next two problems add the difficulty of nonlinear reaction kinetics to the problem. The next problem combines the difficulties imposed by nonlinear kinetics with relatively large residuals at the solution. The final problem is the most difficult since the dynamic system exhibits a limit cycle and a large number of local minima have been identified.

15.3.2 General Formulation

Objective Function

$$\min_{\hat{\boldsymbol{x}}_\mu, \boldsymbol{\theta}} \sum_{\mu=1}^{r} \sum_{i=1}^{m} (\hat{x}_{\mu,i} - x_{\mu,i})^2$$

Constraints

Dynamic Model

$$\boldsymbol{f}(\frac{d\boldsymbol{z}}{dt}, \boldsymbol{z}, \boldsymbol{\theta}) = \boldsymbol{0} \qquad \boldsymbol{z}(t_o) = \boldsymbol{z}_o$$

Point constraints

$$@\ t = t_\mu \qquad z_i - \hat{x}_{\mu,i} = 0 \qquad i = 1, \ldots, m \qquad \mu = 1, \ldots, r$$

Variable Definitions

$\boldsymbol{f}$ is a system of l differential-algebraic functions which represent the nonlinear model, $\boldsymbol{z}$ is a vector of i dynamic variables, $\boldsymbol{\theta}$ is a vector of p parameters, and $\hat{\boldsymbol{x}}_\mu$ is a vector of i fitted data variables at the μ^{th} data point. $\boldsymbol{x}_\mu$ is a vector of i experimentally observed values at the μ^{th} data point, and $\boldsymbol{\sigma}$ is a vector of i values which represent the experimental standard deviation of these observations. $t \in (t_o, t_f)$ and t_μ is the time associated with the μ^{th} observation.

15.3.3 Test Problem 1

This model represents the first order irreversible chain reaction:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Only the concentrations of components A and B were measured, therefore component C does not appear in the model used for estimation. This model appears in Tjoa and Biegler (1991a).

Formulation

Objective Function

$$\min_{\hat{\boldsymbol{x}}_\mu, \boldsymbol{\theta}} \sum_{\mu=1}^{10} \sum_{i=1}^{2} (\hat{x}_{\mu,i} - x_{\mu,i})^2$$

Constraints

Dynamic Model

$$\begin{aligned} \frac{dz_1}{dt} &= -\theta_1 z_1 \\ \frac{dz_2}{dt} &= \theta_1 z_1 - \theta_2 z_2 \end{aligned}$$

Point constraints

$$@\ t = t_\mu \qquad z_i - \hat{x}_{\mu,i} = 0 \qquad i = 1,2 \quad \mu = 1,\ldots,10$$

Initial conditions

$$\boldsymbol{z}_o = (1,0)$$

Variable Bounds

$$\begin{aligned} 0 \le \hat{\boldsymbol{x}}_\mu \le 1 \\ 0 \le \boldsymbol{\theta} \le 10 \end{aligned}$$

Variable Definitions

z_1 and z_2 are the mole fractions of the components A and B respectively. θ_1 and θ_2 are the rate constants of the first and second reactions respectively.

Data

μ	1	2	3	4	5	6	7	8	9	10
t_μ	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
x_1	0.606	0.368	0.223	0.135	0.082	0.050	0.030	0.018	0.011	0.007
x_2	0.373	0.564	0.647	0.669	0.656	0.624	0.583	0.539	0.494	0.451

Problem Statistics

No. of continuous variables	2
No. of dynamic variables	2
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	2
No. of point constraints	20

Best Known Solution

- Objective Function: 1.18584×10^{-6}
- Parameters
  $\boldsymbol{\theta} = (5.0035, 1.0000)^T$
- Fitted Data Variables
  Matches data to the given precision

15.3.4 Test Problem 2

This model represents the first order reversible chain reaction:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C$$

This model appears in Tjoa and Biegler (1991a).

Formulation

Model

$$\begin{aligned}
\frac{dz_1}{dt} &= -\theta_1 z_1 + \theta_2 z_2 \\
\frac{dz_2}{dt} &= \theta_1 z_1 - (\theta_2 + \theta_3) z_2 + \theta_4 z_3 \\
\frac{dz_3}{dt} &= -\theta_4 z_3 + \theta_3 z_2
\end{aligned}$$

Initial conditions

$$\boldsymbol{z}_o = (1, 0, 0)$$

Variable Bounds

$$0 \leq \hat{\boldsymbol{x}}_\mu \leq 1$$
$$(0,0,10,10) \leq \boldsymbol{\theta} \leq (10,10,50,50)$$

Variable Definitions

z_1, z_2, and z_3 are the mole fractions of the components A, B, and C respectively. θ_1 and θ_3 are the rate constants of the first and second forward reactions, and θ_2 and θ_4 are the rate constants of the reverse reactions.

Data

μ	1	2	3	4	5	6	7
t_μ	0.05	0.1	0.15	0.2	0.25	0.3	0.35
$x_{\mu,1}$	0.8241	0.6852	0.5747	0.4867	0.4166	0.3608	0.3164
$x_{\mu,2}$	0.0937	0.1345	0.1654	0.1899	0.2094	0.2249	0.2373
$x_{\mu,3}$	0.0821	0.1802	0.2598	0.3233	0.3738	0.4141	0.4461
μ	8	9	10	11	12	13	14
t_μ	0.4	0.45	0.5	0.55	0.6	0.65	0.7
$x_{\mu,1}$	0.2810	0.2529	0.2304	0.2126	0.1984	0.1870	0.1870
$x_{\mu,2}$	0.2472	0.2550	0.2613	0.2662	0.2702	0.2733	0.2759
$x_{\mu,3}$	0.4717	0.4920	0.5082	0.5210	0.5313	0.5395	0.5460
μ	15	16	17	18	19	20	
t_μ	0.75	0.8	0.85	0.9	0.95	1.0	
$x_{\mu,1}$	0.1709	0.1651	0.1606	0.1570	0.1541	0.1518	
$x_{\mu,2}$	0.2779	0.2794	0.2807	0.2817	0.2825	0.2832	
$x_{\mu,3}$	0.5511	0.5553	0.5585	0.5612	0.5632	0.5649	

Problem Statistics

No. of continuous variables	4
No. of dynamic variables	3
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	3
No. of point constraints	60

Best Known Solution

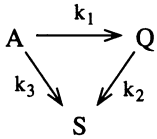
- Objective Function: 1.8897×10^{-7}
- Parameters

  $\boldsymbol{\theta} = (4.000, 2.000, 40.013, 20.007)^T$

- Fitted Data Variables
  Matches data to the given precision

15.3.5 Test Problem 3 : Catalytic Cracking of Gas Oil

This model represents the catalytic cracking of gas oil (A) to gasoline (Q) and other side products (S).



Only the concentrations of A and Q were measured, therefore the concentration of S does not appear in the model for estimation. This model appears in Tjoa and Biegler (1991a).

Formulation

Model

$$
\begin{aligned}
\frac{dz_1}{dt} &= -(\theta_1 + \theta_3)z_1^2 \\
\frac{dz_2}{dt} &= \theta_1 z_1^2 - \theta_2 z_2
\end{aligned}
$$

Initial conditions

$$\boldsymbol{z}_o = (1, 0)$$

Variable Bounds

$$
\begin{aligned}
0 \leq \hat{\boldsymbol{x}}_\mu \leq 1 \\
0 \leq \boldsymbol{\theta} \leq 20
\end{aligned}
$$

Variable Definitions

z_1 and z_2 are the mole fractions of the components A and Q respectively. θ_1, θ_2, and θ_3 are the rate constants of the respective reactions.

Data

μ	1	2	3	4	5	6	7
t_μ	0.025	0.05	0.075	0.10	0.125	0.150	0.175
$x_{\mu,1}$	0.7307	0.5982	0.4678	0.4267	0.3436	0.3126	0.2808
$x_{\mu,2}$	0.1954	0.2808	0.3175	0.3047	0.2991	0.2619	0.2391

μ	8	9	10	11	12	13	14
t_μ	0.20	0.225	0.250	0.30	0.35	0.40	0.45
$x_{\mu,1}$	0.2692	0.2210	0.2122	0.1903	0.1735	0.1615	0.1240
$x_{\mu,2}$	0.2210	0.1898	0.1801	0.1503	0.1030	0.0964	0.0581
μ	15	16	17	18	19	20	
t_μ	0.50	0.55	0.65	0.75	0.85	0.95	
$x_{\mu,1}$	0.1190	0.1109	0.0890	0.0820	0.0745	0.0639	
$x_{\mu,2}$	0.0471	0.0413	0.0367	0.0219	0.0124	0.0089	

Problem Statistics

No. of continuous variables	3
No. of dynamic variables	2
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	2
No. of point constraints	40

Best Known Solution

- Objective Function: 2.65567×10^{-3}
- Parameters
  $\boldsymbol{\theta} = (12.214, 7.9798, 2.2216)^T$
- Fitted Data Variables

μ	1	2	3	4	5	6	7
$\hat{x}_{\mu,1}$	0.7348	0.5808	0.4802	0.4093	0.3566	0.3159	0.2836
$\hat{x}_{\mu,2}$	0.2014	0.2822	0.3079	0.3064	0.2912	0.2696	0.2456

μ	8	9	10	11	12	13	14
$\hat{x}_{\mu,1}$	0.2573	0.2354	0.2170	0.1876	0.1652	0.1476	0.1334
$\hat{x}_{\mu,2}$	0.2213	0.1980	0.1763	0.1386	0.1085	0.0850	0.0669

μ	15	16	17	18	19	20
$\hat{x}_{\mu,1}$	0.1217	0.1119	0.0963	0.0846	0.0754	0.0680
$\hat{x}_{\mu,2}$	0.0530	0.0424	0.0280	0.0193	0.0140	0.0106

15.3.6 Test Problem 4 : Bellman's Problem

This problem describes a reversible homogeneous gas phase reaction of the form:

$$2NO + O_2 \rightleftharpoons 2NO_2$$

The model equation is the result of many normalizations. This model originally appeared in Bellman et al. (1967) as well as in Tjoa and Biegler (1991a) and Varah (1982).

Formulation

Model

$$\frac{dz}{dt} = \theta_1(126.2 - z)(91.9 - z)^2 - \theta_2 z^2$$

Initial conditions

$$z_o = 0$$

Variable Bounds

$$x_\mu - 5 \le \hat{x}_\mu \le x_\mu + 5$$
$$0 \le \boldsymbol{\theta} \le 0.1$$

Data

μ	1	2	3	4	5	6	7
t_μ	1.0	2.0	3.0	4.0	5.0	6.0	7.0
x_μ	1.4	6.3	10.4	14.2	17.6	21.4	23.0
μ	8	9	10	11	12	13	14
t_μ	9.0	11.0	14.0	19.0	24.0	29.0	39.0
x_μ	27.0	30.4	34.4	38.8	41.6	43.5	45.3

Problem Statistics

No. of continuous variables	2
No. of dynamic variables	1
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	1
No. of point constraints	14

Best Known Solution

- Objective Function: 22.03094
- Parameters
  $\boldsymbol{\theta} = (4.5704 \times 10^{-6}, 2.7845 \times 10^{-4})^T$

- Fitted Data Variables

μ	1	2	3	4	5	6	7
$\hat{x}_\mu$	4.54	8.51	12.01	15.12	17.89	20.38	22.62

μ	8	9	10	11	12	13	14
$\hat{x}_\mu$	26.49	29.69	33.55	38.18	41.32	43.49	46.07

15.3.7 Test Problem 5 : Methanol-to-Hydrocarbons Process

This model represents the conversion of methanol to various hydrocarbons. The simplified kinetic model used here is:

$$
\begin{aligned}
A &\xrightarrow{k_1} B \\
A+B &\xrightarrow{k_2} C \\
C+B &\xrightarrow{k_3} P \\
A &\xrightarrow{k_4} C \\
A &\xrightarrow{k_5} P \\
A+B &\xrightarrow{k_6} P
\end{aligned}
$$

In this model, A represents the oxygenates, B is $\ddot{C}H_2$, C is the olefins, and P denotes the paraffins, aromatics, and other products. The differential equation model is formulated under the assumption of simple kinetics and a quasi-steady state for the intermediate B. The model appears in Maria (1989).

Formulation

Model

$$
\begin{aligned}
\frac{dz_1}{dt} &= -\left(2\theta_1 - \frac{\theta_1 z_2}{(\theta_2+\theta_5)z_1 + z_2} + \theta_3 + \theta_4\right) z_1 \\
\frac{dz_2}{dt} &= \frac{\theta_1 z_1(\theta_2 z_1 - z_2)}{(\theta_2+\theta_5)z_1 + z_2} + \theta_3 z_1 \\
\frac{dz_3}{dt} &= \frac{\theta_1 z_1(z_2 + \theta_5 z_1)}{(\theta_2+\theta_5)z_1 + z_2} + \theta_4 z_1
\end{aligned}
$$

Initial conditions

$$\boldsymbol{z}_o = (1,0,0)$$

Variable Bounds

$$
\begin{aligned}
0 \le \hat{\boldsymbol{x}}_\mu \le 1 \\
0 \le \boldsymbol{\theta} \le 100
\end{aligned}
$$

Variable Definitions

z_1, z_2, and z_3 are the mole fractions of the components A, C, and P respectively. The parameter vector $\boldsymbol{\theta}$ is defined as:

$$\boldsymbol{\theta} \equiv (k_1, \frac{k_2}{k_3}, k_4, k_5, \frac{k_6}{k_3})$$

Data

μ	1	2	3	4	5	6	7	8
t_μ	0.050	0.065	0.080	0.123	0.233	0.273	0.354	0.397
$x_{\mu,1}$	0.461	0.426	0.383	0.305	0.195	0.170	0.139	0.112
$x_{\mu,2}$	0.114	0.135	0.157	0.194	0.231	0.234	0.228	0.228
$x_{\mu,3}$	0.018	0.035	0.045	0.047	0.084	0.095	0.111	0.134
μ	9	10	11	12	13	14	15	16
t_μ	0.418	0.502	0.553	0.681	0.750	0.916	0.937	1.122
$x_{\mu,1}$	0.112	0.090	0.082	0.066	0.053	0.043	0.041	0.029
$x_{\mu,2}$	0.226	0.220	0.214	0.178	0.188	0.183	0.184	0.166
$x_{\mu,3}$	0.168	0.148	0.157	0.206	0.206	0.214	0.213	0.230

Problem Statistics

No. of continuous variables	5
No. of dynamic variables	3
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	3
No. of point constraints	48

Best Known Solution

- Objective Function: 0.10693
- Parameters
  $\boldsymbol{\theta} = (5.2407, 1.2176, 0, 0, 0)^T$
- Fitted Data Variables

μ	1	2	3	4	5	6	7	8
$\hat{x}_{\mu,1}$	0.607	0.528	0.460	0.316	0.133	0.100	0.058	0.044
$\hat{x}_{\mu,2}$	0.169	0.195	0.214	0.243	0.246	0.240	0.226	0.220
$\hat{x}_{\mu,3}$	0.018	0.028	0.037	0.066	0.125	0.140	0.163	0.172

μ	9	10	11	12	13	14	15	16
$\hat{x}_{\mu,1}$	0.039	0.023	0.017	0.008	0.006	0.002	0.002	0.000
$\hat{x}_{\mu,2}$	0.217	0.207	0.203	0.196	0.194	0.191	0.190	0.189
$\hat{x}_{\mu,3}$	0.176	0.187	0.192	0.200	0.202	0.205	0.206	0.207

15.3.8 Test Problem 6 : Lotka-Volterra Problem

This problem involves a two parameter predator-prey model similar to those used in ecology. The model determines the population over time of the two different species (the predators, and the prey) given parameters relating to the interaction between them. The state profiles at the solution are cyclic and out of phase with each other. The parameter estimation problem in this model was studied by Luus (1998).

Formulation

Model

$$\begin{aligned} \frac{dz_1}{dt} &= \theta_1 z_1 (1 - z_2) \\ \frac{dz_2}{dt} &= \theta_2 z_2 (z_1 - 1) \end{aligned}$$

Initial conditions

$$\boldsymbol{z}_o = (1.2, 1.1)$$

Variable Bounds

$$\begin{aligned} 0.5 \leq \hat{\boldsymbol{x}}_\mu \leq 1.5 \\ 0 \leq \boldsymbol{\theta} \leq 10 \end{aligned}$$

Variable Definitions

z_1 represents the population of the prey, and z_2 the population of the predator. The parameters $\boldsymbol{\theta}$ are related to the birth, death, and interaction rates of the two species.

Data

μ	1	2	3	4	5
t_μ	1	2	3	4	5
$x_{\mu,1}$	0.7990	0.8731	1.2487	1.0362	0.7483
$x_{\mu,2}$	1.0758	0.8711	0.9393	1.1468	1.0027

μ	6	7	8	9	10
t_μ	6	7	8	9	10
$x_{\mu,1}$	1.0024	1.2816	0.8944	0.7852	1.1527
$x_{\mu,2}$	0.8577	1.0274	1.1369	0.9325	0.9074

Problem Statistics

No. of continuous variables	2
No. of dynamic variables	2
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	2
No. of point constraints	20
No. of known solutions	23

Best Known Solution

- Objective Function: 1.24924×10^{-3}
- Parameters
  $\boldsymbol{\theta} = (3.2434, 0.9209)^T$
- Fitted Data Variables

μ	1	2	3	4	5
$\hat{x}_{\mu,1}$	0.7980	0.8643	1.2538	1.0385	0.7608
$\hat{x}_{\mu,2}$	1.0794	0.8876	0.9402	1.1443	1.0032

μ	6	7	8	9	10
$\hat{x}_{\mu,1}$	0.9976	1.2785	0.8841	0.7907	1.1515
$\hat{x}_{\mu,2}$	0.8670	1.0282	1.1288	0.9315	0.8883

15.4 Optimal Control Problems

15.4.1 Introduction

Optimal Control problems arise often in many different fields in the engineering and sciences. This class of problems has been well studied from both theoretical and computational perspectives. The books by Hager and Pardalos (1998), Polak (1997, 1971), Dontchev (1983), Alekseev et al. (1987), and Bryson and Ho (1988) offer the reader a sample of the available material. Examples taken from the chemical engineering field, include such problems as the temperature control of a batch or plug flow reactor system, or the optimal catalyst mix in a tubular reactor. The models used to describe these types of systems are almost always nonlinear in nature. This often results in the existence of multiple local minima in the area of interest.

All of the example problems which follow exhibit at least two local minima. The first is a simple single differential equation model with constant control and the minimization of a concave objective function. The second problem adds the difficulty of a time varying control, while the third, which deals with the control of a CSTR, adds a very nonlinear differential algebraic system. The fourth problem is not only an optimal temperature control problem in a PFR, but also a design problem since the size of the reactor is also an optimization variable. The final example, the bifunctional catalyst problem, is the most challenging since it has been shown to contain well over 100 local minima. Additional difficulty arises from the small separation, on the order of 10^{-5}, between many of the local minima.

15.4.2 Test Problem 1

This example is of a simple control problem with one state and one control variable.

Formulation

Objective function

$$\min_{u} -z(t_f)^2$$

Constraints

$$\frac{dz}{dt} = -z^2 + u$$

Initial Conditions

$$z(t_o) = 9$$

Control

u is a constant over the whole time horizon.

Variable bounds

$$\begin{array}{c} -5 \le u \le 5 \\ -12 \le z \le 9 \\ t \in [0, 1] \end{array}$$

Problem Statistics

No. of continuous variables	1
No. of dynamic variables	1
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	1
No. of known solutions	2

Best Known Solution

- Objective function: -8.23623

- Control variable
  $u = -5$

15.4.3 Test Problem 2 : Singular Control Problem

This example represents a nonlinear singular control problem and appears in Luus (1990b) as well as in Rosen and Luus (1992).

Formulation

Objective function

$$\min_{\boldsymbol{w}} \; z_4(t_f)$$

Constraints

$$\begin{aligned}
\frac{dz_1}{dt} &= z_2 \\
\frac{dz_2}{dt} &= -z_3 u + 16t - 8 \\
\frac{dz_3}{dt} &= u \\
\frac{dz_4}{dt} &= z_1^2 + z_2^2 + 0.0005\left(z_2 + 16t - 8 - 0.1 z_3 u^2\right)^2
\end{aligned}$$

Initial Conditions

$$z(t_o) = (0, -1, -\sqrt{5}, 0)$$

Control

u is piecewise constant over 10 intervals:
$u \;=\; w_i \quad$ for $\quad t_i \leq t < t_{i+1}$
$t_i = (0,\ 0.1,\ 0.2,\ 0.3,\ 0.4,\ 0.5,\ 0.6,\ 0.7,\ 0.8,\ 0.9,\ 1)$

Variable bounds

$$-4 \leq \boldsymbol{w} \leq 10$$
$$t \in [0, 1]$$

Problem Statistics

No. of continuous variables	10
No. of dynamic variables	4
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	4
No. of known solutions	2

Best Known Solution

- Objective function: 0.120114
- Control variables
  $\boldsymbol{w} = (10, 7.728, 5.266, -0.764, 0.132, 0.133, -0.835, 6.764, 6.221, 5.414)$

15.4.4 Test Problem 3 : CSTR Problem

This example represents a continuous stirred tank reactor model and appears in Luus (1990b).

Formulation

Objective function

$$\min_{\boldsymbol{w}} \; z_3(t_f)$$

Constraints

$$\begin{aligned}
\frac{dz_1}{dt} &= -(z_1 + 0.25) + (z_2 + 0.5)\exp\left[\frac{25z_1}{z_1+2}\right] - (1+u)(z_1 + 0.25) \\
\frac{dz_2}{dt} &= 0.5 - z_2 - (z_2 + 0.5)\exp\left[\frac{25z_1}{z_1+2}\right] \\
\frac{dz_3}{dt} &= z_1^2 + z_2^2 + 0.1u^2
\end{aligned}$$

Initial Conditions

$$z(t_o) = (0.09, 0.09, 0)$$

Control

u is piecewise linear over 10 intervals:
$u \;=\; w_i + \frac{w_{i+1}-w_i}{t_{i+1}-t_i}(t - t_i) \quad \text{for} \quad t_i \leq t < t_{i+1}$

$t_i = (0, 0.078, 0.156, 0.234, 0.312, 0.39, 0.468, 0.546, 0.624, 0.702, 0.78)$

Variable bounds

$$-0.5 \leq \boldsymbol{w} \leq 5$$
$$t \in [0, 0.78]$$

Variable Definitions

z_1 represents the deviation from the dimensionless steady-state temperature, z_2 the deviation from the dimensionless steady-state concentration, and u is the scaled coolant flowrate.

Problem Statistics

No. of continuous variables	11
No. of dynamic variables	3
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	3
No. of known solutions	2

Best Known Solution

- Objective function: 0.13317
- Control variables

$\boldsymbol{w} = (4.27, 2.22, 1.38, 0.887, 0.584, 0.379, 0.237, 0.137, 0.068, 0.023, -0.002)$

15.4.5 Test Problem 4 : Oil Shale Pyrolysis

This model describes the determination of the optimal temperature profile and residence time for the following reaction system:

$$\begin{aligned}
A_1 &\xrightarrow{k_1} A_2 \\
A_2 &\xrightarrow{k_2} A_3 \\
A_1 + A_2 &\xrightarrow{k_3} A_2 + A_2 \\
A_1 + A_2 &\xrightarrow{k_4} A_3 + A_2 \\
A_1 + A_2 &\xrightarrow{k_5} A_4 + A_2
\end{aligned}$$

Only components A_1 and A_2 are included in the model. This example was studied by Luus (1990b); Rosen and Luus (1992); Carrasco and Banga (1997).

Formulation

Objective function

$$\min_{w,p} \; -z_2(t_f)$$

Constraints

$$\begin{aligned}
\frac{dz_1}{dt} &= -p\left(k_1 z_1 + k_3 z_1 z_2 + k_4 z_1 z_2 + k_5 z_1 z_2\right) \\
\frac{dz_2}{dt} &= p\left(k_1 z_1 - k_2 z_2 + k_3 z_1 z_2\right) \\
k_i &= a_i \exp\left[\frac{-b_i}{Ru}\right] \qquad \forall i = 1 \ldots 5
\end{aligned}$$

Initial Conditions

$$z(t_o) = (1, 0)$$

Control

u is piecewise constant over 10 intervals:

$u = w_i$ for $t_i \le t < t_{i+1}$

$t_i = (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1)$

Variable bounds

$$\begin{aligned}
698.15 \le \boldsymbol{w} \le 748.15 \\
7 \le p \le 11 \\
t \in [0, 1]
\end{aligned}$$

Variable Definitions

z_1 and z_2 are the mole fractions of components A_1 and A_2 respectively. The control u is the temperature of the reactor, and p is the residence time. a_i and b_i are the Arrhenius constants for reaction i.

Data

$\ln a_i = (8.86,\ 24.25,\ 23.67,\ 18.75,\ 20.70)$

$b_i/R = (10215.4,\ 18820.5,\ 17008.9,\ 14190.8,\ 15599.8)$

Problem Statistics

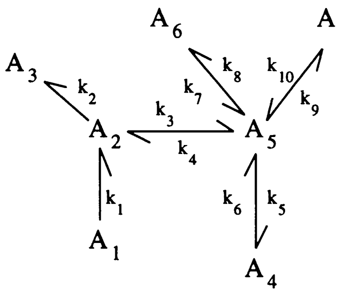
No. of continuous variables	12
No. of dynamic variables	7
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	7
No. of known solutions	5

Best Known Solution

- Objective function: -0.353606
- Residence time: $p = 8.3501$
- Control variables
  $w =$ (698.15, 698.15, 698.15, 748.15, 748.15, 699.20, 698.15, 698.15, 698.15, 698.15)

15.4.6 Test Problem 5 : Bifunctional Catalyst Blend Problem

This example concerns the optimization of a bifunctional catalyst in converting methylcyclopentane to benzene. The catalyst contains a hydrogenation component and a isomerization component. The object is to determine the mixture of the two along the length of the reactor which maximizes the concentration of the desired product, A_7, in the following reaction scheme:



This problem has been studied by Luus et al. (1992), Bojkov and Luus (1993), and Luus and Bojkov (1994). Even though this example is relatively small (7 states and 1 control), it has been shown to exhibit a very large number of local minima.

Formulation

Objective function

$$\min_{w} \; -z_7(t_f)$$

Constraints

$$
\begin{aligned}
\frac{dz_1}{dt} &= -k_1 z_1 \\
\frac{dz_2}{dt} &= k_1 z_1 - (k_2 + k_3) z_2 + k_4 z_5 \\
\frac{dz_3}{dt} &= k_2 z_2 \\
\frac{dz_4}{dt} &= -k_6 z_4 + k_5 z_5 \\
\frac{dz_5}{dt} &= k_3 z_2 + k_6 z_4 - (k_4 + k_5 + k_8 + k_9) z_5 + k_7 z_6 + k_{10} z_7 \\
\frac{dz_6}{dt} &= k_8 z_5 - k_7 z_6 \\
\frac{dz_7}{dt} &= k_9 z_5 - k_{10} z_7 \\
k_i &= \left(c_{i,1} + c_{i,2} u + c_{i,3} u^2 + c_{i,4} u^3\right) v_r \qquad \forall i = 1 \ldots 10
\end{aligned}
$$

Initial Conditions

$$z(t_o) = (1, 0, 0, 0, 0, 0, 0)$$

Control

u is piecewise constant over 10 intervals:

$u = w_i \quad \text{for} \quad t_i \leq t < t_{i+1}$

$t_i = (0,\ 0.1,\ 0.2,\ 0.3,\ 0.4,\ 0.5,\ 0.6,\ 0.7,\ 0.8,\ 0.9,\ 1)$

Variable bounds

$$0.6 \leq \boldsymbol{w} \leq 0.9$$
$$t \in [0, 1]$$

Variable Definitions

z_i is the mole fraction of the component A_i, and the control, u, is the mass fraction of hydrogenation component present in the catalyst. v_r is the characteristic volume of the reactor determined by the total mass of catalyst in the reactor divided by the molar flowrate of methylcyclopentane into the reactor. c_{ij} are experimentally determined constants which relate the catalyst blend to the reaction rate constants using a cubic equation.

Data

$$v_r = 2000 \ \frac{g \cdot h}{mol}$$

$c_{i,j} =$

$$\begin{pmatrix}
0.2918487\times10^{-2} & -0.8045787\times10^{-2} & 0.6749947\times10^{-2} & -0.1416647\times10^{-2} \\
0.9509977\times10^{1} & -0.3500994\times10^{2} & 0.4283329\times10^{2} & -0.1733333\times10^{2} \\
0.2682093\times10^{2} & -0.9556079\times10^{2} & 0.1130398\times10^{3} & -0.4429997\times10^{2} \\
0.2087241\times10^{3} & -0.7198052\times10^{3} & 0.8277466\times10^{3} & -0.3166655\times10^{3} \\
0.1350005\times10^{1} & -0.6850027\times10^{1} & 0.1216671\times10^{2} & -0.6666689\times10^{1} \\
0.1921995\times10^{-1} & -0.7945320\times10^{-1} & 0.1105666 & -0.5033333\times10^{-1} \\
0.1323596 & -0.4696255 & 0.5539323 & -0.2166664 \\
0.7339981\times10^{1} & -0.2527328\times10^{2} & 0.2993329\times10^{2} & -0.1199999\times10^{2} \\
-0.3950534 & 0.1679353\times10^{1} & -0.1777829\times10^{1} & 0.4974987 \\
-0.2504665\times10^{-4} & 0.1005854\times10^{-1} & -0.1986696\times10^{-1} & 0.9833470\times10^{-2}
\end{pmatrix}$$

Problem Statistics

No. of continuous variables	10
No. of dynamic variables	17
No. of linear equalities	-
No. of convex inequalities	-
No. of nonlinear equalities	-
No. of nonconvex inequalities	-
No. of dynamic constraints	17
No. of known solutions	> 300

Best Known Solution

- Objective function: -10.09582×10^{-3}
- Control variables
  $\boldsymbol{w} = (0.66595, 0.67352, 0.67500, 0.9, 0.9, 0.9, 0.9, 0.9, 0.9, 0.9)$

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