THE UNIVERSITY OF CALGARY

STEADY STATE SIMULATION OF CHEMICAL PROCESSES

by

ANUP KUMAR GUPTA

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN ENGINEERING

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA, CANADA November, 1990

C ANUP KUMAR GUPTA 1990



The University of Calgary Libraries and Cultural Resources supplies documents under the fair dealing and library exceptions of the Copyright Act. The documents are for individual research purposes only, with any further reproduction prohibited.

ABSTRACT

The steady state simulation of single and multistage separation is examined in this investigation. In particular, processes a new criterion formulation of the stability for multiphase reacting/ is This formulation non-reacting systems presented. permits the simultaneous computation of stability and flash calculations for single stage separation processes. Furthermore, the formulation is extended for simulation of multistage separation processes involving the multiple formulations subsequently utilized phases. These are to develop algorithms for single and multistage multiphase separation processes. For single stage processes, algorithms for isothermal-isobaric and multiphase isenthalpic-isobaric flash presented. are Algorithms for multistage multiphase separation processes developed in this work permit the simulation of three-phase and two-phase distillation columns. absorbers and reboiled absorbers. The algorithms are evaluated using a number of test cases. Applications of the algorithms are illustrated.

The new development of the stability criterion has led to the formulation of a set of coupled nonlinear algebraic equations which describe both the stability and the equilibrium calculations of reacting and non-reacting systems. Two algorithms for the simultaneous solution and multiphase isothermal-isobaric flash calculations of stability are presented. These algorithms differ in the manner in which the mole fraction summation and the stability equations are solved. The first these equations by using algorithm solves an active set solution strategy while the second one utilizes the Newton-Raphson method. The

(iii)

is extended handle isenthalpic second algorithm to the flash computations in non-reacting systems. The effectiveness and efficiency of the proposed algorithms are illustrated by solving several typical multiphase problems. Furthermore, the active set algorithm is utilized to study a number of typical phase equilibrium problems encountered in gas processing and petrochemical industries, in enhanced oil recovery schemes and in systems containing gas hydrates.

formulation of simultaneous The stability and equilibrium calculations for single stage separation processes is extended to permit the formulation for multistage multiphase separation processes. New independent variables which represent the total moles of a component leaving a stage are introduced. An algorithm based on the Newton-Raphson method is proposed for the solution of the coupled nonlinear equations. The algorithm is utilized to simulate three and two phase distillation columns, absorbers and reboiled absorbers. The performance of the two phase multistage algorithm is compared with some of the existing algorithms. It is found to be efficient and effective. The three phase distillation algorithm is easily able to handle the appearance or disappearance of a phase during the computations.

An acceleration technique, based on the Dominant Eigenvalue Method of Orbach and Crowe (1971), is evaluated for computational efficiency for single stage flash calculation. It is found to be efficient.

This investigation provides a unified approach for the steady state simulation of multiphase single and multistage separation processes.

(iv)

ACKNOWLEDGEMENTS

The author wishes to acknowledge and express his sincere gratitude to Professor P. R. Bishnoi for his support, encouragement and continuous supervision of this project.

The author is also thankful to Professor N. Kalogerakis for his valuable advice and support throughout the project.

The author takes this opportunity to thank Professor R. A. Heidemann for his encouragement during this work.

The author would also like to acknowledge Professor Warren D. Seider for suggesting the method for the alternative derivation, given in the Appendix A, of the stability equations.

The financial support provided by the Natural Sciences and Engineering Research Council of Canada and the Department of Chemical and Petroleum Engineering is greatly appreciated. Dedicated to my parents

Mohan Lal Gupta

•

and

Mridula Gupta

TABLE OF CONTENTS

ABSTRACT ACKNOWLEDG LIST OF TABLI LIST OF FIGUR	EMENT ES .ES	Page (iii) (v) (xi) (xiv)
NOMENCLATU	RE	(xvii)
CHAPTER 1 -IN	TRODUCTION	1
CHAPTER 2 -EC FI	UILIBRIUM CALCULATIONS FOR TWO PHASE ASH COMPUTATIONS	
2.	Literature Review	5
2.:	2 Problem Statement	8
2.:	8 Methods of Solution	
2.:	3.1 Successive Substitution on K-factors	9
2.:	3.2 Successive Substitution on Liquid and Vapor Mole Fractions	10
2.4	Proposed Solution Scheme	12
2.:	5 Numerical Experience	15
2.0	5 Discussion	25
2.7	7 Summary	26
CHAPTER 3 - M SI E(ULTIPHASE EQUILIBRIUM COMPUTATIONS - MULTANEOUS PHASE STABILITY AND QUILIBRIUM CALCULATIONS	
3.	Literature Review	27
3.2	Problem Statement	30
3.3	A New Development of Phase Stability Criteria	33

	3.4	Formulation of Equations	
	3.4.1	Coupled Isothermal-Isobaric Equilibrium and Stability Calculations	36
	3.4.2	Chemical Equilibrium Relations	37
	3.5	Governing Equations	38
	3.6	Advantages of Proposed Formulation	40
	3.7	Summary	41
CHAPTER 4 -	AN A OF PI	CTIVE SET METHOD FOR THE CALCULATION HASE STABILITY AND FLASH COMPUTATION	N S
	4.1	Proposed Algorithm	42
	4.2	Initialization of the Proposed Algorithm	48
	4.3	Evaluation of the Proposed Algorithm	
	4.3.1	Updating the Compositions in a Single Loop	52
	4.3.2	Comparison with Conventional Method of Alternate Stability and Flash Calculations	54
	4.3.3	Numerical Examples	63
	4.3.4	Discussion of Results	63
	4.4	Applications of the Algorithm	
	4.4.1	Enhanced Oil Recovery Applications	65
	4.4.2	Cryogenic Natural Gas Applications	72
	4.4.3	Application to Chemical Industry	81
	4.4.4	Applications to Systems containing Gas Hydrates	84
	4.5	Summary	89
CHAPTER 5 -	A SIM	ULTANEOUS SOLUTION METHOD FOR THE	
	CALC COMF	ULATION OF PHASE STABILITY AND FLASH PUTATIONS	
	5.1	Analysis of the Stability Equation	91
	5.2	Modifications Required for Simultaneous Solution	

.

	5.2.1	Switching of the solution between the α θ axes	93
	5.2.2	Singular Jacobian	95
	5.2.3	Ill-conditioned Jacobian	95
	5.3	Isothermal-Isobaric Specifications for	
	521	Reactive and Non-Reactive Systems	06
	5.3.1	Evaluation of the Proposed Algorithm	90 97
	5.4	Isenthalpic Specifications for Non-Reactive Systems	21
	5.4.1	Proposed Algorithm	112
	5.4.2	Evaluation of the Proposed Algorithm	113
	5.5	Discussion of the Results	118
	5.6	Summary	120
CHAPTER 6 -	MATH MULT	IEMATICAL MODELING OF MULTISTAGE TIPHASE SEPARATION PROCESSES	
	6.1	Literature Review	121
	6.2	Problem Statement	128
	6.3	Formulation of Equations	131
	6.4	Governing Equations	135
	6.5	Specification Equations	138
	6.6	Advantages of Proposed Formulation	141
	6.6 Su	ımmary	141
CHAPTER 7 -	A ME' SEPAI	THOD FOR THE SOLUTION OF MULTISTAGE RATION PROBLEMS	
	7.1	Two Phase Separation Column	
	7.1.1	Proposed Algorithm	143
	7.1.2	Evaluation of the Proposed Algorithm	146

	7.2	Three Phase Separation Column	
	7.2.1	Proposed Algorithm	153
	7.2.2	Evaluation of the Algorithm	155
	7.3	Discussion of Results	170
	7.4	Summary	173
CHAPTER 8 -	CON	CLUSIONS AND RECOMMENDATIONS	
	8.1	Conclusions	174
	8.2	Recommendations	177
REFERENCES			179
APPENDIX A	An A Equat	lternative Derivation of the Stability ions	191
APPENDIX B	Select	ion of the Equilibrium Ratios	193
APPENDIX C	Deriv	atives for the Single Stage Flash	195
APPENDIX D	Deriv Proce	atives for the Multistage Separation sses	200
APPENDIX E	Evalu appro	ations of the coefficients for the ximate thermodynamic model	215

LIST OF TABLES

Table	Title	Page
2.1	Compositions (mol %) of Mixtures A and B	17
2.2	Number of iterations for Mixture A at 158.9 K	18
2.3	Number of Thermodynamic Evaluation for Mixture A at 158.9 K	18
2.4	Conditions for the selected points for Mixture B	21
2.5	Number of iterations for Mixture B	21
2.6	Number of Thermodynamic Evaluations for Mixture B	22
4.1	Compositions of Test Mixtures	51
4.2	Number of Thermodynamic Evaluations for the selected points for Mixture A using one and two loops for updating phase compositions	53
4.3	Calculated Equilibrium Phase Fractions at 25 ⁰ C for Mixture B	57
4.4	Number of Thermodynamic Evaluations for Mixture B	57
4.5	Calculated compositions of the various phases at 25 ⁰ C and 7100 kPa for Mixture B	58
4.6	Four Phase Calculations For Mixture C at 25 ⁰ C	60
4.7	Calculated compositions of the various phases at 25 ⁰ C and 7100 kPa for Mixture C	61
4.8	Three Phase Calculations For Mixture D	62

4.9	Compositions of the various phases at -122.25°C and 6129 kPa for Mixture D	62
4.10	Binary interactions parameters for Trebble-Bishnoi Equation of State (1988)	66
4.11	Three Phase Calculations For the mixture of Carbon dioxide, nitrogen and n-nonadecane at 21 ⁰ C	69
4.12	Compositions of the various phases at 26 ^o C and 5670 kPa for Ethanol, Water and Carbon Dioxide System	80
4.13	Equilibrium Phase Compositions (mol %) for a Mixture containing 50, 49.9 AND 0.1 mol % OF H ₂ O, CH ₄ AND C ₃ H ₈ .	85
4.14a	Condensate Composition	86
4.14b	Feed Contents	86
4.15	Equilibrium Phase Compositions (mol %) for Feed Mixture A at 278 K and 1.7 MPa.	87
4.16	Equilibrium Phase Compositions (mol %) for Feed Mixture B at 278 K and 2.9 MPa.	87
5.1	Equilibrium phase compositions (mol %) for the CH_4 - CO_2 - H_2S mixture at 6060 kPa	98
5.2	Equilibrium phase compositions (mol %) for the ethanol-ethylacetate-water mixture at 101.32 kPa	102
5.3	Equilibrium phase compositions (mol %) for the the reacting system at 473.15 K and 30 MPa	107
5.4	Equilibrium phase compositions (mol %) for the the reacting system at 473.15 K and 10.13 MPa	108

5.5	Equilibrium phase compositions (mol %) for the the reacting system at 535 K and 20 MPa	109
5.6	Calculated temperatures and stability variables for the n-pentane and water system at 1000 kPa	115
7.1a	Specifications of the Two Phase Multistage Separation Problems	147
7.1b	Specifications for the Two Phase Multistage Separation Problems	148
7.2	Number of Iterations and Thermodynamic Evaluations for the test problems	150
7.3a	Number of Thermodynamic Evaluations required by various Solution Procedures	152
7.3b	Number of Inverse operations required by various Solution Procedures	152
7.4	Specifications for the Three Phase Multistage Separation Problems	156
7.5	Comparison of results for the mixture of Water, n-Propanol and n-Butanol	157
7.6	Phase Compositions (mol %) for the mixture of Water, n-Propanol and n-Butanol	158
7.7	The results for the mixture of Water, Butyl- acetate and n-Butanol	166
7.8	Equilibrium Phase Compositions (mol %) for the mixture of Water, Butylacetate and n-Butanol	167

LIST OF FIGURES

Figure	Title	Page
2.1	Computational Flow Diagram of the Proposed Algorithm	16
2.2	Phase Envelope and Constant Quality Curves for Mixture B	20
2.3	Approach to convergence for Mixture B at 6890 KPa and 220.22 K	24
4.1	Computational Flow Diagram of the Algorithm	44
4.2	Phase Fractions for Mixture B at 25 C	56
4.3	Phase Fractions for Mixture C at 25 C	59
4.4	Phase Compositions for the liquid-liquid-vapor region of C02 + Nitrogen + n-Nonadecane at 21°C	67
4.5	Molar volume for the liquid-liquid-vapor region of C02 + Nitrogen + n-Nonadecane at 21°C	68
4.6	Phase Compositions for the liquid-liquid-vapor region of C02 + Propane + n-nonadecane at 24°C	70
4.7	Molar volume for the liquid-liquid-vapor region of C02 + Propane + n-Nonadecane at 24°C	71
4.8	Phase Compositions for the liquid-liquid-vapor region of Methane + Nitrogen + Propane at -152°C	73
4.9	Molar volume for the liquid-liquid-vapor) region of Methane + Nitrogen + Propane at -152°C	74
4.10	Phase Compositions for the liquid-liquid-vapor	75

	region of Methane + Nitrogen + n-Hexane at $-103^{\circ}C$	
4.11	Molar volume for the liquid-liquid-vapor region of Methane + Nitrogen + n-Hexane at -103°C	76
4.12	Phase Equilibrium behavior for the system Carbon Dioxide – Ethanol	78
4.13	Phase Equilibria of Water, Ethanol, Carbon Dioxide	79
4.14	Phase Equilibrium behavior for the system Carbon Dioxide – 2-proponol	82
4.15	Phase Equilibria of Water, Carbon Dioxide, 2-propanol at 60°C	83
5.1	Exact and Modified Solution of the Stability Equation	94
5.2	Vapor Phase Fraction and Stability Variable during iterations for the CO_2 -CH ₄ -H ₂ S Mixture at 6060 kPa and 212.5 K	99
5.3	Phase Fraction and Stability Variable during iterations for the CO_2 -CH ₄ -H ₂ S Mixture at 6060 kPa and 212.75 K	100
5.4	Vapor Fraction and Stability Variable during iterations for the Ethanol-Ethylacetate- Water Mixture at 101.32 kPa and 343.46 K	103
5.5	Ethylacetate Rich Liquid Fraction and Stability Variable during iterations for the Ethanol-Ethylacetate-Water Mixture at 101.32 kPa and 343.46 K	104

5.6	Phase Fractions and Stability Variables during Iterations for Methanol Synthesis Reaction at 535 K & 20 MPa	110
5.7	Vapor Fraction and Stability Variable during iterations for the Ethanol-Ethylacetate– Water Mixture at 101.32 kPa and $H_{spec}/R = -4141.76$ K	114
5.8	Enthalpy-Temperature diagram for equimolar n-Pentane and water at 1000 kPa calculated using isenthalpic flash computations	116
6.1	Equilibrium stage model	126
6.2	A Schematic Representation of Stage j	127
7.1	Approach to convergence for Problem 2 with Partial and Full Convergence of Inner Loop	151
7.2	Water Rich Liquid Phase Fraction and Stability Variable for the Mixture of Water, n-Propanol and n-Butanol	161
7.3	Phase Fraction of the Second Liquid Phase for the Mixture of Water, n-Propanol and n-Butanol	162
7.4	Stability Variable of the Second Liquid Phase for the Mixture of Water, n-Propanol and n-Butanol	163
7.5	Approach to convergence for the Mixture of Water, n-Propanol and n-Butanol	164
7.6	Water Rich Liquid Phase Fraction and Stability Variable for the Mixture of Water, Butylacetate and n-Butanol	168
7.7	Approach to convergence for the Mixture of Water, Butylacetate and n-Butanol	169

NOMENCLATURE

Symbols

Description

b	constant vector
В	iteration matrix in Chapter 2;
	Bottom flow rate in multistage processes
\mathbf{B}_{ij}	parameter in the thermodynamic model
d	defined by Equation (B.8)
D	defined by Equation (3.29) or Equation (6.21)
e	absolute average error
Ε	error vector at any iteration; in multistage processes
	residual in Enthalpy Balance Equation
f _{ii}	fugacity of component i in phase j
F	function to be zeroed in Chapter 2
F	mole of feed
g	defined by Equation (2.9)
G	Gibbs free energy
G*	defined by Equation (3.9)
Hı	hydrate phase of structure I
Нп	hydrate phase of structure II
J	Jacobian for the phase
K	chemical reaction constant vector
K	equilibrium ratio of component i in phases j
L	mole of phase j
La	aqueous liquid phase
Lh	hydrocarbon liquid phase
m	moles of component leaving a stage
Μ	Residual in the Component Material Balance Equation
n	number of moles
N	number of components
р	pressure
Ρ	pressure in atm

Residual in the phase summation equation Ρ total moles q external enthalpy added Q R number of reactions, Universal Gas constant; Reflux ratio in multistage processes R Residuals in the equations S Residual in the Summation Equation Number of Stages S Т temperature T Residual in the stability equation unknown vector u V vapor Phase accentric factor W withdrawal ratio wr mole fraction of component i in phase j X_{ij} X, updated component mole fraction vector for phase j assumed component mole fraction vector for phase j X, Ñ. calculated component mole fraction vector for phase j liquid mole fraction X mole fraction of component i in vapor У_{іі} **у** _ј updated component mole fraction vector in vapor phase assumed component mole fraction vector in vapor phase У_і Ϋ́, calculated component mole fraction vector in vapor phase vapor mole fraction У slack variables in Appendix A y_k component mole feed vector Z

Greek letters

α	molar phase fraction
α_{j}	molar fraction of phase j
β	vector of β (defined by Equation (4.1))
δ	incipient phase definition tolerance;

	kronecker delta in the Appendices C and D		
Δ	refers to change		
3	prescribed tolerance, a small number (1.0×10^{-10})		
$\boldsymbol{\phi}_{ii}$	fugacity coefficient of component i in phase j		
Λ	dominant eigenvalue of matrix B		
λ	Lagrange multipliers		
υ	stoichiometric coefficient		
ບຼ	number of cavities of type m per water molecule in the hydrate		
π	number of phases		
ξ	extent of reaction		
θ	stability variables given by Equation 3.18		
$\boldsymbol{\varTheta}_{\mathtt{mk}}$	fraction of cavity of type m occupied by gas component k		
μ	chemical potential		
ω	acceleration parameter		
Subscripts			
c	critical constant		
f	feed		
i	component index		
j	phase index; component index in Appendix B; stage index		
k	phase index		
1	liquid phase, phase index		
l	cavity type		
m	reaction index ; phase index		
р	reaction index in Appendix C		
pcond	partial Condenser		
r	reference phase index		
reb	reboiler		
S	reaction index; specified value in Chapter 6 & 7		
spec	specified value		
t	total		
tcond	total condenser		
v	vapor phase		
w	water		
1	vapor phase		

2 liquid phase

Superscripts

- (v) iteration index
 - * exact solution in Chapter 2
- * property in pure state
- standard state of ideal gas at 1 atm
- b base conditions

CHAPTER 1 INTRODUCTION

Steady-state simulation of chemical processes has played a very the design of chemical important role in plants. The steady-state simulation programs are powerful design tools. In addition, they can be easily used to evaluate the performance of existing chemical processes. These simulation programs frequently have to deal with multiple liquid require phases. Hence, they the incorporation of a multiphase equilibrium flash calculation routine, which has to be robust and efficient. Moreover. the development of a reliable multiphase flash algorithm can be utilized to design an effective three phase distillation algorithm. Another application of multiphase equilibrium computations is in the simulation of enhanced oil recovery schemes. In this case, multiple liquid phases can be formed and they have to be accounted for in the simulation. In view of the practical importance of the multiphase computations for chemical and petroleum industry, the of effective efficient development an and methodology for the computations of multiphase equilibrium in single and multi-stage chemical processes was undertaken in this investigation.

Isothermal-isobaric flash calculation involving a vapor and a liquid phase is the most commonly used equilibrium computation. The method of successive substitution for these computations is investigated in Chapter 2. Successive substitution on the equilibrium ratios and mole fractions is examined. An efficient and easy-to-implement acceleration scheme is proposed for the successive substitution method with the liquid and the vapor mole fractions as the iteration variables. The performance of this scheme is compared with some of the existing acceleration schemes which iterate upon equilibrium ratios.

Computations of phase equilibria with chemically reacting species is of interest in various applications in the chemical industry. A common problem in the calculations of chemical and phase equilibria is that the number of phases which are present at equilibrium are not known a In Chapter 3, an alternative development of the stability priori. for multiphase reacting/non-reacting systems criterion is presented. This new formulation enables the performance of simultaneous stability multiphase computations at fixed pressure and temperature. and An augmented set of coupled nonlinear algebraic equations is obtained which describes both the stability and multiphase isothermal-isobaric flash calculations for reacting and non-reacting mixtures. The stability variable is introduced in the stability equation and its relevance in determining the stability of a phase is shown.

Based on the formulation of Chapter 3, an active set solution method is proposed for the simultaneous phase stability and flash calculations in Chapter 4. The active set method partitions the phase fractions and the stability variables between an active set and a non-active set. The stability equations are solved by switching the variables between the active and the non-active set as the computation proceeds. The effectiveness efficiency of the proposed solution and method are illustrated by solving a number of multiphase problems. The application of the algorithm is illustrated by solving a number of typical phase equilibrium problems encountered in the gas processing and petroleum industries, and in enhanced oil recovery schemes using Trebble-Bishnoi equation of state. In addition, the application of the method to multiphase computations in systems containing solid hydrates, liquids and vapor phases is illustrated.

An algorithm which utilizes the Newton-Raphson procedure for the simultaneous solution of stability and flash computations in reacting/non-reacting systems is discussed in Chapter 5. The stability equation is suitably transformed to alleviate the problems associated with the ill-conditioning and the singularity of the Jacobian near the phase boundaries. The algorithm is extended to handle the isenthalpic flash computations in non-reacting systems. The effectiveness of the is demonstrated algorithm by solving proposed multiphase isothermal-isobaric flash problems for reactive and non-reactive and multiphase isenthalpic flash problems for systems. non-reactive systems.

In 6, the formulation of single-stage stability Chapter and isothermal-isobaric flash is extended for the simulation of multi-stage Variables similar to those used separation processes. in the computations of single stage flash are introduced for the multistage variables are then utilized These processes. to write the material balance, energy balance. equilibrium, summation and the stability the multistage separation processes. The for modeling equations advantages of the proposed formulation for the modeling of two and three phase multistage separation schemes are discussed.

An algorithm for the solution of coupled nonlinear algebraic equations for multistage multiphase separation computations is given in Chapter 7. Two phase absorbers, reboiled absorbers and distillation columns are simulated. The performance of the two phase algorithm is compared with three of the existing methods. A similar algorithm is utilized for three phase distillation calculations. The effectiveness of proposed algorithm for three-phase distillation the computations is illustrated by solving two test problems.

The conclusions drawn in this study and the recommendations for further work are presented in Chapter 8.

of the behavior Modeling multiphase requires a suitable thermodynamic model to describe the various phases. In this study, various cubic equation of states (EOS) like Trebble-Bishnoi (Trebble and Bishnoi. 1988). Peng-Robinson (Peng and Robinson. 1976) and Soave-Redlich-Kwong (Soave, 1972) Equations of State have been used to model different phases. In addition, for some of the problems, activity coefficient models like NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) have also been utilized.

All the algorithms utilized in this study were implemented using C language on a Zenith Z-386 microcomputer. Microsoft C compiler (version 4.0) was used for compiling with the Intel 80287 coprocessor option. All the computations were performed using double precision arithmetic.

CHAPTER 2

EQUILIBRIUM CALCULATIONS FOR TWO PHASE FLASH COMPUTATIONS

Successive substitution methods and various acceleration schemes for the vapor-liquid flash computations are discussed in this chapter. An efficient and easy to implement acceleration scheme for successive substitution method is proposed. The computational efficiency of this acceleration scheme is compared with other acceleration procedures.

2.1 LITERATURE REVIEW

Successive substitution method, with the equilibrium ratios as the iteration variables, is the most commonly used procedure for converging two phase flash calculations. This procedure converges rapidly for the problems where the equilibrium ratios are weakly dependent on phase compositions. However, the method is slow converging for non-ideal mixtures particularly in the critical region (Michelsen, 1982b; Heidemann, 1983).

Alternative procedures based on the Newton-Raphson method have been proposed by Hirose et al. (1978) and Asselineau et al. (1979). Hirose et al. considered non-idealities of both the vapor and liquid phases and simultaneously solved for all the variables using the Newton-Raphson procedure. Asselineau et al. applied the Newton-Raphson procedure to dew-point and bubble-point calculations.

Newton-Raphson procedure is applicable to a wider class of problems. However, it requires the evaluation of Jacobian matrix at every

iteration. The required partial derivatives for the Jacobian matrix can either be evaluated analytically or numerically through the use of finite differences. The numerical evaluation of the derivatives can consume a considerable amount of the computer time. The time saved by the higher rate of convergence may not necessarily be compensated by that required for calculating the derivatives. Quasi-Newton methods. such as those of Broyden (1965, 1971), are an alternative. These methods successively improve approximations Jacobian matrix without to the calculating the derivatives involved. This method has been applied by Nghiem and Heidemann (1982) for accelerating convergence in multiphase computations. Boston and Britt (1978) have employed the Broyden's method in converging the "inside-out" algorithm for equilibrium computations.

Quasi-Newton methods require storage and manipulation of matrices at every iteration. The Dominant Eigenvalue Method, which has been shown to be equivalent to Quasi-Newton method (Crowe, 1984), is an attractive alternative. Crowe has proposed dominant eigenvalue algorithm which is an order of magnitude faster and produces results during iterations identical to those generated with the Broyden's method. The increased speed of the algorithm is obtained by replacing matrix-vector products by scalar-vector and vector-vector products. Furthermore, the algorithm requires storage of one vector per iteration compared with the storage of current estimate of the Jacobian matrix in the Broyden's method. The use of General Dominant Eigenvalue Method of Crowe and Nishio (1975) has been recommended by Michelsen (1982b) to promote the convergence of the successive substitution method.

Mehra et al. (1983) showed that the successive substitution with the

equilibrium ratios as the iteration variables can be regarded as a method of steepest descent for free energy minimization. They then formulated an acceleration scheme based on the gradient of the Gibbs free energy function.

Rijkers and Heidemann (1986) examined the convergence behavior of several alternative flash algorithms and determined the effect of the initiation procedure on obtaining the trivial solution.

Recently, Joulia et al. (1986) proposed a hybrid method which utilizes Schubert's method (a Quasi-Newton updating technique for sparse Jacobians) to accelerate the rate of convergence for two phase flash calculations. Their method is a combination of two simultaneous solution methods. These methods are based on a linearization of the system of equations with or without the partial derivatives of equilibrium ratios with respect to compositions. The flash computations are started by neglecting the partial derivatives of equilibrium ratios with respect to compositions. A switch-over is performed to a solution method in which the composition derivatives of equilibrium ratios are included. In their method the Jacobian matrix is updated using Schubert's method (1970).

Kinoshita and Takamatsu (1986) proposed a new algorithm based on the Newton-Raphson procedure for the vapor liquid equilibrium flash calculations. The liquid and vapor mole fractions were used as the iteration variables, and the functions to be zeroed were chosen so that the Jacobian matrix is diagonally dominant with diagonal elements close to unity. Their solution procedure will be examined in more detail in this Chapter since this method can easily be extended to multiphase computations. Furthermore, it will be shown (Gupta et al., 1988) that

7

an acceleration scheme based on the Dominant Eigenvalue Method of Orbach and Crowe (1971) can be utilized instead of the Newton-Raphson procedure for updating the phase compositions.

2.2 PROBLEM STATEMENT

The basic equations describing the two phase isothermal-isobaric flash calculations are given below :

Component material balances :

$$z_i = (1 - \alpha) x_i + \alpha y_i$$
 (i = 1,...,N). (2.1)

Mole fraction Summation :

$$\sum_{i=1}^{N} (y_i - x_i) = 0.$$
 (2.2)

Equilibrium relations :

$$y_i = K_i x_i$$
 (i = 1,...,N) (2.3)

where

$$K_{i} = \phi_{i2} / \phi_{i1} . \qquad (2.4)$$

The fugacity coefficients, ϕ_{ij} , are obtained from the thermodynamic model employed.

For the isothermal-isobaric flash problem, the feed compositions, z, the pressure and the temperature are specified. The liquid and vapor phase compositions, x and y, and the vapor fraction, α , are obtained by solving the above 2N+1 equations.

2.3 METHODS OF SOLUTION

2.3.1 Successive Substitution on K-factors

Equations (2.1) and (2.3) are combined to eliminate the vapor composition, y_i , yielding

$$\mathbf{x}_{i} = \frac{\mathbf{z}_{i}}{1 + (\mathbf{K}_{i} - 1) \alpha}$$
 (i = 1,...,N). (2.5)

Equations (2.2), (2.3) and (2.5) are then combined to yield an equation for the vapor fraction, α , namely

$$\sum_{i=1}^{N} \frac{(K_{i} - 1) z_{i}}{1 + (K_{i} - 1) \alpha} = 0.$$
(2.6)

The method is initialized by assuming values for the equilibrium ratios. Equation (2.6) is solved for the vapor fraction, α , using some iterative scheme like Newton-Raphson. Subsequently, the liquid and the vapor compositions are calculated from equation (2.5) and (2.3). The new K values are then calculated using equation (2.4). These steps are repeated, until the sum of squares of the difference of logarithm of fugacities is within given tolerance. This procedure is successive substitution with the equilibrium ratios as the iteration variables. We shall refer to this method as SS-K.

The rate of convergence of successive substitution method can be improved by a simple method suggested by Mehra et al. (1983). An acceleration parameter, γ , is introduced in the updating of the equilibrium ratios. Using this accelerated procedure, the equilibrium ratios are updated by

$$\mathbf{K}_{i}^{(\boldsymbol{v})} = \mathbf{K}_{i}^{(\boldsymbol{v}-1)} (\mathbf{f}_{i1}^{\prime} / \mathbf{f}_{i2}^{\prime})^{\boldsymbol{\gamma}}, \qquad (2.7)$$

where, f_{i1} and f_{i2} are the fugacities of component i in the two phases. The acceleration parameter is related to the gradient of the Gibbs free energy and is calculated from

$$\gamma^{(\upsilon)} = \left| \frac{\sum [g_i^{(\upsilon-1)}]^2}{\sum [g_i^{(\upsilon-1)} g_i^{(\upsilon)}] - \sum [g_i^{(\upsilon-1)}]^2} \right| \gamma^{(\upsilon-1)}, \quad (2.8)$$

where

$$g_i = \ln f_{i2} - \ln f_{i1}$$
 (2.9)

Note that the acceleration parameter of one corresponds to the successive substitution method. This method of acceleration is referred to as Acc-SS-KM.

The General Dominant Eigenvalue Method of Crowe and Nishio (1975) has been used by many investigators to accelerate the convergence of equilibrium computations. Michelsen (1982) has suggested using the General Dominant Eigenvalue Method of order two, for accelerating the convergence of successive substitution methods. In his implementation, one acceleration step is applied after every five steps of successive substitution. If convergence is not achieved within 12 iterations, the Newton-Raphson method is used thereafter. This acceleration procedure will be referred to as Acc-SS-K2.

2.3.2. Successive Substitution on Liquid and Vapor Mole Fractions

A successive substitution algorithm, which iterates upon the vapor

and the liquid compositions, has been proposed by Kinoshita and Takamatsu (1986). The algorithm obtains the phase fraction by solving Equation (2.6). The remaining 2N unknowns (mole fractions of the vapor and the liquid phases) are partitioned into two groups. The functions to be zeroed are the difference between the assumed and the calculated values of the mole fractions, namely

$$\mathbf{F}_{\mathbf{y}}(\mathbf{y}) = \mathbf{y}^{(\mathbf{v})} - \mathbf{\bar{y}}^{(\mathbf{v})}$$
(2.10)

and,

$$\mathbf{F}_{2}(\mathbf{x}) = \mathbf{x}^{(U)} - \dot{\mathbf{x}}^{(U)}.$$
 (2.11)

The solution of the flash problem is obtained by solving \mathbf{F}_1 for y and then solving \mathbf{F}_2 for x.

The vapor and liquid compositions are updated by

$$\mathbf{y}^{(U+1)} = \mathbf{y}^{(U)} + \Delta \mathbf{y}$$
 (2.12)

and

$$\mathbf{x}^{(\boldsymbol{\nu}+1)} = \mathbf{x}^{(\boldsymbol{\nu})} + \Delta \mathbf{x}$$
(2.13)

where $\Delta \mathbf{y}$ and $\Delta \mathbf{x}$ are obtained from

$$\Delta \mathbf{y} = -\mathbf{J}_1^{-1} \mathbf{F}_1 \tag{2.14}$$

and

$$\Delta \mathbf{x} = -\mathbf{J}_2^{-1} \mathbf{F}_2. \tag{2.15}$$

In equation (2.14) and (2.15), J_1 and J_2 are the Jacobian matrices. The iterative calculations are considered to be converged when the average absolute errors defined by

$$\mathbf{e}_{1} = \sum_{i=1}^{N} |\mathbf{F}_{i1}| / \mathbf{N} = ||\mathbf{E}_{1}| | / \mathbf{N}$$
(2.16)

and

$$e_2 = \sum_{i=1}^{N} |F_{i2}| / N = ||E_2|| / N$$
 (2.17)

are within a prescribed limit, ε .

A successive substitution with vapor and liquid mole fractions as the iterative variables will result when J_1 and J_2 in Equations (2.14) and (2.15) are set to the identity matrix. We shall refer to this method as the KT-U method.

When the full Jacobian is used to update the liquid phase compositions and the unit matrix is used for updating vapor phase compositions, we refer the method as the KT-J.

2.4 PROPOSED SOLUTION SCHEME

The KT-J method, being a Newton-Raphson method, requires a good initial estimate of the unknown variables to ensure convergence. In addition, the required computational effort for the evaluation of the Jacobian matrices can easily outweigh the computational gains due to faster convergence. On the other hand, the KT-U method does not require a good initial estimate. However, since it is a first order method, its rate of convergence is slow.

The acceleration of the KT-U method can be based on the observation that for successive substitution methods the change in the vector of unknowns becomes a geometric series as the solution is approached. This can be demonstrated by a Taylor series expansion of a function G, given

12

by

$$\mathbf{u}^{(\upsilon+1)} = \mathbf{G}(\mathbf{u}^{(\upsilon)}),$$
 (2.18)

about an arbitrary point \mathbf{u}_1 in the neighborhood of the solution. This expansion is given by

$$\mathbf{u}^{(\upsilon+1)} = \mathbf{G}(\mathbf{u}_{1}^{(\upsilon)}) + \mathbf{B} (\mathbf{u}^{(\upsilon)} - \mathbf{u}_{1})$$
(2.19)

where $\mathbf{B} = \frac{\partial \mathbf{G}}{\partial \mathbf{u}}$, evaluated at $\mathbf{u} = \mathbf{u}_1$. The solution vector iterates, $\mathbf{u}^{(U)}$, can be approximated eventually by

$$\mathbf{u}^{(U+1)} = \mathbf{B} \, \mathbf{u}^{(U)} + \mathbf{b},$$
 (2.20)

where

$$\mathbf{b} = \mathbf{G}(\mathbf{u}_{1}^{(0)}) - \mathbf{B} \mathbf{u}_{1}.$$
 (2.21)

Then, the error at any iteration, v + 1, is given by

$$\mathbf{E}^{(\boldsymbol{\nu}+1)} = \mathbf{u}^{(\boldsymbol{\nu}+1)} - \mathbf{u}^* = \mathbf{B} \mathbf{E}^{(\boldsymbol{\nu})}$$
(2.22)

which can be written in terms of the initial error as

$$\mathbf{E}^{(\upsilon+1)} = \mathbf{B}^{\upsilon} \mathbf{E}^{(\upsilon)}.$$
 (2.23)

The change in each iteration depends on the value of the largest eigenvalue of the iteration matrix, **B**, being used. For the iterative process to be convergent the necessary and sufficient condition is that the absolute value of the maximum eigenvalue, Λ , of matrix **B** be strictly less than one. An acceleration method based on the use of the dominant eigenvalue (DEM) has been suggested by Orbach and Crowe (1971) and applied to accelerate the solution of flowsheeting problems with recycles.

The dominant eigenvalue of matrix \mathbf{B} for the convergent iterative scheme can be approximated by

$$|\Lambda| = ||\mathbf{E}_{1}^{(v)}||/||\mathbf{E}_{1}^{(v-1)}||.$$
(2.24)

Equation (2.24) can be derived from equation (15) of Orbach and Crowe (1971).

In the acceleration scheme proposed here, the norms of the error vectors for the variables y and x are obtained from equations (2.16) and (2.17). Thus, the corresponding eigenvalues can be written as,

$$|\Lambda_1| = \mathbf{e}_1^{(\upsilon)} / \mathbf{e}_1^{(\upsilon-1)}$$
 (2.25)

and

$$| \Lambda_2 | = \mathbf{e}_2^{(0)} / \mathbf{e}_2^{(0-1)}.$$
 (2.26)

Therefore, for a convergent process, the acceleration factors for the vectors y and x are given by

$$\omega_{1} = \frac{1}{1 - \Lambda_{1}}$$
(2.27)

and

$$\omega_2 = \frac{1}{1 - \Lambda_2}.$$
(2.28)

The mole fractions in the vapor and the liquid phases can be updated by

$$\hat{\mathbf{y}}^{(\boldsymbol{\nu})} = (1 - \omega_1) \, \mathbf{y}^{(\boldsymbol{\nu})} + \, \omega_1 \bar{\mathbf{y}}^{(\boldsymbol{\nu})}$$
(2.29)

and

$$\hat{\mathbf{x}}^{(0)} = (1 - \omega_2) \, \mathbf{x}^{(0)} + \, \omega_2 \, \bar{\mathbf{x}}^{(0)}.$$
(2.30)

The acceleration may be applied periodically so that after each

promotion step the change in the vector of unknowns becomes a geometric series again (Orbach and Crowe, 1971). The change calculated during a promotion step may not be bounded by any maximum limit.

Unlike other acceleration methods (Mehra et al., 1983), the proposed scheme does not require any storage or multiplication of vectors and matrices. Very few calculations are required beyond the use of the error norms between two consecutive iterations. These error norms are used for checking the convergence and hence are already available.

The proposed accelerated successive substitution algorithm is referred to as Acc-SS-xy and is shown in Figure 2.1.

In addition, the use of General Dominant Eigenvalue Method of Crowe and Nishio (1975) in updating the liquid and vapor phase compositions which uses two eigenvalues has also been implemented. This method will be referred to as Acc-SS-xy2.

2.5 NUMERICAL EXPERIENCE

The seven algorithms (KT-U, KT-J, SS-K, Acc-SS-KM, Acc-SS-K2, Acc-SS-xy and Acc-SS-xy2) are compared in the following example problems using two mixtures, namely, Mixture A and Mixture B. The Peng-Robinson equation of state (Peng and Robinson, 1976) was used to model the two phases. The pure component properties were obtained from Reid et al. (1987). The ideal equilibrium ratios based on Raoult's Law were used to generate the initial estimates of the liquid and vapor mole fractions. The solution was considered to be converged when the errors as defined in equation (2.16) and (2.17) are less than 1 x 10^{-6} . In SS-K and Acc-SS-KM the convergence was checked for both the vapor and the liquid mole fractions instead of the K-factors, which is the usual procedure.



Figure 2.1: Computational Flow Diagram of the Proposed Algorithm

16

Component	Mixture A 1.40	Mixture B
N ₂		
CO2	0.00	10.00
CH4	94.30	86.08
C ₂ H ₆	2.70	2.47
C ₃ H ₈	0.74	0.67
n-C ₄ H ₁₀	0.49	0.45
n-C ₅ H ₁₂	0.10	0.24
n-C ₆ H ₁₄	0.27	0.09

Table 2.1 : Compositions (mol %) of Mixtures A and B

.

-
Pressure									
Suc	. Subs.	Accelera	ated Succes	sive Substitu	ition				
SS-K	KT-U [*]	Acc-SS-KM	Acc-SS-K2	Acc-SS-xy*	Acc-SS-xy2	KT-J [*]			
4	4	4	4	4	- 4	3			
7	7	4	6	5	5	4			
11	11	6	6	5	7	4			
5	5	4	5	4	4	3			
	ure SS-K 4 7 11 5	Suc. Subs. SS-K KT-U* 4 4 7 7 11 11 5 5	Suc. Subs. Acceleration SS-K KT-U* Acc-SS-KM 4 4 4 7 7 4 11 11 6 5 5 4	Suc. Subs. Accelerated Succes SS-K KT-U* Acc-SS-KMAcc-SS-K2 4 4 4 7 7 4 6 11 11 6 6 5 5 4 5	Suc. Subs. Accelerated Successive Substitut SS-K KT-U* Acc-SS-KMAcc-SS-K2 Acc-SS-xy* 4 4 4 4 7 7 4 6 5 11 11 6 6 5 5 5 4 5 4	areSuc. Subs.Accelerated Successive SubstitutionSS-KKT-U*Acc-SS-KMAcc-SS-K2Acc-SS-xy*Acc-SS-xy244444477465511116657554544			

Table 2.2 : Number of iterations for Mixture A at 158.9 K

* For liquid updates

Table 2.3 : Number of Thermodynamic Evaluation for Mixture A at 158.9 K

Pressure								
(kPa)	Sı	uc. Subs.	Accele	rated Succes	sive Substitu	ution		
	SS-I	K KT-U	Acc-SS-KM	[Acc-SS-K2	Acc-SS-xy	Acc-SS-xy2	KT-J	
101	8	7	8	8	7	7	14	
507	14	12	8	12	10	10	16	
1013	22	19	12	12	11	13	17	
1520	10	12	8	10	11	11	17	

This allowed us to conduct proper comparisons of the performance of the different methods.

It should be pointed out that not only the number of iterations should be compared but the total number of the necessary thermodynamic evaluations should also be monitored. It is these calls to the thermodynamic routines which take the bulk of the time and hence need to be compared for the different methods.

Mixture A:

Flash calculations are carried out for a seven component mixture consisting of six hydrocarbons and nitrogen at 158.9 K and various pressures. The composition of the mixture is given in Table 2.1. This mixture was also studied by Kinoshita and Takamatsu (1986).

The number of iterations required for convergence of the various methods is shown in Table 2.2. As seen, the SS-K and KT-U methods require the same number of iterations to converge. Acc-SS-KM, Acc-SS-K2, Acc-SS-xy and Acc-SS-xy2 also require about the same number of iterations. KT-J performed better than the other accelerated methods.

The number of the required thermodynamic evaluations are shown in Table 2.3. The evaluations necessary to obtain the Jacobian matrix for the KT-J method are included in the shown numbers. The number of the evaluations required for KT-U and SS-K are comparable. Acc-SS-KM, Acc-SS-xy and Acc-SS-xy2 also required about the same number of thermodynamic evaluations. KT-J required considerably larger numbers of evaluations compared to any of the other methods. Acceleration using two dominant eigenvalues of equilibrium ratios or phase compositions was not particularly better than the use of a single dominant eigenvalue for



Figure 2.2: Phase Envelope and Constant Quality Curves for Mixture B

Point	Pressure	Temperature	Vapor Mole
	(kPa)	(K)	Fraction
1	6890	220.22	0.9902
2		230.35	0.9901
3	6080	211.92	0.4994
4		235.03	0.9913
5	5066	202.23	0.0123
6		204.67	0.5008
7		235.84	0.9915
8	2027	170.29	0.0102
9		173.20	0.4993
10		220.15	0.9899

Table 2.4 : Conditions for the selected points for Mixture B

Table 2.5 : Number of iterations for Mixture B

Point	t						
	Suc. SS-K	Subs. KT-U [®]	Acceler Acc-SS-KN	ated Success A Acc-SS-K2	ive Substitut Acc-SS-xy*	tion Acc-SS-xy2	KT-J [*]
1	88	60	30	26	13	10	6
2	27	26	17	13	13	11	30
3	69	75	25	16	19	16	14
4	16	16	10	11	9	8	9
5	23	23	23	10	7	7	5
6	22	23	12	11	7	7	5
7	12	12	9	7	8	7	6
8	10	10	6	6	7	7	4
9	10	10	6	6	6	5	3
10	8	8	6	6	6	6	4

* For liquid updates

Point							
	Suc.	c. Subs. Accelerated Successive Substitution					
	SS-K	KT-U	Acc-SS-KM A	Acc-SS-K2	Acc-SS-xy	Acc-SS-x	y2 KT-J
1	178	89	60	52	29	24	40
2	54	51	34	26	30	27	69
3	138	379*	50	32	73	132	167
4	32	31	20	22	21	20	28
5	46	70	46	20	25	24	35
6	44	61	24	22	25	24	30
7	24	22	18	14	17	16	22
8	20	17	12	12	13	13	17
9	20	16	12	12	12	11	16
10	16	14	12	12	12	12	17
* vapo	or upda	ntes exce	eds the limit	on the	maximum nu	mber of	iterations

Table 2.6 : Number of Thermodynamic Evaluations for Mixture B

-

allowed.

this problem, at the conditions studied.

Mixture B:

Flash calculations are performed for a seven component mixture of a typical natural gas at various pressures and temperatures. The composition of the mixture is given in Table 2.1. The phase envelope of this mixture and the constant quality lines of vapor mole fractions of 0.01, 0.5 and 0.99 are shown in Figure 2.2. In Figure 2.2, only vapor and a liquid phases are considered, the possible formation of a solid phase or another liquid phase is not considered.

The pressure and temperature conditions at which flash computations are performed for Mixture B are shown in Table 2.4. These are chosen to keep the vapor fractions approximately constant at 0.01, 0.5 and 0.99.

The number of iterations required for the flash calculations are shown in Table 2.5. As seen, the number of iterations required at 2027 kPa is nearly the same for Acc-SS-KM, Acc-SS-K2, Acc-SS-xy and Acc-SS-xy2 while KT-J required fewer iterations. At higher pressures Acc-SS-xy performs better than Acc-SS-KM. Similarly, Acc-SS-xy2 performs better than Acc-SS-K2. Acc-SS-K2 and Acc-SS-xy2 perform better than Acc-SS-KM and Acc-SS-xy respectively. The performance of KT-J method is generally better than the other methods, in terms of number of iterations.

As shown in Table 2.6, for most of the points examined, KT-U requires fewer thermodynamic evaluations as compared to SS-K. The number of thermodynamic evaluations necessary for Acc-SS-KM and Acc-SS-xy are comparable. Similarly, those required for Acc-SS-K2 and Acc-SS-xy2 are also about the same. This is true at all points considered, except at



Figure 2.3 : Approach to convergence for Mixture B at 6890 kPa and 220.22 K

point 3, which is close to the critical point. Acc-SS-xy for point 3 showed initial divergence and absolute value of the acceleration parameter had to be used to force convergence. The KT-J method, with the Jacobian matrix evaluated only once (after one step of KT-U), required larger number of thermodynamic evaluations than the other accelerated methods.

Convergence behavior at 6890 kPa and 220.22 K for Mixture B is shown in Figure 2.3, where the errors defined by equation (2.17) are shown for all the accelerated methods.

2.6 DISCUSSION

The results from the example problems studied show that the computational effort required by KT-U and SS-K are comparable. The convergence rate of KT-U is slightly better initially than that of SS-K, though ultimately in both the methods the rate of convergence becomes constant. The computational effort required by Acc-SS-xy and Acc-SS-KM are about the same. The use of two eigenvalues to promote convergence is computationally slightly more efficient than the use of one eigenvalue. The updating of the liquid compositions by a true Jacobian requires more computational effort than the other accelerated methods.

Both Acc-SS-KM and Acc-SS-K2 exhibit oscillatory behavior for Mixture B, as seen in Figure 2.3. For Acc-SS-KM, this behavior can be curbed to some extent by placing a bound on the maximum step length allowed. In this work, we have used the same bound as that suggested by Mehra et al. (1983). If the acceleration is used only periodically, Acc-SS-xy does not require any bounds on the maximum change which is allowed for each step. In these example problems, we observed that taking a promotion step after every three iterations was the best. Cyclic acceleration has been observed to perform better by Soliman (1979) for recycle systems, and has previously been employed by Michelsen (1982b) with GDEM.

For the implementation of the acceleration schemes, Acc-SS-xy2, Acc-SS-K2 and Acc-SS-xy require the storage of 4n, 2n and 2 variables respectively.

In Chapter 4, it will be shown that it is computationally more efficient to update the liquid and vapor compositions in a single loop rather than using two separate loops to update the compositions.

2.7 SUMMARY

An acceleration scheme, based on the method of Orbach and Crowe (1971), for the successive substitution method which uses liquid and vapor compositions as the iteration variables for isobaric-isothermal flash calculations, is presented. The proposed algorithm with this acceleration scheme shows a slight oscillatory behavior, if periodic acceleration is employed. The number of iterations required for convergence is often less than the number required by the method which uses K-factors as the iteration variables. However. the number of thermodynamic evaluations is comparable with that of Mehra et al. (1983) and is more than that of Michelsen (1982b, 1987). No storage and multiplication of vectors is necessary to incorporate the acceleration scheme. The norm of the error which is used to check for the convergence is simply used in the updating formula.

CHAPTER 3

MULTIPHASE EQUILIBRIUM COMPUTATIONS - SIMULTANEOUS PHASE STABILITY AND EQUILIBRIUM CALCULATIONS

Α new development of stability criterion for multiphase reacting/non-reacting systems is presented in this chapter. This criterion is utilized to derive a modified set of equations, which allow for the simultaneous solution of phase stability and flash computations. Advantages of this new formulation are discussed. A brief literature review of methods for multiphase equilibrium computations in reacting/non-reacting systems is presented.

3.1 LITERATURE REVIEW

For the solution of the isothermal-isobaric multiphase flash problem two approaches have been used. The first of these is based on the minimization of the total Gibbs free energy with material constraints. The methods of Heidemann (1974), Gautam and Seider (1979), Soares et al. (1982), Michelsen (1982b) and Trangenstein (1987) are based on this approach. Heidemann proposed a three phase flash calculation methodology based on the direct minimization of Gibbs free energy. Gautam and Seider used the RAND method to solve the problem. A quadratic approximation of the Gibbs free energy is developed around the current point and Lagrange multipliers are introduced for the equality constraints. The stationary point conditions are then utilized to obtain a linear set of equations, which are solved. Any composition dependence of the fugacity coefficients is neglected in their scheme. Soares et al. utilized a

minimization procedure based on a Newton-Raphson algorithm in which the Marquardt method is used to control the correction vector. Michelsen used a second-order minimization algorithm of Murray (1972) in his computational procedure. Murray's method uses Newton's direction for descent when the Hessian is positive definite and modifies this direction when it is indefinite. Trangenstein proposed a new algorithm for the minimization of the Gibbs free energy involving at the most two phases. This method modifies the Newton's direction only if it is orthogonal to the steepest descent direction and when the Hessian is indefinite at the same time.

The second approach for multiphase computations is to solve a set of nonlinear equations which are obtained from material balance and the necessary conditions for the minimization of the total Gibbs fee energy. Henley and Rosen (1969) presented a rigorous three-phase flash calculation procedure which is an extension of the conventional two methodology. (1980)phase flash calculation Mauri describes a three-phase calculation algorithm based on the Henley-Rosen method that considers all possible phase conditions. Risnes and Dalen (1984) describe a successive substitution method for calculating multiphase flash equilibrium. Nghiem and Li (1984) used Quasi-Newton Successive Substitution method for computations of phase equilibria for systems with any number of phases. Fussel (1979) utilized minimum variable Newton-Raphson method for calculating multiphase equilibria. Wu and Bishnoi (1986a) proposed to solve the mass and the equilibrium equations simultaneously using the Newton-Raphson method. They obtained the required Jacobian matrix analytically. A combination of equation solving

approach and unconstrained minimization was used by Ammar and Renon (1987) for the two phase isothermal flash. Mehra et al. (1982) proposed a scheme which is a composite of accelerated form of successive substitution and a second order method. The second order method utilized is a hybrid of steepest descent and Newton's method, patterned after the Levenberg-Marquardt procedure.

Flash calculation at specified pressure and enthalpy (isenthalpic flash) have received much less attention than isothermal-isobaric flash computations. For the isenthalpic flash computations either a series of isothermal flash calculations are performed until the enthalpy balance equation is satisfied or the enthalpy and the material balance equations are solved simultaneously for the temperature and phase splits. Agarwal et al. (1989) compared both the schemes for multiphase isenthalpic flash calculations. They concluded that the method which performs series of more robust isothermal flashes but is is it much slower than simultaneous solution strategy. Michelsen (1987) has extended his stepwise procedure for the isothermal flash, to multiphase adiabatic and isentropic flash calculations. He suggested using accelerated successive substitution and switching to a second order convergence method to achieve final convergence for isenthalpic flash computations.

In recent years a number of calculation procedures have been proposed for the solution of chemical and phase equilibria. Smith and general strategies solving chemical Missen (1988) discuss the for problems. Smith (1980) classifies chemical equilibrium equilibrium stoichiometric non-stoichiometric. formulations either or to be Stoichiometric formulations require a knowledge of the stoichiometric

coefficients of a linearly independent set of reactions and utilize the extent of the reactions as the independent variables. On the other hand, the non-stoichiometric formulations elemental abundance constraints in calculations. studies used in the Recent iп this area are have concentrated on the reliability and efficiency of the employed iterative computational procedures. Castier et al. (1989) have used the second order Murray's method (1972) for minimization with the stoichiometric formulation. Very recently, Michelsen (1989) presented two algorithms which utilize a duality transformation of the Gibbs energy function for the calculation of multiphase ideal solution chemical equilibrium.

A common problem in the calculations of chemical and phase equilibria is that the number of phases which are present at equilibrium are not known a priori. Two solution strategies have been applied. In the first one, a non-linear programming approach is used to minimize the Gibbs energy function with a large number of phases (Lantagne et al., 1988; Castillo and Grossmann, 1981). The second approach is to sequentially add a phase in the computations and test the stability of the solution (Gautam and Seider, 1979; Castier et al., 1989; Michelsen 1982a; Wu and Bishnoi, 1986a; Nghiem and Li, 1984).

In the present work, an alternative development of the stability criterion will be presented. This would allow for the simultaneous calculation of stability and flash computations.

3.2 PROBLEM STATEMENT

In general, phase equilibrium calculations at specified temperature and pressure require the determination of the number of moles (n_{ik}) of each component i in phase k which minimize the Gibbs free energy over all possible states. For a multicomponent multiphase system the Gibbs free energy function is given by

$$\mathbf{G} = \sum_{\mathbf{k}=1}^{\pi} \sum_{i=1}^{N} \mathbf{n}_{i\mathbf{k}} \,\mu_{i\mathbf{k}} \tag{3.1}$$

where μ_{ik} is the chemical potential of component i in phase k, N is the number of components present in the mixture and π is the total number of phases. The moles of each component, n_{ik} , which minimize the Gibbs free energy should also satisfy the following constraints :

- (1) Material balance constraints
 - (a) Non-reacting Systems : In this case, the total number of moles of each component must be conserved, hence, we have

$$\sum_{k=1}^{\pi} \mathbf{n}_{ik} = \mathbf{z}_{i} \qquad (i = 1,...,N). \qquad (3.2a)$$

(b) Reacting Systems : In this case, the moles of a component will not be conserved due to chemical reactions. Therefore, the total number of moles of each component, n_i , is related to the moles of the component in the feed, z_i , through the extent of the chemical reactions taking place, namely

$$\mathbf{n}_{i} = \sum_{k=1}^{\pi} \mathbf{n}_{ik} = \mathbf{z}_{i} + \sum_{m=1}^{R} \boldsymbol{v}_{im} \boldsymbol{\xi}_{m} \quad (i = 1,...,N), \quad (3.2b)$$

where v_{im} is the stoichiometric coefficient and ξ_m is the extent of the mth reaction. It is noted that Equation (3.2b) is also valid for non-reacting systems when ξ_m is set equal to zero, and hence, we shall refer to Equation (3.2b) for non-

reacting systems as well.

(2) Non-negative constraints.

The number of moles of a component in a phase cannot be negative. Hence,

$$n_{ik} \ge 0$$
 (i = 1,...,N; k = 1, ..., π). (3.3)

It is a common practice to specify the number of phases and then solve the above stated minimization problem. The material balance constraints, Equation (3.2b), are often eliminated by introducing a reference phase (r) and solving for the number of moles of each component in this phase (n_{ir}) . Therefore, substituting the number of moles in the reference phase into Equation (3.1), we obtain

$$G = \sum_{i=1}^{N} z_{i} \mu_{ir} + \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} n_{ik} (\mu_{ik} - \mu_{ir}) + \sum_{\substack{m=1 \ i=1}}^{R} \sum_{i=1}^{N} v_{im} \xi_{m} \mu_{ir}.$$
 (3.4)

Thus, the constrained minimization of G, given by Equation (3.1), subject to Constraints (3.2b) and (3.3) is converted to an unconstrained one in which G given by Equation (3.4) is minimized. It is assumed that the nonnegative constraints are always satisfied for an acceptable solution.

The minimum of the Gibbs free energy is to be computed over all *possible states*. Since it is not known a *priori* which phases exist in equilibrium, a common practice is to test the solution obtained by the above minimization for stability by adding a new phase (Gautam and Seider, 1979).

In the next section, we shall show that the stability and flash

computations can be performed simultaneously by considering an additional constraint in the minimization problem.

3.3 A NEW DEVELOPMENT OF PHASE STABILITY CRITERIA

Consider a closed system at fixed temperature and pressure in which a maximum of π phases may coexist. Let the phase fractions of each of the (π -1) phases be specified which may be zero for some of the phases. The phase fraction for the remaining phase, which is assumed to be the reference phase, is obtained from the phase summation equation,

$$\alpha_{r} = 1 - \sum_{\substack{k=1\\k \neq r}}^{\pi} \alpha_{k}.$$
(3.5)

At this point the additional constraints which represent specified phase splits can be incorporated. Thus, the problem of minimizing the Gibbs free energy, G, given by Equation (3.4), can be stated as

$$\begin{array}{ccc}
\operatorname{Min} & \left\{ & G & \right\}, & (3.6) \\
& & & \\ & & \\ & & (i = 1, \dots, N) \\
& & (k = 1, \dots, \pi; \ k \neq r) \\
& & (m = 1, \dots, R)
\end{array}$$

subject to the additional constraints of the specified phase splits,

- -

$$\alpha_{k} = \sum_{i=1}^{N} n_{ik} / n_{i} \qquad (k = 1, ..., \pi; k \neq r)$$
(3.7)

and the nonnegative Constraints (3.3). In Equation (3.7) n_t is the total number of moles, namely

$$\mathbf{n}_{t} = \sum_{i=1}^{N} \mathbf{n}_{i} = \sum_{i=1}^{N} \mathbf{z}_{i} + \sum_{i=1}^{N} \sum_{m=1}^{R} \boldsymbol{v}_{im} \boldsymbol{\xi}_{m}.$$
 (3.8)

The above constrained minimization problem can now be converted to an unconstrained minimization problem by defining the Lagrangian, G^* , as

$$G^{*} = G + \sum_{\substack{k=1\\k\neq r}}^{\pi} \lambda_{k} \left[\alpha_{k} - \sum_{i=1}^{N} n_{ik}/n_{i} \right], \qquad (3.9)$$

where λ_k are the Lagrange multipliers. Again, the inequality constraints (3.3), must be satisfied to have an acceptable solution.

The conditions for the stationary points of the Lagrangian G^* are obtained by setting the derivatives of G^* with respect to n_{ik} , λ_k and ξ_m equal to zero. Two of these conditions,

$$\frac{\partial G^{*}}{\partial n}_{ik} = 0 \qquad (i = 1,...,N; k = 1,...,\pi; k \neq r) \qquad (3.10)$$

and

$$\frac{\partial G^*}{\partial \xi_m} = 0 \qquad (m = 1,...,R), \qquad (3.11)$$

are used below to establish relations for stability and chemical reaction equilibrium respectively. The derivative with respect to λ_k gives back the imposed constraints (Equation 3.7).

Equation (3.10) after some manipulation yields

$$\lambda_{k} / n_{t} = \mu_{ik} - \mu_{ir} = RT \ln (f_{ik} / f_{ir})$$

$$(i = 1,...,N; k = 1,...,\pi; k \neq r). \quad (3.12)$$

It is noted here that λ_{μ} has the same value for all the components in

34

the phase. It will now be shown that the variables λ_k can be used to determine the stability of the phase k in a system.

At the optimum, where the Gibbs free energy is minimum for the specified phase splits (constrained minimum), the following conditions are satisfied (Rao, 1984),

$$\frac{\partial G}{\partial \alpha_{k}} = \lambda_{k} \qquad (k = 1,...,\pi; k \neq r). \qquad (3.13)$$

Equation (3.13) implies that if a negative value is obtained for a λ_k , then the value of G can be further decreased by increasing the amount of phase k. Hence, a new set of phase splits can be specified in order to obtain a new minimum with a lower value of G.

Using Equation (3.13), we next show that for any phase k at the minimum (unconstrained) of G, either α_k or λ_k has to be zero. Whenever, α_k is strictly positive (i.e. phase k is present), the Gibbs free energy of the system would not decrease only if λ_k is zero. In other words, if λ_k is different from zero then one can always select a perturbation in α_k to decrease the Gibbs free energy of the system, which is contrary to the hypothesis that G was minimized. Hence, λ_k must be zero. Similarly, whenever α_k is zero (i.e. phase k is not present), the Gibbs free energy would not decrease only if λ_k is positive or zero.

Therefore, the relationship between the phase fraction, α_k , and the stability variables, λ_k , at the desired (unconstrained) minimum of G can be written as

$$\alpha_k \lambda_k - 0$$
 (k - 1,..., π ; k \neq r) (3.14)

subject to,

 $\alpha_k \ge 0 \quad \text{and} \quad \lambda_k \ge 0.$ (3.15)

Equations (3.14) and (3.15) can alternatively be derived by converting the inequality constraints, $\alpha_k \geq 0$, into equality constraints by introducing slack variables and redefining the Lagrangian, G^{*}, as shown in the Appendix A. It is noted that Equations (3.14) and (3.15) are commonly known as Kuhn-Tucker conditions.

The stability of a phase k can thus be determined by the above analysis. If at the solution it is determined that λ_k is positive, then the phase k can not coexist in equilibrium with the other phases. Hence, phase k under such conditions is unstable. The variables λ_k , can therefore determine the stability of phase k. Physically, λ_k/n_t represents the distance between the tangent hyperplane originated at the reference phase composition and the Gibbs free energy surface at the kth phase composition. Since $\lambda_k \geq 0$, the formulation dictates that the common tangent plane should never be above the Gibbs free energy surface.

In an alternate approach, Michelsen (1982a) developed a stability criterion for the phase equilibrium problem by examining the stationary points of the distances between the Gibbs free energy surface and the tangent hyperplane.

3.4 FORMULATION OF EQUATIONS

3.4.1 Coupled Isothermal-Isobaric Equilibrium and Stability Calculations

In the previous section, we have shown that at the minimum of G, the phase fractions and the stability variables must satisfy Equations (3.14) and (3.15). Next we shall develop the required equations for

coupling the isothermal-isobaric equilibrium and stability calculations. The K-factor is defined as

$$\mathbf{K}_{\mathbf{i}\mathbf{k}} = \boldsymbol{\phi}_{\mathbf{i}\mathbf{r}} / \boldsymbol{\phi}_{\mathbf{i}\mathbf{k}} . \tag{3.16}$$

The fugacity coefficients can be expressed in terms of mole fractions and fugacities. Using Equations (3.16) and (3.12) we obtain,

$$\mathbf{x}_{ik} = K_{ik} \mathbf{x}_{ir} \mathbf{e}^{k}$$
 (i = 1,...,N; k = 1,..., π ; k \neq r) (3.17)

where θ_{k} is defined as

$$\theta_{k} \equiv \lambda_{k} / (n_{t} RT). \qquad (3.18)$$

Equations (3.14) and (3.15) may be rewritten in terms of θ_k to obtain,

$$\alpha_{\mathbf{k}} \theta_{\mathbf{k}} = 0 \qquad (\mathbf{k} = 1, \dots, \pi; \mathbf{k} \neq \mathbf{r}) \tag{3.19}$$

subject to

$$\alpha_k \ge 0 \quad \text{and} \quad \theta_k \ge 0.$$
 (3.20)

It should be noted that when phase k is present θ_{k} is zero. Equation (3.17) then reduces to the well known equilibrium relationship. Equations (3.17), (3.19) and (3.20) allow the coupling of the flash isothermal-isobaric equilibrium calculations with the stability calculations. The resulting set of the governing nonlinear equations is given in the next section.

3.4.2 Chemical Equilibrium Relations

Equation (3.11) along with Equation (3.14) yields

$$\sum_{i=1}^{N} v_{im} \mu_{ir} = 0 \qquad (m = 1,...,R). \qquad (3.21)$$

Equation (3.21) can be written as,

$$\sum_{i=1}^{N} v_{im} \ln (f_{ir}) - \ln K_{am} = 0 \qquad (m = 1,...,R) \qquad (3.22)$$

where f_{ir} is the fugacity of component i in the reference phase in atm and K_{am} is the chemical equilibrium constant defined as

$$K_{am} = \exp \left(-\sum_{i=1}^{N} v_{im} G_{i}^{o}/RT\right).$$
 (3.23)

3.5 GOVERNING EQUATIONS

For any reacting/non-reacting system the set of equations that describe the simultaneous equilibrium and stability calculations at constant pressure and temperature is written as follows :

Phase Fraction Summation :

$$\sum_{k=1}^{\pi} \alpha_k = 1. \tag{3.24}$$

Mole Fraction Summation :

$$S_{k} = \sum_{i=1}^{N} (K_{ik} e^{\theta_{k}} - 1) x_{ir} = 0 \qquad (k = 1, ..., \pi; k \neq r) \qquad (3.25)$$

with

$$\mathbf{x}_{ir} = \mathbf{n}_i / (\mathbf{n}_t \mathbf{D}_i)$$
 (i = 1,...,N), (3.26)

where,

$$\mathbf{n}_{i} = \mathbf{z}_{i} + \sum_{m=1}^{R} \boldsymbol{v}_{im} \boldsymbol{\xi}_{m}$$
 (i = 1,...,N), (3.27)

$$\mathbf{n}_{t} = \sum_{i=1}^{N} \mathbf{n}_{i}, \qquad (3.28)$$

.

$$D_{i} = 1 + \sum_{\substack{j=1\\ j \neq r}}^{\pi} (K_{ij} e^{\theta_{j}} - 1) \alpha_{j}, \qquad (3.29)$$

and

$$K_{ik} = \phi_{ir} / \phi_{ik}$$
 (3.30)

Phase Equilibrium and Stability Relations :

$$\mathbf{x}_{ik} = \mathbf{K}_{ik} \mathbf{x}_{ir} \mathbf{e}^{\theta_k}$$
 (i = 1,...,N; k = 1,...,\pi; k \neq r) (3.31)

and

$$\alpha_{k} \theta_{k} = 0$$
 $(k = 1,...,\pi; k \neq r)$ (3.32)

subject to,

$$\alpha_k \ge 0$$
 and $\theta_k \ge 0$. (3.33)

Chemical Equilibrium Relations :

Substituting Equations (3.26), (3.27) and the definition of the fugacity coefficient in Equation (3.22), we obtain

$$\sum_{i=1}^{N} v_{im} \ln \left[(z_i + \sum_{s=1}^{R} v_{is} \xi_s) \phi_{ir} P/(n_t D_i) \right] - \ln K_{am} = 0 \quad (m = 1,...,R).$$
(3. 34)

For the isothermal-isobaric equilibrium and stability problem, the above $(\pi(N+2)-1+R)$ equations are to be solved for the $(\pi(N+2)-1+R)$ unknowns, namely $(\pi) \alpha_k$'s, $(\pi-1) \theta_k$'s, $(N.\pi) \mathbf{x}_{ik}$'s and $(R) \xi_m$'s. It is understood

that for non-reacting systems Equation (3.34) and the unknowns, ξ_m , are removed from the above set. It is also noted that at the final solution (i.e. at the point of minimum Gibbs free energy) the stability variables θ_{μ} will satisfy the following relation :

 $\theta_{k} = \ln (f_{ik}/f_{ir})$ (i = 1,...,N; k = 1,..., π ; k \neq r). (3.35)

3.6 ADVANTAGES OF THE PROPOSED FORMULATION

The proposed formulation provides an alternate approach for the minimum of the Gibbs free energy. Instead of testing the stability of the solution by adding a new phase, this test is performed simultaneously with the phase and chemical equilibria calculations.

The advantages of the proposed formulations are :

- (a) First, it provides a unified set of simultaneous equations that describe phase equilibrium, chemical equilibrium and the stability of the system.
- (b) Second, it provides a "cleaner" and conceptually simpler picture of the system under investigation.
- (c) Finally, it provides a better understanding of the phase behavior of a system because the appearance/disappearance of a phase in the P-T continuum can be readily followed.

Solution methods for the above equations for reacting and non-reacting systems will be the subject of next two chapters. The formulation presented in this chapter is particularly useful for solving three phase distillation towers. This will be discussed in detail in the later chapters.

3.7 SUMMARY

An alternative development of the stability criterion for multiphase systems has been presented which enables simultaneous computation of the stability and the isothermal-isobaric multiphase equilibrium computations for reacting and non-reacting systems.

CHAPTER 4

AN ACTIVE SET METHOD FOR THE CALCULATION OF PHASE STABILITY AND FLASH COMPUTATIONS

In this chapter, an algorithm based on an active set strategy is developed to solve the coupled nonlinear equations derived in the previous chapter. The algorithm updates all the phase compositions in a single loop and does not utilize two separate loops as done in Chapter 2 for two-phase flash computations. For an example problem, it is shown that the updating of the phase compositions in a single loop is more efficient. In addition, a new scheme to generate initial values for the variables is proposed. The effectiveness of the iterative proposed algorithm is demonstrated by solving a number of test problems. For a test problem, the number of thermodynamic evaluations which are required conventional alternate bv the approach of stability and flash calculations is compared with that of the proposed algorithm. The applications of the algorithm to multiphase equilibrium computations in hydrates and typical problems encountered in enhanced oil recovery schemes, supercritical extraction and chemical industry are illustrated.

4.1 PROPOSED ALGORITHM

The proposed algorithm for the multiphase multicomponent flash calculations is based on the formulation presented in the previous chapter. It uses the component mole fractions as the iterative variables. For convenience, let β_{μ} denote a two dimensional vector,

given by

$$\underline{\beta}_{k} = [\alpha_{k}, \theta_{k}]^{\mathrm{T}} \qquad (k = 1, ..., \pi; k \neq r)$$
(4.1)

and,

$$\boldsymbol{\beta}_{r} = [\boldsymbol{\alpha}_{r}, \boldsymbol{0}]^{\mathrm{T}}. \tag{4.2}$$

Namely, it is assumed that the reference phase is always present. The system of $\pi(N+2)$ -1 equations is partitioned into two groups. For given K-factors, the system of Equations (3.25), (3.24) and (3.32) is solved iteratively in an inner loop. Subsequently, using Equation (3.26) and (3.31), all the component mole fractions are obtained in an outer loop. An accelerated successive substitution method, given in Chapter 2 for the two phase equilibrium flash calculations, is utilized for updating the mole fractions. The proposed algorithm is shown in Figure 4.1.

Inner loop of the proposed algorithm

In the inner loop of the proposed algorithm, Equations (3.25), (3.24) and (3.32) are solved for the 2π -1 unknown elements of β . It is proposed that the stability equations, Equation (3.32), be solved using an active set strategy. This would require that one of the elements of β_k (either α_k or θ_k) be set to zero and the other element can be calculated from the other equations. Hence, Equation (3.32) would be satisfied exactly at each iteration.

Using the active set strategy, the following procedure is adopted for solving the summation and the stability equations (Equations 3.25 and 3.32). Initially all the phases are assumed to be present, so all the stability variables, θ , are zero from Equation (3.32). Equations



Figure 4.1 : Computational Flow Diagram of the Algorithm

(3.25) and (3.24) are then solved for the phase fractions, α . In case one of the phase fractions becomes negative it is set to zero and the corresponding value of the stability variable is calculated from Equation (3.25).

The solution of Equations (3.25) and (3.24) for the phase fractions, α , is obtained by nonlinear Gauss-Seidel procedure (Dahlquist and Bjorck, 1974). This solution procedure assumes that each of the S_k (given by Equation 3.25) is a function of only θ_k and α_k . Hence, only one of the Equations (3.25) can be solved at a time for the unknown variable. The iterative process is repeated until either the convergence is obtained on the correction vector or the predefined number of iterations have been exceeded.

The procedure outlined above for calculating phase fractions often converges in a few iterations, typically less than five. However, if convergence has not been obtained within eleven iterations, we switch over to the Newton-Raphson method where all phase fractions are computed simultaneously. The use of Newton-Raphson is often required for systems where the interactions between the phase fractions are very strong. In addition, by implementing the Jacobian the problem of ill-conditioning is readily solved by removing the dependent rows using Gram-Schmidt orthogonalization (Henley and Rosen, 1969). The changes in the phase fractions for the rows which are removed are The set to zero. Newton-Raphson procedure is repeated until all the S_{μ} for the phases present are within a predefined tolerance.

Outer loop of the proposed algorithm

In the outer loop of the proposed algorithm, the component mole fractions for all the π phases are converged upon. Note that in Figure 4.1 all the phase compositions are updated in a single loop and separate loops, as in Chapter 2, for updating the phase compositions are not utilized. The phase compositions are updated by first calculating the component mole fractions for the reference phase using Equation (3.26). Subsequently, component mole fractions for the other π -1 phases are obtained using Equation (3.31). The θ values required in Equation (3.31) will be zero for the phases which are present. The θ values for the phases which are absent ($\alpha_{\rm k} = 0$) are obtained from Equation (3.25), which on rearrangement gives,

$$e^{\theta_{k}} = \frac{\sum_{i=1}^{N} z_{i} / D_{i}}{\sum_{i=1}^{N} K_{ik} z_{i} / D_{i}} . \qquad (4.3)$$

It may be noted that either θ_k or α_k in D_i will be zero. Now using Equation (3.26), we can write Equation (4.3) as

$$e^{\theta_{k}} = 1 / \sum_{i=1}^{N} K_{ik} x_{ir}.$$
(4.4)

It is noted that for the phases which are absent the calculation of component mole fractions using Equations (3.31) and (4.4) is equivalent to calculating the mole fractions with θ equal to zero in Equation (3.31) and then normalizing them.

The updating procedure of the compositions in each phase is similar to the ones used in Chapter 2, i.e., we obtain the function,

$$\mathbf{F}_{j}^{(U)} = \mathbf{x}_{j}^{(U)} - \bar{\mathbf{x}}_{j}^{(U)} \qquad (j = 1,...\pi)$$
(4.5)

where, \mathbf{F}_{j} is the difference between the assumed and the calculated values of the mole fraction vector in phase j. The component mole fractions are updated by

$$\hat{\mathbf{x}}_{j}^{(U)} = (1 - \omega_{j}) \, \mathbf{x}_{j}^{(U)} + \omega_{j} \, \bar{\mathbf{x}}_{j}^{(U)} \qquad (j = 1, ... \pi)$$
(4.6)

The iterative calculations for the component mole fractions are considered to be converged when all the average absolute errors defined by

$$\mathbf{e}_{j} = \sum_{i=1}^{N} |\mathbf{F}_{ij}| / \mathbf{N} \quad (j = 1, ...\pi)$$
 (4.7)

are within a prescribed limit, ε .

The acceleration factor for phase j, ω_j , can again be related to the dominant eigenvalue of the iteration matrix and for the convergent iterative scheme it is given by

$$\omega_{j} = \frac{1}{1 - \Lambda_{j}} \tag{4.8}$$

where

$$A_{j} = \frac{e_{j}^{(0)}}{e_{j}^{(0-1)}}.$$
(4.9)

If the iterative process is convergent, the acceleration is applied

after every two steps of successive substitution to obtain the new values of the component mole fractions.

Once all the component mole fractions are obtained, new values of the fugacity coefficients, ϕ_{ij} , are obtained using the thermodynamic model employed. New values of K_{ij} are then obtained using Equation (3.30).

Collapsing phases

In the iterative computations in the outer loop, some of the phases which appear in the solution may have the same compositions and compressibilities as some of the other phases. The phase fractions of these phases are added together to decrease the number of phases. Subsequent computations are performed only for the distinct phases.

4.2 INITIALIZATION OF THE PROPOSED ALGORITHM

A good initial estimate of the phase fractions and component mole fractions is required for the flash calculations. Here, it is proposed that the distance between the tangent plane and the surface of the Gibbs free energy of mixing should be used as a criterion to select the $(\pi-1)$ set of equilibrium ratios from the N sets of equilibrium ratios which are generated using the method suggested by Michelsen (1982a). The unknown variables viz. the phase fractions and the component mole fractions can then be initialized using Equations (3.25), (3.26), (3.31) and (3.24) with all the stability variables, θ , equal to zero.

The initial estimates of the equilibrium ratios are obtained by following the procedure given below:

Step 1 : Obtain the ideal equilibrium ratios from the Wilson equation

$$\ln K_{ij} = \ln(p_{ci}/p) + 5.373 (1.0 + w_i)(1.0 - T_{ci}/T). \quad (4.10)$$

Step 2 : Calculate the maximum and the minimum pressure which would generate a two phase vapor-liquid split using the ideal equilibrium ratios. If the specified pressure p satisfies $p_{min} , set <math>p^{\#}$ equal to p and go to Step 4.

Step 3 : Obtain the ideal equilibrium ratios from the Wilson equation at $p^{\#}$ such that $p^{\#}$ satisfies $p_{min} < p^{\#} < p_{max}$.

Step 4 : Perform a two phase vapor-liquid equilibrium flash calculation at p[#].

Step 5 : Choose vapor as the reference phase. Obtain N sets of estimates of the equilibrium ratios using the following equation which was suggested by Michelsen (1982a) for initiating stability calculations,

$$K_{ij} = \phi_{ir} / \phi_{ij}^*$$
 (i = 1,...,N; j = 1,...,N) (4.11)

where ϕ_{ij}^{*} is the fugacity coefficient of the pure component i (i.e. components other than component i are present in an infinitesimal amount). All the fugacity coefficients, ϕ_{ij} are calculated in liquid states in Equation (4.11).

Step 6: For the selection of the equilibrium ratios for the liquid phase m (m = 1,..., π -1), calculate d_i using

$$d_{i} = \frac{K_{ii}}{\frac{m-1}{\prod_{k=1}^{m-1} K_{ki}}} z_{i} \phi_{i1}(z) / \phi_{iv}(z) \quad (i = 1,...,N). \quad (4.12)$$

The set of equilibrium ratios which have the highest value of d_i is used to initialize the equilibrium ratios for the phase m (Appendix B). Step 6 is repeated for all the π -1 phases.

After $(\pi-1)$ sets of the equilibrium ratios are chosen, the phase fractions and the component mole fractions for the $\pi-1$ liquid phases are then generated. The following procedure is used for this purpose :

Step 1 : Assume vapor as the reference phase and the values of liquid phase fractions equal to zero.

Step 2 : Calculate phase fraction, α_j , using Equation (3.25) for all the π -1 liquid phases by assuming θ_j to be zero. If negative value of α_j is obtained, set α_j equal to zero and calculate θ_j using Equation (3.25).

Step 3 : Calculate component mole fractions, x_j , using Equation (3.31). In this calculation, the component mole fractions of the reference vapor phase are assumed to be those obtained in Step 1 of the algorithm for generating the equilibrium ratios.

Step 4 : Calculate equilibrium ratios, K_{j} , using Equation (3.30).

4.3 EVALUATION OF THE PROPOSED ALGORITHM

The proposed algorithm was evaluated through a number of test cases and the results of some typical problems are presented herewith. The compositions of the four test mixtures are given in Tables 4.1. The Peng-Robinson equation of state (1976) was used to model the phases for Mixtures A, B and C and the Soave-Redlich-Kwong (Soave, 1972) equation of state for Mixture D.

Component		Mole Perce	ent	
_	Mixture A	Mixture B	Mixture C	Mixture D
N ₂	-	0.10	0.08	30.40
CO	10.00	78.95	63.16	-
CH	86.08	3.44	2.752	54.79
C ₂ H ₆	2.47	0.85	0.68	7.08
C ₃ H ₈	0.67	0.63	0.504	3.67
i-C ₄ H ₁₀	-	0.08	0.064	-
n-C ₄ H ₁₀	0.45	0.69	0.552	2.08
i-C ₅ H ₁₂	-	0.33	0.264	-
n-C ₅ H ₁₂	0.24	0.45	0.360	1.98
n-C ₆ H ₁₂	0.09	-	-	-
C6 ⁺	-	14.48	11.584	-
H ₂ O	-	-	20.000	-

Table 4.1 : Compositions of Test Mixtures

.

The solution was considered to be converged when the residuals defined by Equation (3.25) and the errors as defined in Equation (4.7) are less than 1×10^{-6} and 1×10^{-7} respectively.

4.3.1 Updating the Compositions in a Single Loop (Mixture A)

In Chapter 2, the liquid and the vapor phase compositions are updated and accelerated in two separate loops. This example shows how the number of thermodynamic evaluations is affected by updating the phase compositions in a single loop rather than in two separate loops.

Flash computations were performed on a seven component mixture of a typical natural gas of compositions given in Table 4.1 at various pressures and temperatures. This mixture was studied in Chapter 2 and hence we decided to compare the performance of the proposed algorithm with the results obtained previously. Table 4.2 shows the number of thermodynamic evaluations required for convergence with the algorithm with a single loop at various pressures and temperatures. A tolerance of 1×10^{-6} was utilized in the outer loop. The results are compared with those obtained using two loops for updating and accelerating the phase compositions (from Table 2.6 with Acc-SS-xy method). Except for the first point, the number of thermodynamic evaluations which are necessary for the algorithm with one loop are less than those required by the algorithm which utilizes two separate loops for updating and accelerating phase compositions.

Hence, for all the multiphase flash problems a single loop is utilized for updating and accelerating phase compositions.

Point	Pressure	Temperature	Evaluat	ions
	(kPa)	(K)	Two Loops	Single Loop
1	6890	220.22	29	64
2		230.35	30	17
3	6080	211.92	73	26
4		235.03	21	16
5	5066	202.23	25	16
6		204.67	25	19
7		235.84	17	14
8	2027	170.29	13	12
9		173.20	12	11
10		220.15	12	10

Table 4.2 : Number of Thermodynamic Evaluations for the selected pointsfor Mixture A using one and two loops for updating phasecompositions

.
4.3.2 Comparison with Conventional Method of Alternate Stability and Flash Calculations (Mixture B)

The compositions of a reservoir oil, shown in Table 4.1 as Mixture B, has been studied by Mehra et al. (1982). This mixture is rich in carbon dioxide and shows three phases at certain conditions (Shelton and Yarborough, 1977).

Flash calculations were carried out for this system at 25° C and The various pressures. equilibrium phase fractions calculated bv specifying three phases are summarized in Table 4.3 and also shown in Figure 4.2. It is noted that the phase fractions of the phases which were found to be absent were obtained as zero. The values of θ for the absent phases are also given in the table. As seen, the θ value for the absent phase is positive, indicating that the phase is unstable compared with any of the phases which are present.

The number of thermodynamic evaluations which are required by the present method is compared with those required by the conventional method of performing alternate stability and flash calculations. The results are given in Table 4.4. The computational procedure utilized for the alternate stability and flash calculations is as follows:

Step 1 : Test the stability of the feed in the liquid state with respect to a new phase in the vapor state. The required equilibrium ratios for this calculation are obtained using the Wilson equation. If feed is found to be unstable, go to Step 3.

Step 2 : Test the stability of the feed in the liquid state with respect to a new phase in the liquid state. To perform this stability test, two sets of equilibrium ratios corresponding to the lightest and the heaviest hydrocarbon in the mixture are provided from the ratios generated using Michelsen (1982a) method. If the feed is found to be stable, only one phase exists.

Step 3 : Perform a two phase flash calculations.

Step 4 : Test the stability of each of the generated phases of the two phase flash solution until either one of the phases is found to be unstable or all the constituent phases are found to be stable.

Step 5 : If in Step 4 one of the phases is found to be unstable, perform a three phase flash calculations.

Step 6 : If both the phases of the two phase flash solution are found to be stable, then only two phases exist in equilibrium.

Table 4.4 shows that by performing the stability and the flash calculations simultaneously the required thermodynamic evaluations are approximately reduced by at least half when compared to the conventional method. Here, it should be noted that the acceleration procedure as used in the simultaneous calculations is used in both the stability and the flash computations of the conventional algorithm. Compositions of the three phases obtained at 25° C and 7100 kPa are given in Table 4.5. The phase fractions and their compressibility factors are also shown in the table.



Figure 4.2 : Phase Fractions for Mixture B AT 25 C

Point	Pressure	sure Phase Fraction			θ For	
	(kPa)	Vapor	Hydrocarbon Rich Liquid	CO ₂ Rich Liquid	The Absent Phase [#]	
1	6500	0.6087	0.3913	0	0.0077	
2	6600	0.6033	0.3967	0	0.0040	
3	6700	0.5983	0.4017	0	0.0006	
4	6800	0.4749	0.3994	0.1257	-	
5	6900	0.3300	0.3963	0.2737	-	
6	7000	0.1952	0.3939	0.4109	-	
7	7100	0.0692	0.3921	0.5387	-	
8	7200	0	0.3915	0.6085	0.0011	
9	7300	0	0.3920	0.6080	*	
* Vap	or phase sam	ne as CO ₂	rich liquid			
# Nun	nber of pha	ses specified	= 3.			

Table 4.3 : Calculated Equilibrium Phase Fractions at 25^oC for Mixture B

Table 4.4 : Number of Thermodynamic Evaluations for Mix	ture	B
---	------	---

Point	Phases Specified $= 3$				
	Simultaneous	Conventional			
1	27	51			
2	28	52			
3	28	54			
4	24	71			
5	24	74			
6	23	58			
7	22	63			
8	28	56			
9	36	75			

Component			
	Vapor	Liquid	Liquid
N ₂	0.2615	0.04320	0.1207
CO2	90.7102	58.1383	92.5879
CH4	6.7462	2.1350	3.9654
C ₂ H ₆	1.0033	0.7339	0.9148
C ₃ H ₈	0.5133	0.6318	0.6436
i-C ₄ H ₁₀	0.0519	0.0849	0.0801
n-C ₄ H ₁₀	0.3867	0.7826	0.6615
i-C ₂ H ₁₂	0.1431	0.3977	0.3047
n-C ₅ H ₁₂	0.1756	0.5618	0.4039
C6 ⁺	0.0083	36.4908	0.3174
Phase Fractions	0.0692	0.3921	0.5387
Compressibility Factor	0.4428	0.3855	0.2150

Table 4.5 : Calculated compositions of the various phases at 25° C and 7100 kPa for Mixture B



Figure 4.3 : Phase Fractions for Mixture C at 25 C

Pressure	ssure Phase Fraction						θ For
(kPa)	Vapor		Liquid		Ν	N	The Absent
	H	(ydrocarboi	n CO ₂	Water		·	Phase [#]
6500	0.4873	0.3132	0	0.1995	7	23	0.0047
6600	0.4830	0.3175	0	0.1995	7	24	0.0009
6700	0.3943	0.3161	0.0904	0.1992	7	24	-
6800	0.2831	0.3136	0.2045	0.1988	7	24	-
6900	0.1821	0.3117	0.3077	0.1985	7	24	-
7000	0.0903	0.3103	0.4012	0.1982	7	23	-
7100	0.0054	0.3092	0.4874	0.1980	7	24	-
7200	0	0.3095	0.4925	0.1980	7	23	0.0026
7300	0	0.3099	0.4921	0.1980	15	31	*

Table 4.6 : Four Phase Calculations For Mixture C at $25^{\circ}C$

* Vapor phase same as CO_2 rich liquid

N : Total Number of Iterations

 N_t : Number of Thermodynamic Evaluations

Phases Specified = 4

Component		rcent			
	Vapor	Liquid	Liquid	Liquid	
N ₂	0.3001	0.0484	0.1301	0.0000	
CO2	89.9410	57.5136	92.0085	0.2446	
CH4	7.3467	2.2901	4.1124	0.0000	
C ₂ H ₆	1.0198	0.7443	0.9118	0.0000	
C ₃ H ₈	0.5038	0.6250	0.6320	0.0000	
i-C ₄ H ₁₀	0.0500	0.0830	0.0781	0.0000	
n-C ₄ H ₁₀	0.3699	0.7619	0.6451	0.0000	
i-C ₅ H ₁₂	0.1348	0.3844	0.2963	0.0000	
n-C ₅ H ₁₂	0.1647	0.5417	0.3931	0.0000	
C6 ⁺	0.0074	36.9265	0.3448	0.0000	
H ₂ O	0.1618	0.0811	0.4478	99.7554	
Phase Fractions	0.0054	0.3092	0.4874	0.1980	
Compressibility Factor	0.4534	0.3882	0.2087	0.06078	

Table 4.7 : Calculated compositions of the various phases at 25°C and7100 kPa for Mixture C

Pressure	Temperature	Phase Fraction					θ For
(kPa)	(°C)	Vapor Liquid		Liquid			The Absent
					Ν	\mathbf{N}_{t}	Phase
4053	-121.45	0.0524	0.7931	0.1545	54	115	
	-122.25	0	0.5388	0.4612	40	106	0.0008
6129	-104.15	0.0001	0.6580	0.3419	77	179	-

Table 4.8 : Three Phase Calculations For Mixture D

N : Total Number of Iterations

N_t: Number of Thermodynamic Evaluations

Phases Specified = 3

Table 4.9 : Compositions of the various phases at -105.15^oC and 6129 kPa for Mixture D

Component			
	Vapor	Liquid	Liquid
N ₂	48.2718	22.5853	45.4377
CH4	49.1900	56.6382	51.2336
C ₂ H ₆	1.9970	9.4558	2.5083
C ₃ H ₈	0.4122	5.2671	0.5967
n-C ₄ H ₁₀	0.0941	3.0796	0.1566
n-C ₅ H ₁₂	0.0349	2.9741	0.0672
Phase Fractions	0.0001	0.6580	0.3419
Compressibility			
Factor	0.3515	0.2297	0.3190

4.3.3 Numerical Examples

A Four Phase Example (Mixture C) :

Mixture C is a mixture of water and hydrocarbons and was studied by Mehra et al. (1982). Such systems can form four phases in petroleum reservoirs. The mixture was flashed at 25° C and various pressures. The results are summarized in Table 4.6 and Figure 4.3, and the compositions of the coexistent phases at 25° C and 7100 kPa are given in Table 4.7. As seen, a right number of phases is predicted and the final convergence is obtained in a reasonable number of iterations.

A Three Phase Example (Mixture D) :

Mixture D, a nitrogen-rich light hydrocarbon mixture, has been studied by Michelsen (1982b) using Soave-Redlich-Kwong (Soave, 1972). This mixture shows highly complex behavior and has two separate narrow three-phase regions and its pressure-temperature phase envelope has been reported by Michelsen (1982b). In this work the mixture is flashed at the same three conditions of pressure and temperature as those reported by Michelsen. The results are summarized in Table 4.8. The compositions, phase fraction and the compressibility factors for the three coexistent phases at -104.15°C and 6129 kPa are given in Table 4.9. As seen from Table 4.8, the final solution is obtained in all the cases studied. The solution. however, larger number of iterations requires and thermodynamic evaluations as compared with Mixture B and Mixture C.

4.3.4 Discussion of Results

A comparison of the proposed computational scheme with the conventional method of performing alternate phase stability and the

flash calculations shows that for Mixture B a savings of fifty percent or more can be effected in the computational effort. This computational efficiency is expected since no individual subproblems need be converged. For example, for a system in which three phases are present, the conventional algorithm would converge a two phase subproblem only later to find that the two phase solution is not stable and then would perform a three phase flash calculations. The proposed computational scheme would simultaneously calculate the compositions and the phase fractions for all the three phases. The information which we obtain regarding the stability of the solution obtained is the same in both the cases. It should be noted, that the procedure suggested by Michelsen (1982a) for determining the stability of a phase or of a flash solution can be obtained using the proposed algorithm. In this case, the phase for the new phase would be specified fraction as zero and the corresponding theta for the phase would be calculated.

The proposed algorithm is able to solve the problems which exhibit a narrow three phase region on the pressure-temperature plane and the differences in the Gibbs free energy between different minima are extremely small (sometimes of the order of 10^{-10}). Michelsen (1982b) had to use the second-order minimization algorithm of Murray (1972) to achieve convergence on the problems studied for Mixture D.

4.4 APPLICATIONS OF THE ALGORITHM

The application of the algorithm for simultaneously performing multiphase flash and phase stability calculations is illustrated by solving a number of typical phase equilibrium problems. It is applied to compute the phase behavior of six ternary systems (Gupta and Bishnoi, 1989). These systems are typically encountered in enhanced oil recovery (EOR) schemes, cryogenic processing of natural gases and dehydration of alcohol using carbon dioxide at elevated pressures. In addition, the algorithm is utilized for the isothermal-isobaric flash computations for systems containing solid hydrates in presence of other fluid phases.

A recently proposed Trebble-Bishnoi equation of state has been used to model all the fluid phases, with the binary interaction parameters obtained either from the vapor-liquid equilibrium or liquid-liquid equilibrium data. The interaction parameters for the binary mixtures are presented in Table 4.10. They are either regressed using vapor-liquid or liquid-liquid equilibrium data obtained from the literature. The or experimental data for two of the binary systems are not available in the literature, hence, for these systems the parameters evaluated using similar systems have been used.

4.4.1 Enhanced Oil Recovery Applications

In the EOR schemes, it is important to know the effect of nitrogen and propane on the phase behavior of the reservoir fluid. Hence, two mixtures are considered - a ternary system of carbon dioxide, nitrogen and n-nonadecane and a system of carbon dioxide, propane and nonadecane.

In Figure 4.4, the experimental liquid-liquid-vapor (LLV) compositions (Fall and Luks, 1986) at 21° C and various pressures for the mixture of carbon dioxide, nitrogen and n-nonadecane are compared with those calculated. The compositions are calculated by repeated flash computations. Figure 4.4 shows an excellent agreement between the experimental and the calculated compositions for the three phases.

Components	Ka	Kb	Kc	Kd	Data or Parameter Source
Carbon dioxide - n-Nonadecane	0	0	0.1	0	Fallet al. (1985)
Carbon dioxide - Nitrogen	0	0 1241	0.1	0	Vorizane et al. (1985)
Nitrogen - n-Nonadecane ¹	0	0	0.3156	0.0721	Sultonov et al. (1972), Makranczy et al. (1976), Tremper & Prausnitz (1976)
Carbon dioxide - Propane	0.1459	0.0243	0	0	Trebble & Bishnoi (1988)
Propane - n-Nonadecane ²	0	0	0.2517	0.0517	Chapplow & Prausnitz (1974), Ng et al. (1969)
Nitrogen - Methane	0.0289	0	0	0	Kidnay et al. (1975)
Methane - Propane	-0.0135	0	0	0	Trebble & Bishnoi (1988)
Nitrogen - Propane	-0.075	0	0	0.1433	Llave et al. (1985)
Methane - n-Hexane	-0.025	0	0	0	Merill et al. (1984)
Nitrogen - n-Hexane	0.0572	0	0	-0.1434	Poston & Mcketta (1966)
Ethanol - Water	0	0.0885	0	0	Trebble & Bishnoi (1988)
Ethanol - Carbon dioxide	0.0670	0	0	0	Panagiotopoulos & Reid (1987)
Carbon dioxide - Water	0	0	0	-0.1652	Englezos (1990)
2-Propanol - Water	0	0.1330	0	0	DaSie (1988)
2-Propanol - Carbon dioxide	0.0900	0	0	0	Radosz (1986)

Table 4.10 : Binary interactions parameters for Trebble-Bishnoi Equation of State (1988)

1) For nitrogen - n-hexadecane system 2) For propane - eicosane system



Figure 4.4 : Phase Compositions for the liquid-liquid-vapor region of CO2 + nitrogen + n-nonadecane at 21 C



Pressure		Phase Fra	θ For	
(kPa)	Vapor	CO ₂ Rich Liquid	Hydrocarbon Rich Liquid	The Absent Phase
		Rich Liquid	Kiel Liquid	
5000	0.8879	0.1121	0	0.0711
5600	0.8730	0.1270	0	0.0213
6200	0.0331	0.8370	0.1299	-
	Pressure (kPa) 5000 5600 6200	Pressure (kPa) Vapor 5000 0.8879 5600 0.8730 6200 0.0331	Pressure (kPa) Vapor Phase Fra CO ₂ Rich Liquid 5000 0.8879 0.1121 5600 0.8730 0.1270 6200 0.0331 0.8370	Pressure (kPa)VaporPhase Fraction CO2 Rich LiquidHydrocarbon Rich Liquid50000.88790.1121056000.87300.1270062000.03310.83700.1299

Table 4.11 : Three Phase Calculations For the mixture of carbon dioxide, nitrogen and n-nonadecane at 21⁰C



Figure 4.6 : Phase Compositions for the liquid-liquid-vapor region of CO2 + propane + n-nonadecane at 24 C



Figure 4.7 : Molar volume for the liquid—liquid—vapor region of CO2 + propane + n—nonadecane at 24 C

Figure 4.5 compares the experimental and the calculated molar volumes for the mixture of carbon dioxide, nitrogen and n-nonadecane. The predictions for the molar volumes are within 3.4%, 3.4% and 1.8% of the experimental values for the vapor and the two liquid phases.

The results of flashing the mixture of carbon dioxide, nitrogen and n-nonadecane having a feed composition of 95 mole percent carbon dioxide and 4 mole percent nonadecane at 21° C and three pressures are summarized in Table 4.11. The equilibrium phase fractions calculated for the phases which are present and the values of θ for the absent phase are given in the table. As seen, the theta value for the absent phase is positive, indicating that the phase is unstable. The final convergence was obtained within 14 iterations and 37 thermodynamic evaluations for all the three conditions shown.

Figure 4.6 compares the calculated compositions of the three phases with the experimental values (Fall and Luks, 1986) for the mixture of carbon dioxide, propane and nonadecane. The convergence is obtained in 16 iterations except at 6000 kPa where 31 iterations are required. Good agreement between the calculated and the experimental phase compositions is obtained.

The experimental and the calculated molar volumes for the mixture of carbon dioxide, propane and nonadecane are compared in Figure 4.7. The predictions are within 1.6%, 8.6% and 6.3% of the experimental values for the two liquid and the vapor phases.

4.4.2 Cryogenic Natural Gas Applications

The multiphase flash algorithm is utilized to predict the LLV phase and volumetric behavior of two ternary prototype liquefied natural gas



,

Figure 4.8 : Phase Compositions for the liquid—liquid—vapor region of methane + nitrogen + propane at -152.15 C



74







Figure 4.11 : Molar volume for the liquid—liquid—vapor region of methane + nitrogen + n—hexane at

(LNG) systems. The systems studied are - mixture of methane, propane and nitrogen and mixture of methane, n-hexane and nitrogen. Both mixtures contain nitrogen, which is known to induce LLV behavior in LNG systems (Luks et al., 1983).

The experimental phase compositions (Llave et al., 1987) for the mixture of methane, propane and nitrogen at -152.15° C and various pressures are compared with the predicted values in Figure 4.8. The calculated curves are obtained by repeated flash calculations, and the converged solution, in each case, is obtained in approximately 10 iterations and requires approximately 30 thermodynamic evaluations.

Figure 4.9 compares the experimental and the predicted molar volumes for the two liquid phases. As seen, the calculated and the experimental molar volumes are in good agreement (within 1.7% and 2.9%). The calculated vapor phase molar volumes are also shown. The corresponding experimental data, however, are not available.

The experimental (Merrill et al., 1984) and the calculated phase compositions for the mixture of methane, n-hexane and nitrogen at -103.15° C and various pressures is presented in Figure 4.10. The multiphase flash algorithm approximately required 15 iterations and 38 thermodynamic evaluations to converge to the solution.

Figure 4.11 presents the predicted and the experimental molar volumes at -103.15° C and various pressures for the mixture of methane, n-hexane and nitrogen. The experimental vapor volumes are not available. The predicted liquid volumes are within 7.0% and 2.2% of the experimental values. At 4900 kPa the two liquid phases have molar volumes which are close. Also, note the reversal in the calculated





Component		Mole Percent					
	Feed	Vapor	Liquid	Liquid			
Ethanol	25.00	0.4461	47.3317	11.6436			
CO,	70.00	99.4635	42.1804	86.8645			
Water	5.00	0.0904	10.4879	1.4919			
Phase Fractions		0.0995	0.4055	0.4950			
Molar Volur (m ³ /m	nes * 10 ⁶ ol)	245.04	44.27	47.86			

Table 4.12 : Compositions of the various phases at 26°C and 5670 kPafor Ethanol, Water and Carbon dioxide System

,

densities for the two liquid phases.

4.4.3 Applications to Chemical Industry

In chemical industry. multiphase behavior can occur in the highly supercritical-fluid extraction. when compressible fluids are utilized for separation around the critical region of the extractant. One potential application of the supercritical fluid extraction is the separation of the alcohols from dilute aqueous solutions. We correlate and predict some of the experimental results for separation of ethanol from water and 2-propanol from water using supercritical carbon dioxide.

calculated Figure 4.12 presents the and the experimental (Panagiotopoulos and Reid, 1987) compositions for the carbon dioxide-ethanol temperatures. binary three As seen. excellent at agreement is obtained between the experimental and the calculated compositions, except in the critical region for the 64.95^oC isotherm.

In Figure 4.13, the experimental data of Gilbert and Paulaitis (1986) for ethanol, water and carbon dioxide system is presented at 35° C which is close to the critical temperature of carbon dioxide. The continuous line, shown in the figure represent the predictions obtained by repeated flash calculations. As seen from Figure 4.13, the predicted compositions are generally in excellent agreement with the experimental measurements except at higher ethanol concentrations in the ethanol rich phase.

Table 4.12 presents the calculated three phase compositions for the ternary of ethanol, water and carbon dioxide at $26^{\circ}C$ and 5670 kPa. The phase fractions and the molar volumes are also shown in the table. No experimental equilibrium LLV composition data for this system exists in



. .



Figure 4.15 : Phase Equilibria of water, carbon dioxide and 2-propanol at 60 C

Shavarts Efremova the literature. However. and (1970) measured which gas-liquid and liquid-liquid critical end points bound the gas-liquid-liquid three phase region and observed a tricritical point at 47.4°C and 9170 kPa. The LLV separation in ethanol-water system in the presence of compressed carbon dioxide represents an alternative method which can be utilized for dehydrating ethanol (Paulaitis et al., 1984). The algorithm converged to the three phase solution in 63 iterations even though the three phase region is very narrow. Hence, the algorithm may be utilized for studying the alternative separation scheme for dehydrating ethanol.

The calculated and the experimental binary vapor-liquid equilibrium data for 2-propanol and carbon dioxide are shown in Figure 4.14 at four temperatures (Radosz, 1986). As seen, there is a good agreement between the calculated and the experimental compositions except at high pressures where EOS predicts less solubility of carbon dioxide in the liquid phase than those measured experimentally.

Phase compositions for the LLV equilibrium for the water, 2-propanol and carbon dioxide at 60° C and three pressures are shown in Figure 4.15. Experimental data points are the measurements reported by DiAndreth et al. (1987), and vertices of the triangles are the calculated compositions of the three phases. As seen, the calculated three phase region is much larger than the one obtained experimentally.

4.4.4 APPLICATION TO SYSTEMS CONTAINING GAS HYDRATES

The algorithm is utilized to simultaneously examine five possible phases which could exist at equilibrium. These phases are hydrate structure I (HI), hydrate structure II (HII), aqueous liquid (La),

TABLE 4.13 : Equilibrium Phase Compositions (mol %) for a Mixture
containing 50, 49.9 and 0.1 mol % of H2O, CH4 and

Component	Pressure	v	La	Hı	Нп
CH	2.4	99.81	0.08		11.40
C,H,		0.16	0.00		1.91
H ₂ O		0.03	99.92		86.69
CH	3.7	99.94		14.30	13.16
C,H,		0.04		0.00	0.61
H ₂ O		0.02		85.70	86.23
CH	16.1	99.75		14.66	
C,H,		0.24		0.00	
H ₂ O		0.01		85.34	

с₃н₈.

Component	mol %
CH	13.00
C,H	10.00
ĊŢĤ	10.00
⋼ -ĊݛĤ	8.00
_□ -C H	4.00
□-C H	52.95
CO	2.00
N ₂	0.05

TABLE 4.14A :Condensate Composition

TABLE 4.14B : Feed Contents

Feed Mixture	m Condensate	o l e Water	s Methanol
A	100	60	-
В	100	60	3.6

Component	Vapor	Aqueous liquid	Hydrocarbon liquid	Hydrate II
CH	74.63	< 0.005	6.69	7.23
C,H,	15.92	< 0.005	10.18	0.57
ĊŢH	3.19	< 0.005	7.99	4.26
	0.96	< 0.005	8.88	-
	0.14	< 0.005	4.45	-
	0.53	< 0.005	59.01	-
CO	3.80	0.0017	2.00	0.13
N ₂	0.77	< 0.005	0.02	0.01
но́	0.06	99.9983	0.78	87.80

•

TABLE 4.15 : Equilibrium Phase Compositions (mol %) for FeedMixture A at 278 K and 1.7 MPa.

TABLE 4.16 : Equilibrium Phase Compositions (mol %) for FeedMixture B at 278 K and 2.9 MPa.

Component	Vapor	Aqueous liquid	Hydrocarbon liquid	Hydrate II
CH	82.15	< 0.005	12.30	8.44
C, H,	10.31	< 0.005	9.97	0.45
ĊŢĤ	2.77	< 0.005	9.73	4.21
n-C, H	0.66	< 0.005	8.02	-
	0.10	< 0.005	4.01	-
n-CZH	0.43	< 0.005	53.06	-
CO	2.47	< 0.005	1.99	0.09
N	1.04	< 0.005	0.05	0.02
НO	0.04	93.97	0.70	86.79
Снзон	0.03	6.03	0.17	-

hydrocarbon liquid (Lb) and vapor (V). The solid hydrates of structure I and II are treated as two separate solid solution phases and are described by the model of van der Waals and Platteeuw (1959). All fluid phases (vapor, aqueous liquid and hydrocarbon liquid) are described by the equation of state (EOS) of Trebble and Bishnoi (1988). Equation of interaction parameters for additional systems state are taken from Englezos (1990). The equilibrium distribution ratio for the solid hydrate phases is obtained using Equation (3.30) with the ϕ_{ii} (j=HI or HII) obtained from

$$\boldsymbol{\phi}_{ij} = \mathbf{f}_{ij} / (\mathbf{x}_{ij} \mathbf{P}), \tag{4.13}$$

where

$$\mathbf{x}_{ij} = \sum_{l} v_{l} \Theta_{li} / (1 + \sum_{m} v_{m} \sum_{k} \Theta_{mk}).$$
(4.14)

In Equation (4.13) the fugacity of water is obtained from the van der Waals - Platteeuw model (for further details see Englezos, 1990). For the other components in the hydrate, the fugacity is taken equal to the fugacity in the reference phase.

Two systems are studied : a *methane-propane-water* system and mixtures of *oil condensate* with water and methanol. These examples are taken from Bishnoi et al. (1989).

The calculated equilibrium phase compositions for the *methane-propane-water* system at 274 K and 2.3, 2.4 and 16.1 MPa are given in Table 4.13. At the pressure of 2.4 MPa, a vapor phase, an aqueous liquid phase and hydrate II is present. A further increase in pressure to 3.7 MPa, the aqueous liquid phase disappears and hydrate I is formed. At a still higher pressure of 16.1 MPa leads to the

disappearance of hydrate II phase.

For the system of gas condensate, two mixtures are considered. The composition of the condensate is given in Table 4.14A while the feed contents of the mixtures is presented in Table 4.14B. Tables 4.15 and 4.16 gives the calculated equilibrium compositions for these mixtures. Note that in both the tables, four phases are present. Furthermore, Feed B contains methanol which acts as a inhibitor for hydrate formation. Table 4.16 shows that aqueous rich liquid contains about 6 molar percent of methanol.

4.5 SUMMARY

An algorithm based on the alternative development of the stability criterion for multiphase systems is presented. The effect of updating and accelerating the phase compositions in a single loop on the required number of thermodynamic evaluations is examined. A new scheme for the initialization of the iterative variables is also proposed. The scheme utilizes the distance between the Gibbs free energy and the tangent hyperplane as a criterion to select the required equilibrium ratios for the $(\pi$ -1) phases.

The proposed algorithm is tested on a number of multiphase problems. A comparison of the number of the thermodynamic evaluations necessary by the proposed algorithm with the conventional method of performing alternate stability and flash calculations is made for a test example. The proposed algorithm leads to a computational savings of more than fifty percent.

The application of the algorithm is illustrated by solving typical problems encountered in enhanced oil recovery, natural gas processing
and petrochemical industry. The thermodynamic model employed for all the computations is the recently proposed Trebble-Bishnoi equation of state. The phase and volumetric behavior of six ternary systems are compared with the experimental data from the literature. Good agreement between the experimental and the calculated phase compositions and the molar volumes is obtained for most of the problems studied. In addition, applications of the algorithm to multiphase flash computations in systems containing gas hydrates is demonstrated.

The algorithm is found to be effective and efficient and hence, may be used to perform multiphase flash computations.

CHAPTER 5

A SIMULTANEOUS SOLUTION METHOD FOR THE CALCULATION OF PHASE STABILITY AND FLASH COMPUTATIONS

The algorithm presented in the previous chapter is modified so as to simultaneously solve the stability and the summation equations using the procedure. is utilized Newton-Raphson It to perform multiphase isothermal-isobaric flash computations in reactive and **non-re**active systems (Gupta et al., 1990a). In addition, the algorithm is extended for the isenthalpic flash computations in non-reacting systems (Gupta et al., 1990b). The effectiveness of the proposed calculation procedure is demonstrated by several examples.

5.1 ANALYSIS OF THE STABILITY EQUATION

The stability equation (Equation 3.32) requires for any phase k that either the phase fraction (α_k) or the stability variable (θ_k) or both must be zero. Equations (3.32) and (3.33) together require the solution to lie on either the non-negative α -axis or the non-negative θ -axis (Figure 5.1a). This implies that during the computations when the phase fraction becomes zero, the stability variable for the phase must become either a positive number for an unstable phase or zero for an incipient phase. Similarly, when the stability variable becomes zero, the phase fraction for the phase must become either a positive number for a stable phase or zero for an incipient phase. The non-linear Equations (3.32) and (3.33) do allow the appearance and the disappearance of a phase during the computations. Hence, Equations (3.32) and (3.33) permit "switching" of the solution from the α -axis to the θ -axis when a phase disappears and from the θ -axis to the α -axis when a phase appears.

For the simultaneous solution of the summation and stability equations it is necessary to linearize Equation (3.32). The linearized form of Equation (3.32), however, does not allow the switching of the solution between α and θ axes. Another problem with the linearized form of Equation (3.32) is that it would lead to a singular Jacobian when $\alpha_k = \theta_k = 0$. The problem of singularity in the Jacobian may occur during the iterations whenever both α_k and θ_k become equal to zero or at the final solution itself when an incipient phase is present. It should be noted that in a computer implementation, a phase would be considered incipient when one of the variables (α_{k}, θ_{k}) is zero and the other one is less than or equal to a small user specified tolerance (δ). In addition to the above two problems, when the solution or the path to the solution is near phase boundaries (i.e. when one of the variables α_k , θ_k is zero and the other has a very small value) the linearized form of Equation (3.32) ill-conditioned Jacobian which is yields an detrimental to the convergence of the solution.

The problems of "switching" of the solution between the α and θ axes, the singularity of the Jacobian at $\alpha_k = \theta_k = 0$, and the ill-conditioning of the Jacobian near the phase boundaries can readily be handled by "solving" the stability equations by partitioning the variables into an *active* and a *non-active* set. For example, if α_k is in the active set and during the computations becomes "zero" then α_k is placed in the non-active set and the corresponding θ_k is brought into the active set. We have utilized this strategy to solve multiphase problems in non-reacting systems in Chapter 4. In the present Chapter we propose an algorithm which allows the simultaneous solution of the

stability and summation equations. Such a development is important when wishes extend the solution algorithm one to to non-isothermal non-isobaric flash problems or to multiphase multistage equilibrium the simultaneous solution of the simulations. For summation and stability equations it is necessary to modify Equation (3.32) and the solution domain in order to overcome the above mentioned problems. Next, the modifications which are necessary for this purpose are given.

5.2 MODIFICATIONS REQUIRED FOR SIMULTANEOUS SOLUTION 5.2.1 Switching of the solution between the α and θ axes

The "switching" of the solution between the two axes can be accomplished by modifying the solution of Equation (3.32).In particular, we select a small positive number, ε , and whenever α becomes less or equal to ε while θ_k is zero, both α_k and θ_k are set equal to ε . In other words, the solution segment $[0,\varepsilon]$ on the α -axis is mapped into the point A $(\varepsilon,\varepsilon)$ shown in Figure 5.1b. Similarly, the solution segment $[0,\varepsilon]$ on the θ -axis is also mapped into the same point A. For a special case, when both α_k and θ_k are less than ε , then the solution remains at point A. The modification allows the switching of the solution between the axes. The suggested value of ε is 1.0 x 10⁻¹⁰ and it should always be less than the convergence tolerance. It is noted that at point A the linearized form of Equation (3.32) becomes

$$\Delta \alpha_{k} + \Delta \theta_{k} = -\varepsilon. \tag{5.1}$$

Using Equation (5.1) and non-negative conditions on α_k and θ_k (Equation 3.33) it can be shown that in the next iteration the solution would either lie on the α -axis, or on the θ -axis or remain at point A (Figure



(a) exact solution of $\alpha \theta = 0$







(c) incipient phase definition tolerance (δ) δ and ε should satisfy $\delta > \varepsilon \sqrt{2}$



5.1b). Hence, this would allow the solution to switch automatically between the α and the θ axes whenever necessary.

5.2.2 Singular Jacobian

The problem of singular Jacobian when $\alpha_k = \theta_k = 0$ is also overcome when the above technique is implemented for switching the axes. Namely, during the computations both α_k and θ_k would never become equal to zero since the small square region denoted by (0,0) and (ε,ε) is removed from the solution domain (see Figure 5.1b). In a case where an incipient phase is present the solution will converge either on the point (ε,ε) or on the α or θ axes in the interval [ε,δ] (see Figure 5.1c).

5.2.3 Ill-conditioned Jacobian

The problem of ill-conditioning of the Jacobian when either α_k or θ_k takes very small values is not overcome by the previous modification since ε is a very small number. The conditioning of Jacobian can be significantly improved by modifying Equation (3.32) to

$$\alpha_{\mathbf{k}} \theta_{\mathbf{k}} / (\alpha_{\mathbf{k}} + \theta_{\mathbf{k}}) = 0.$$
(5.2)

The modified stability equation (Equation 5.2) describes equivalently to Equation (3.32) the appearance and disappearance of a phase. The advantage of using Equation (5.2) is that its partial derivatives with respect to α_k or θ_k are either 0 or 1. The proposed technique developed for Equation (3.32) for switching the solution between the α and θ axes must also be used with the linearized form of Equation (5.2).

5.3 ISOTHERMAL-ISOBARIC SPECIFICATIONS FOR REACTIVE AND NON-REACTIVE SYSTEM

5.3.1 Proposed Algorithm

The proposed solution procedure is similar to the one presented in Chapter 4. It partitions the system of $(\pi(N+2)-1+R)$ equations into two groups. The summation, stability and chemical equilibrium equations are solved in an inner loop. Subsequently all the component mole fractions are obtained in an outer loop.

The proposed computational procedure modifies the inner loop of the algorithm as presented in Chapter 4. It solves the summation and the stability equations simultaneously utilizing the Newton-Raphson procedure rather than using the active set strategy. Previously, we have discussed the modifications which are required for this purpose. In particular, we had modified the stability equation and the solution domain so that it could be solved using the Newton-Raphson procedure.

For given values of fugacity coefficients, Equations (3.24), (3.25), fractions, α_{ν} , stability (5.2) and (3.34) are solved for phase variables, θ_{μ} , and extent of the reaction, ξ_{μ} . This computation is performed in the inner loop of the proposed algorithm. As mentioned before, the Newton-Raphson procedure is utilized for this purpose. The Jacobian obtained required matrix is analytically. The required derivatives are given in Appendix C. Subsequently, using Equations (3.26) and (3.31), all the component mole fractions are obtained and updated in an outer loop. The updating procedure of the mole fractions in each phase utilizes an acceleration factor based on the dominant eigenvalue of the iteration matrix, as described in Chapter 4. Once all the component mole fractions are updated, the new values of K_{ij} are obtained from Equation (3.16) and the thermodynamic model employed. The iterative calculations are considered to have converged when all the residuals in the Newton-Raphson procedure and the average absolute errors in the component mole fractions are within a prescribed limit, typically 1 x 10⁻⁶.

5.3.2 Evaluation of the Proposed Algorithm

The isothermal-isobaric flash algorithm is evaluated through a number of test cases and the results of two typical problems are presented here. The Trebble-Bishnoi equation of state (1988) is used to model all the phases.

Non-Reacting Systems

A Mixture of Methane-Carbon dioxide and Hydrogen Sulfide

The algorithm was applied to study a mixture of 49.89, 9.88 and 40.23 mole percent *methane*, carbon dioxide and hydrogen sulfide. Ng et al. (1985) obtained experimentally the two and three phase boundaries of this mixture and reported a narrow three phase region. Table 5.1 gives the calculated equilibrium phase compositions and phase fractions for this mixture. The temperatures selected are around the three phase boundary at 6060 kPa. At 212.05 K, two liquid phases are present and a vapor phase is just absent (θ is 6.9 x 10⁻⁶). The vapor phase appears with an increase in temperature. At 212.4 K, two liquid and a vapor phases are present. A further increase in temperature to 212.75 K leads to the disappearance of the methane-rich liquid (θ is 9.2 x 10⁻⁶).

TEMPERATURE		CH ₄	CO,	H ₂ S	PHASE
(K)	PHASE	•	2	2	FRACTION
212.05	VAPOR	87.35	6.45	6.20	0.0000
	LIQUID	18.65	10.97	70.38	0.4932
	LIQUID	80.29	8.82	10.89	0.5068
212.40	VAPOR	87.22	6.66	6.12	0.2656
	LIQUID	19.26	11.68	69.06	0.5238
	LIQUID	79.00	9.47	11.53	0.2106
212.75	VAPOR	87.12	6.84	6.04	0.4466
	LIQUID	19.84	12.33	67.83	0.5534
	LIQUID	77.86	10.05	12.09	0.0000
	FEED	49.89	9.88	40.23	

Table 5.1Equilibrium phase compositions (mol %) for the
CH4-CO2-H2S mixture at 6060 kPa



Figure 5.2 : Vapor Phase Fraction (a) and Stability Variable (0) during Iterations for the CO2-CH4-H2S Mixture at 6060 kPa and 212.05 K



Figure 5.3 : Phase Fraction (a) and Stability Variable O) during Iterations for the CO2-CH4-H2S Mixture at 6060 kPa and 212.75 K

The changes in the phase fraction and the stability variable for the vapor phase during the iterations at 212.05 K are shown in Figure 5.2. In the beginning, the phase fraction for the vapor phase is zero and the stability variable is non-zero. In the 8th iteration vapor phase appears and the stability variable becomes zero. After the 12th iteration, the vapor phase disappears and the stability variable for the vapor phase attains a non-zero positive value. The phase fractions for the two liquid phases are non-zero throughout the computations and hence are not shown.

In Figure 5.3 the phase fractions and the stability variables for the vapor and the methane-rich liquid at 212.75 K are shown. Initially only two liquid phases are present. Vapor phase appears in the 3rd iteration and methane-rich liquid disappears in the 7th iteration. Three phases are present between the 3rd and the 7th iterations.

It should be noted that at 212.05 K and 212.75 K, the value of the stability variable for the absent phase is positive at the solution, indicating that the computed equilibrium is stable. Also, as seen in the figures the appearance and disappearance of a phase during the computations is easily handled by the algorithm.

A Mixture of Ethanol-Ethyl acetate-Water

A three component mixture of 10.7, 30.1 and 59.2 mole percent ethanol, ethyl acetate and water is flashed at 101.32 kPa and various temperatures. This mixture has been studied by Soares et al. (1982). They obtained the phase splits by minimization of the Gibbs free energy of the system using the NRTL model for the liquid phases. In this study, modelled all the phases for the mixture we have using the

TEMPERATURE		ETHANOL	ETHYL	WATER	PHASE
(K)	PHASE		ACETATE		FRACTION
343.45	VAPOR	13.21	57.80	28.99	0.0000
	LIQUID1	9.76	22.46	67.78	0.7801
	LIQUID2	14.04	57.21	28.75	0.2199
343.46	VAPOR	13.30	57.72	28.98	0.1229
	LIQUID1	9.87	22.52	67.61	0.7825
	LIQUID2	14.15	56.96	28.89	0.0946
343.47	VAPOR	13.38	57.63	28.99	0.2158
	LIQUID1	9.96	22.52	67.52	0.7842
	LIQUID2	14.27	56.67	29.06	0.0000
 Experiment	al [*]				
	VAPOR	11.0	60.0	29.0	
	LIQUID1	9.8	9.9	80.3	
	LIQUID2	11.6	46.6	41.8	
	FEED	10.70	30.10	59.20	

Table 5.2 : Equilibrium phase compositions (mol %) for the
ethanol-ethylacetate-water mixture at 101.32 kPa

.

* Experimental Temperature is 343.42 K



Figure 5.4 : Vapor Fraction (a) and Stability Variable (0) during Iterations for the Ethanol-Ethyl acetate-Water Mixture at 101.32 kPa and 343.46 K



Figure 5.5 : Ethyl acetate Rich Liquid Fraction (a) and Stability Variable O) during Iterations for the Ethanol-Ethyl acetate-Water Mixture at 101.32 kPa and 343.46 K

Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1988). Table 5.2 gives the calculated compositions and phase fractions for this mixture. At 343.46 K, two liquid phases and a vapor phase are present. A slight decrease of temperature to 343.45 K leads to the disappearance of the vapor phase (θ is 3.6 x 10⁻⁴) while a small increase in temperature to 343.47 K leads to the disappearance of ethylacetate rich liquid (θ is 2.2 x 10⁻⁴). Note that in Table 5.2, the calculated compositions of the vapor and the ethyl acetate rich liquid are very similar. Zandijcke and Verhoeye (1974) have reported that this mixture shows an azeotrope at a composition of 11.5 mole percent ethanol and 59.5 mole percent ethyl acetate and a temperature of 343.35 K.

The compositions of the coexistent phases at 343.42 K and 101.32 kPa are compared with the experimental values of Zandijcke and Verhoeye (1974) in Table 5.2.

In Figures 5.4 and 5.5 the changes in the phase fractions and the stability variables during the iterations at 343.46 K are shown. Figure 5.4 shows that the phase fraction of the vapor phase is non-zero initially and the stability variable is zero. In the 5th iteration vapor phase disappears and the stability variable becomes non-zero. After the 6th iteration vapor phase reappears and the stability variable becomes zero. Figure 5.5 depicts the appearance and disappearance of ethyl during the computations. Initially, acetate rich liauid the phase fraction of the ethyl acetate liquid is zero and the stability variable is non-zero. In the 3rd iteration the ethyl acetate rich liquid appears, disappears in the 6th iteration and appears again in the 9th iteration. Finally, a solution in which both the vapor and ethyl acetate rich liquid are present is obtained.

As seen, the appearance and disappearance of a phase is easily handled for this system.

Reacting Systems

Mixtures of methane, carbon monoxide, hydrogen, carbon dioxide, water and n-octadecane are studied by utilizing the proposed algorithm. Formation of methanol is examined by considering the following two reactions :

 $\begin{array}{rll} \mathrm{CO} &+& 2\mathrm{H}_2 \ \Leftrightarrow \ \mathrm{CH}_3\mathrm{OH} \\ \mathrm{CO}_2 &+& \mathrm{H}_2 \ \Leftrightarrow \ \mathrm{CO} \ + \ \mathrm{H}_2\mathrm{O}. \end{array}$

Chemical equilibrium constants (K_{a}) for the reactions are calculated using the data given by Reid et al. (1987).

In Tables 5.3 and 5.4, the feed compositions and the calculated equilibrium phase compositions are shown. Castier et al. (1989) studied these mixtures at the conditions shown in the tables. In Table 5.3, the mixture does not contain n-octadecane. At equilibrium there are two phases, namely vapor and methanol-rich liquid. In Table 5.4, the mixture contains n-octadecane and results in three phases. The results shown in the tables are similar to those reported by Castier et al.

The feed mixture of Table 5.4 is also studied at 535 K and 20 MPa. The condition is chosen because one of the phases, the water-rich liquid, disappears during the computations. As shown in Table 5.5, a vapor phase and a hydrocarbon-rich liquid phase coexist while a water-rich liquid phase is absent (θ is 1.1 x 10⁻²). It is noted from the table that the extent of the second reaction, ξ_2 , is negative at these conditions, indicating that the reaction occurs in the reverse

COMPONENT	FEED	VAPOR	LIQUID
CH	3.00	9.15	1.56
CO	15.00	0.01	< 0.005
H ₂	74.00	66.93	4.02
co,	8.00	0.04	0.01
Сн он	0.00	20.40	67.09
H ₂ O	0.00	3.47	27.32
PHASE FRACT	ION	0.5258	0.4742
COMPRESSIBILITY FACTOR		1.0190	0.3006
MOLES	100.00	28.41	25.62

Table 5.3 : Equilibrium phase compositions (mol %) for

the reacting system at 473.15 K and 30 MPa

.

Note : $\xi_1 = 22.98$, and $\xi_2 = 7.98$.

COMPONENT	FEED	VAPOR	WATER RICH LIQUID	HC LIQUID
CH	2.14	6.08	0.24	1.03
co	10.71	0.11	< 0.005	0.01
H	52.86	58.13	0.52	5.32
co	5.71	4.51	0.20	1.70
Сн он	0.00	16.17	24.38	25.32
н _о	21.43	14.78	74.66	5.49
$C_{18}^{2}H_{38}$	7.15	0.22	< 0.005	61.13
PHASE FRACTION		0.4560	0.3801	0.1639
COMPRESSIBILITY FACTOR		0.9611	0.0660	0.6539
MOLES	100.00	32.21	26.85	11.57

Table 5.4 : Equilibrium phase compositions (mol %) for

the reacting system at 473.15 K and 10.13 MPa

Note : $\xi_1 = 14.68$, and $\xi_2 = 4.01$.

HC = Hydrocarbon Rich

COMPONENT	FEED	VAPOR	WATER RICH LIQUID	HC LIQUID
СН	2.14	2.98	0.15	1.07
co	10.71	0.30	0.01	0.08
H,	52.86	45.49	1.05	12.72
cÔ	5.71	7.86	0.54	4.54
Снон	0.00	12.64	11.14	15.65
н _о	21.43	28.96	87.11	14.71
$C_{18}H_{38}$	7.15	1.77	< 0.005	51.23
PHASE FRACTION		0.8536	0.0000	0.1464
COMPRESSIBIL FACTOR	ITY	0.9236	0.1139	1.0687
MOLES	100.00	67.66	0.00	11.61
$\overline{\mathbf{N}}$	7	0.12		

Table 5.5 : Equilibrium phase compositions (mol %) for

the reacting system at 535 K and 20 MPa

.

Note : $\xi_1 = 10.37$, and $\xi_2 = -0.13$.

HC = Hydrocarbon Rich



.

Figure 5.6 : Phase Fractions (a) and Stability Variables O) during Iterations for Methanol Synthesis Reaction at 535 K & 20 MPa

direction. The variations in the values of the phase fractions for the hydrocarbon-rich and water-rich liquids during the iterations are shown in Figure 5.6. The calculations in the inner loop start with a non-zero value of phase fractions for the vapor and the hydrocarbon-rich liquid phases, and a non-zero value of stability variable for the water-rich The liquid. water-rich liquid appears in the first iteration and subsequently disappears after the 2nd iteration. The stability variable for the water-rich liquid phase attains a non-zero value after the 2nd iteration and finally a solution in which a vapor and a hydrocarbon-rich liquid are present is obtained. Again, the algorithm easily deals with a phase which disappears during the computations.

5.4 ISENTHALPIC SPECIFICATIONS FOR NON-REACTIVE SYSTEM

In this case, the enthalpy of the system is specified instead of its temperature. This requires that the Gibbs free energy be minimum over all possible states with the constraint of enthalpy balance. Hence, the isenthalpic flash problem can be looked upon as a series of isothermal-isobaric flash problems which have to be solved until the enthalpy specification is satisfied. In other words the following enthalpy balance,

$$\frac{\pi}{\sum_{k=1}^{N} \sum_{i=1}^{n} n_{ik} h_{ik} - H_{spec}} = 0,$$
(5.3)

needs to be solved along with the equations describing the isothermal-isobaric flash problem to obtain the additional unknown. The above equation can be rewritten as,

$$n_{t} \sum_{k=1}^{\pi} \sum_{i=1}^{N} \alpha_{k} \mathbf{x}_{ik} \mathbf{h}_{ik} - \mathbf{H}_{spec} = 0.$$
 (5.4)

Substitution of Equation (3.31) into Equation (5.4) yields Enthalpy Balance Relation :

$$n_{t} \sum_{k=1}^{\pi} \sum_{i=1}^{N} \alpha_{k} K_{ik} x_{ir} e^{\theta_{k}} h_{ik} - H_{spec} = 0.$$
(5.5)

For the isenthalpic flash computations in non-reacting mixture, Equations (3.24 - 3.33) and Equation (5.5) are solved for the $\pi(N+2)$ unknowns, namely (π) α_k 's, (π -1) θ_k 's, ($N.\pi$) \mathbf{x}_{ik} 's and temperature.

It is noted that at the point of minimum Gibbs free energy with the enthalpy balance constraint the stability variables θ_k will satisfy the following relation :

$$\theta_{k} = \ln (f_{ik}/f_{ir})$$
 (i = 1,...,N; k = 1,...,\pi; k \neq r). (5.6)

5.4.1 Proposed Algorithm

The proposed solution method solves the enthalpy balance relation (Equation 5.5) simultaneously with the summation (Equation 3.25), the relations (Equation 5.2) and phase summation stability equation (Equation 3.24) in an inner loop for the phase fractions, α_{ν} , stability variables, θ_k , and the temperature, T. The mole fractions, x_{ik} , are The Newton-Raphson procedure calculated in an outer loop. with analytical derivatives is utilized in the inner loop. These derivatives are given in Appendix C. For simplicity and efficiency, approximate thermodynamic models for the equilibrium ratios, K_{ik}, and the partial molar enthalpies, h_{ik}, are used in the inner loop. The approximate models are,

$$\ln (K_{ik}/K_{ik}^{b}) = B_{ik}(T-T^{b})/(TT^{b})$$
(5.7)

and

$$\mathbf{h}_{i\mathbf{k}} = \mathbf{h}_{i\mathbf{k}}^{\mathbf{b}} + (\partial \mathbf{h}_{i\mathbf{k}}^{\dagger} / \partial \mathbf{T})_{\mathbf{T}^{\mathbf{b}}} (\mathbf{T} - \mathbf{T}^{\mathbf{b}}).$$
(5.8)

The details of these models are given in Appendix E. In the outer loop the equilibrium ratios and the partial molar enthalpies are evaluated using the thermodynamic model employed. The temperature derivatives of the equilibrium ratios and the partial molar enthalpies are calculated by numerical perturbations. Of course, in the outer loop, besides the mole fractions the temperature is also checked for convergence.

5.4.2 Evaluation of the Proposed Algorithm

The results of two isenthalpic flash computations are presented next. The Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1988) is utilized to calculate all thermodynamic properties.

A Mixture of Ethanol-Ethyl acetate-Water

The isenthalpic flash algorithm is applied to study the mixture of 10.7, 30.1 and 59.2 mole percent ethanol, ethyl acetate and water with isenthalpic specifications instead of isothermal specifications. The enthalpy corresponding to temperatures 343.45, 343.46 and 343.47 K, i.e., $H_{\rm spec}/R$ is -4141.76 K, -3629.54 K and -3242.39 K (with the enthalpy base of zero for the ideal gas at 0 K), respectively is specified. In addition, a pressure of 101.325 kPa is specified. The solutions, obtained previously with isothermal specification, shown in



H /R	TEMPERATUR	E	THETA FOR THE	ABSENT PHASE
(K)	(K)	VAPOR	WATER RICH LIQUID	PENTANE RICI LIQUID
-3000.0	255.79	3.77	_	•
-2500.0	285.64	2.53	-	-
-2000.0	315.97	1.59	-	-
-1500.0	345.94	0.855	-	-
-1000.0	374.74	0.248	-	-
- 759.0	387.94	< 0.001	-	-
- 500.0	387.97	-	-	-
0.0	387.97	-	-	-
500.0	387.97	-	-	-
860.0	388.00	-	-	< 0.001
1000.0	392.01	-	-	0.086
1500.0	403.65	-	-	0.346
2000.0	412.08	-	-	0.549
2500.0	418.32	-	-	0.711
3000.0	423.06	-	-	0.841
3249.3	425.01	-	< 0.001	0.895
3500.0	445.42	-	0.484	1.083
4000.0	484.61	-	1.267	1.457

Table 5.6 : Calculated temperatures and stability variablesfor the n-PENTANE and WATER system at 1000 kPa

.

R =Universal Gas Constant



Figure 5.8 : Enthalpy-Temperature diagram for equimolar n-Pentane and water at 1000 kPa calculated using isenthalpic flash computations

Table 5.2 are obtained. Figure 5.7 depicts the changes in the temperature, vapor phase fraction and stability variable at a specified enthalpy of -4141.76R K. Initially vapor phase fraction is non-zero and stability variable is zero. After the 1st iteration the vapor phase fraction becomes zero while the stability variable becomes non-zero. In the 13th iteration vapor phase reappears to disappear again in the 19th iteration. Α solution in which vapor phase is absent is finally obtained.

As observed in the above example, the algorithm for isenthalpic flash computations easily deals with the appearance and the disappearance of a phase during the computations.

A Mixture of n-Pentane and Water

The isenthalpic flash algorithm is applied to study an equimolar mixture of n-pentane and water at 1000 kPa. Agarwal et al. (1988) and Michelsen (1987) have applied a stepwise procedure of stability and phase split calculations to study a similar mixture and have reported large oscillations in the calculated temperature during the computations for the narrow-boiling mixtures. Figure 5.8 shows the enthalpy temperature diagram calculated using the proposed algorithm. Table 5.6 stability variables gives the calculated temperatures and at different specifications of the enthalpies. In all cases three phases are specified and convergence is obtained within six iterations. Note that the three phase temperatures are also easily obtained.

5.5 DISCUSSION OF RESULTS

The proposed algorithm has been applied to reacting and non-reacting systems to simultaneously calculate the phase fractions and the stability variables. The simultaneous calculation enables us to handle logically the appearance and disappearance of a phase in multiphase computations.

The proposed algorithm is able to solve problems which exhibit a three phase region the pressure-temperature narrow on plane. Simultaneous solution of the stability variables with the phase fractions is very beneficial near the phase boundary. The value of the stability variable for a phase indicates how "close" are the conditions for the appearance of that phase.

The simultaneous calculation of the stability variables and the phase fractions is particularly suited for multiphase computations in reactive systems. In such cases, it is not necessary to converge the extent of the reactions first and then examine the stability of the system. The proposed algorithm calculates all the phase fractions, the stability variables and the extents of reaction simultaneously.

In addition, the simultaneous computation of the temperature, phase fractions and the stability variables is useful for isenthalpic flash computations. The methods for isenthalpic flash computations based on an alternating use of stability analysis and phase split calculations often have convergence problems for narrow boiling mixtures. Since temperature is not known a priori, the stability test can only be applied at an estimate of the system temperature. This can lead to large oscillations in temperature between iterations, particularly for narrow boiling mixtures. The proposed solution procedure for isenthalpic computations, however, is extremely stable and such convergence problems are not observed.

The proposed computational scheme guarantees that the solution obtained is a stationary point of the Gibbs free energy of the system and hence, besides the global minimum it may correspond to a local minimum. Nonlinear iterative methods which guarantee convergence to the global minimum are unknown. Providing multiple initial guesses for the unknown variables is the only way to increase the probability of finding the global minimum using any iterative method. Specifying less phases than expected may lead to a solution which corresponds to a constrained minimum. Hence, specifying more phases than expected can help avoid this problem at the expense of an increase in the number of thermodynamic evaluations. However, in practice we know that the maximum number of phases generally does not exceed three or four in most applications.

In the proposed algorithm, the stability equation (Equation 3.32) is modified so that it could be solved simultaneously with the summation equations using the Newton-Raphson procedure. Previously in Chapter 4, we solved the stability equations using the "active set" strategy with the summation equations and examined the phase behavior of systems containing gas hydrates as well as other phase equilibrium problems typically encountered in gas processing, the petrochemical industry and in enhanced oil recovery schemes. Simultaneous solution of the stability and summation equations is advantageous as it allows the approach to be extended easily to other specifications of the variables. Furthermore, the proposed solution technique for solving the stability equation can easily be utilized in a three-phase distillation tower algorithm.

Simultaneous computation of stability and phase splits enable us to continuously monitor the stability variables as the computations proceed.

5.6 SUMMARY

The simultaneous computation of stability multiphase and isothermal-isobaric flash for reacting/non-reacting systems is presented. The isothermal flash algorithm is extended for the simultaneous computation of the stability and the isenthalpic flash in non-reacting systems. The effectiveness of both the isothermal and the isenthalpic algorithms to handle the appearance and disappearance of a phase during the computations is demonstrated. The proposed isenthalpic flash algorithm is found to be effective for narrow boiling mixtures and it does not show any oscillations in temperature during iterations.

CHAPTER 6

MATHEMATICAL MODELING OF MULTISTAGE MULTIPHASE SEPARATION PROCESSES

In this chapter, an extension of the formulation of simultaneous stability and flash calculations for single stage separation processes Variables to multistage separation processes is presented. which represent the total moles of a component leaving a stage are introduced. The material, energy, equilibrium, summation and stability equations are then written in terms of phase fractions, stability variables and the newly introduced variables. The advantages of the new formulation for multistage multiphase the modeling of separation processes are discussed.

6.1 LITERATURE REVIEW

For the simulation of steady-state multistage separation processes many rigorous solution methods are available. Most of the solution methods can be classified into two categories : equation decoupling methods and the simultaneous solution methods.

The equation decoupling methods are based on partitioning of the system of equations into subsets and solving the system of equations independently. The classical method proposed by Thiele and Geddes (1933) falls into this category. Their algorithm performs stage by stage calculations from the two ends of the column to the feed stage until the material balance on the feed stage is satisfied. The "bubble-point" method of Wang and Henke (1966), which utilizes the summation equation

to determine the stage temperature, is another example. They arranged the component material balances into a tridiagonal matrix and solved simultaneously using the Thomas algorithm. Their method them is effective only for narrow boiling systems. Sujata (1961) proposed the "sum-rates" method which is particularly effective for wide-boiling systems but is not suitable for narrow boiling systems. In his method the summation equation is solved for the phase rate and the enthalpy balance equation is solved for the stage temperature. Tomich (1970) solved the summation and the enthalpy balance equations simultaneously for the stage temperature and the phase rate using the Newton-Raphson technique. Systems involving both narrow boiling and wide boiling mixtures can be solved using this approach. Boston and Sullivan (1974) proposed an "inside-out" algorithm in which calculations are performed nested loops. In the outside loop the enthalpy and in two the equilibrium ratios are evaluated rigorously while in the inside loop simpler "local" models are used to evaluate the quantities. Saeger and (1986) modified the "inside-out" method by introducing a Bishnoi compositional dependence in the local model. Their method improves the convergence behavior of non-ideal systems for which the original "inside-out" method failed to converge.

solution methods for In the simultaneous the simulation of multistage separation processes all the defining equations are first linearized and then solved simultaneously using the Newton Raphson method. Naphtali and Sandholm (1971) utilized this procedure and grouped the describing equations by stage, resulting in a block-tridiagonal Jacobian. Their method takes the composition dependence of equilibrium

ratios and enthalpy into account, making it suitable for non-ideal systems. However, this method requires large computer storage. Ishii and Otto (1973) decreased the storage requirement by grouping the describing equations by components and making simplifying assumptions about the compositional dependence of the equilibrium ratios and enthalpies. Shah and Bishnoi (1978) demonstrated the applicability of this method for simulation of absorbers, reboiled absorbers and distillation columns for hydrocarbon systems using the Peng-Robinson and Soave-Redlich-Kwong equation of states.

A combination of equation decoupling and simultaneous solution strategy has been proposed by Kinoshita et al. (1983a;1983b) and Wu and Bishnoi (1986). Kinoshita et al. (1983) assumed a set of liquid mole fractions for the whole column and then sequentially solved the summation, energy and the overall material balance equations for the phase flow rates and the stage temperatures. The component material balance equations were subsequently utilized to obtain a new set of liquid mole fractions. The error functions, defined as the difference between the new and the assumed liquid mole fractions, were then simultaneously solved using the Newton's method. Wu and Bishnoi (1986) proposed an algorithm in which the summation and the component material balance equations are solved simultaneously for the stage temperatures and the liquid flow rates using the Newton's method. In the outer loop of their algorithm, the vapor flow rates are calculated using the energy and the overall material balance equations.

For the computation of the three phase distillation problem, both equation decoupling and the simultaneous solution procedure have been proposed in the literature. Block and Hegner (1976) proposed an algorithm which uses the residuals of the component material balance equations to update the overall liquid phase mole fractions using the Newton's method. In the inner loop of the algorithm, they sequentially solved for the liquid splits, stage temperatures and stage flow rates using the summation, energy and the overall material balance equations.

Boston and Shah (1979) modified the two phase "inside out" algorithm of Boston and Sullivan (1974) for three phase distillation calculations. Like distillation the two phase program, it uses approximate thermodynamic models in an internal loop. In the outer loop, the number of liquid phases are determined by performing a stability test on the liquid phase. A similar method was proposed by Ross and Seider (1981) which allows the specification of stage efficiencies and utilizes the phase splitting algorithm of Gautam and Seider (1979) in the outer loop.

A simultaneous solution approach for three phase tower calculations was proposed by Ferraris and Morbidelli (1981). They extended the Naphtali and Sandholm's global Newton-Raphson procedure for two phase calculations to three phase distillation computations. In their algorithm, the number of phases present at equilibrium on each stage has to be specified a priori. This was determined by performing a series of single-stage flash calculations after converging the tower computations and, if found necessary, repeating the tower calculations. Ferraris and Morbidelli (1982) proposed a simplified algorithm for problems in which one of the two liquid phases can be regarded as nearly pure.

Kinoshita et al. (1983b) extended their two phase column algorithm (Kinoshita et al., 1983a) to handle three phases. They utilized the overall liquid phase composition and the phase splitting parameters as introduced by Block and Hegner (1976) in their algorithm.

Pucci et al. (1986) proposed a plate-to-plate calculation procedure distillation calculations. The method for three phase consists of performing plate-to-plate calculation from the reboiler to the overhead condenser, then from the top to the bottom of the column and so on until convergence is achieved. An isobaric-isenthalpic flash algorithm is utilized on each plate to a perform a two-phase or three-phase flash calculations.

Baden and Michelsen (1987) described a method in which three phase calculations can be implemented in any two phase distillation column program, by modifying the calculation of the liquid phase thermodynamic properties. They replaced the activity coefficient of the liquid phase by the pseudo activity coefficients based on the total composition of the two liquid phases. Schuil and Bool (1985), in a similar approach, presented a mixed K-value model which could be utilized in any two phase distillation column program.

Stewart (1987) proposed collocation Swartz and a method for distillation. their method multiphase In the phase boundaries are included as unknowns in the system of column equations. These phase boundaries are calculated simultaneously with the other variables.

More recently, Cairns and Furzer (1990) proposed a method based on Naphtali-Sandholm algorithm for the simulation of three phase distillation columns. They utilize average liquid mole fractions as the primary variables in the algorithm. Michelsen's phase stability test (Michelsen, 1982a) is performed on each stage to determine if phase


Figure 6.1 : Equilibrium Stage Model



Figure 6.2 : A Schematic Representation of Stage j (1=Vapor; k=2,3,... π : Liquid)

splitting will occur.

A common problem with all the methods proposed in the literature for the simulation of three phase distillation columns is that the number of phases which are present on a stage are *not* known *a priori*. The number of phases is determined by performing a stability test in an outside loop. A phase can appear and disappear during computations and this causes numerical problems in these methods.

In the present work a new method for the simulation of multistage multiphase separation processes is described. The method *simultaneously* performs the phase stability and equilibrium computations during the iterations. The appearance and disappearance of a phase is easily handled by calculating the stability variable for the phase. For this purpose the stability criterion, developed in Chapter 3, is utilized. The proposed method is based on a new formulation of the describing equations. The formulation uses the number of moles of a component leaving a stage as the primary variables. An algorithm for implementing the formulation for the two and three phase separation processes will be given in Chapter 7. The algorithm solves all the model equations using the Newton-Raphson procedure.

6.2 PROBLEM STATEMENT

The schematic column shown in Figure 6.1 is used to develop model equations. It has S stages numbered from the top to bottom. A diagram of the equilibrium stage is shown in Figure 6.2. Each stage has a feed stream, a vapor side stream and liquid side streams. Note that there are $(\pi$ -1) liquid side streams as there are $(\pi$ -1) liquid phases leaving the stage.

The computation of multistage *multiphase* separation processes requires the determination of the number of moles (n_{ikj}) of each component i in phase k leaving stage j. In addition, like isenthalpic flash calculations, the temperature of stage j (T_j) is unknown and the combined enthalpy of the streams leaving the stage is specified. This requires that for the stage j, as for the single stage separation processes, the combined Gibbs free energy of the streams leaving the stage is minimum over all possible states with the constraint of enthalpy balance. As in Chapter 3, for a multicomponent multiphase system the Gibbs free energy function for the stage j is given by

$$\mathbf{G}_{\mathbf{j}} = \sum_{\mathbf{k}=1}^{\pi} \sum_{i=1}^{N} \mathbf{n}_{\mathbf{i}\mathbf{k}\mathbf{j}} \ \boldsymbol{\mu}_{\mathbf{i}\mathbf{k}\mathbf{j}}$$
(6.1)

where μ_{ikj} is the chemical potential of component i in phase k, N is the number of components present in the mixture and π is the total number of phases. The moles of each component in phase k leaving the stage j, n_{ikj} , which minimize the Gibbs free energy, should satisfy the following constraints :

(1) Material balance constraints

π

In this case, since there is no accumulation of a component on a stage, the total moles of each component leaving the stage j are equal to the moles entering the stage. Hence, we have

$$\sum_{k=1}^{N} n_{ikj} = q_{ij} \quad (i = 1,...,N), \quad (6.2)$$

where, q_{ij} is the total moles of component *i* entering stage *j* and is given by

$$q_{ij} = z_{ij} + (1 - wr_{1j+1}) n_{i1j+1} + \sum_{k=2}^{\pi} (1 - wr_{kj-1}) n_{ikj-1}^{*}$$
(6.3)

In Equation (6.3), z_{ij} are the moles of the component i in the external feed and wr_{kj} is the withdrawal ratio of phase k. In Equation (6.3), phase index 1 refers to the vapor phase and phase indices greater than one refer to liquid phases.

(2) Energy balance constraint

In this case, the total energy on stage j is conserved. That is, the energy entering the stage is equal to that leaving. This gives

$$\sum_{k=1}^{\pi} \sum_{i=1}^{N} \mathbf{n}_{ikj} \mathbf{h}_{ikj} = \mathbf{H}_{sj}, \qquad (6.4)$$

where h_{ikj} is the partial molal enthalpy of component i in phase k and H_{sj} is the "specified" enthalpy of the stage j. H_{sj} is the sum of external energy added, Q_j , the enthalpy entering the stage j from the stages j+1 and j-1 and the enthalpy of external feed to the stage j. It is given by,

$$H_{sj} = Q_{j} + H_{f} + (1 - wr_{1j+1}) \sum_{i=1}^{N} n_{i1j+1} h_{i1j+1}$$
$$+ \sum_{k=2}^{\pi} (1 - wr_{kj-1}) \sum_{i=1}^{N} n_{ikj-1} h_{ikj-1}$$
$$(i = 1,...,N).$$
(6.5)

(3) Non-negative constraints

The number of moles of a component in a phase cannot be negative. Hence,

130

$$\mathbf{n}_{ikj} \ge 0$$
 (i = 1,...,N; k = 1, ..., π). (6.6)

As with the single stage flash, the material balance constraints, given by Equation (6.2), can be eliminated through the introduction of a reference phase (r). Substituting the number of moles in the reference phase (n_{iri}) into Equation (6.1), we obtain

$$G_{j} = \sum_{i=1}^{N} q_{ij} \mu_{irj} + \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} n_{ikj} (\mu_{ikj} - \mu_{irj}).$$
(6.7)

Therefore, for the computation of multiphase equilibria in multistage separation processes the Gibbs free energy for each stage given by Equation (6.7) has to be minimized subject to the enthalpy balance constraint on the stage given by Equation (6.4). It is assumed that the nonnegative constraints, given by Constraints (6.6), are satisfied for an acceptable solution.

The above constrained minimization problem is similar to the single stage isenthalpic flash computations. The problem can be looked upon as a series of isothermal-isobaric flash problems, which have to be solved until the enthalpy specification is satisfied. In the next section, we shall show that the simultaneous phase stability and equilibrium computations for the single stage processes can easily be extended to the simulation of multistage separation processes.

6.3 FORMULATION OF EQUATIONS

The minimization of the Gibbs free energy, given by Equation (6.7), for multistage processes is very similar to the minimization of the Gibbs free energy function (given by Equation 3.4) for single stage processes. The number of moles of component i entering stage j, q_{ii} , is the same as the number of moles of component i fed to a single stage flash, z_i. The only difference between the two minimization problems is that the minimization problem given by Equation (6.7) has an additional constraint of enthalpy balance with an additional unknown variable, the stage temperature (T_i) . As in Section 5.3 for isenthalpic single stage the enthalpy balance constraint computations, can be utilized to evaluate the stage temperature. If this is done, then the minimization problem for multistage processes (given by Equation 6.7) becomes exactly the same as the unconstrained minimization problem for the single stage processes (given by Equation 3.4). This would imply that the equations derived in Chapter 3 for the simultaneous phase stability and equilibrium computations for single stage isothermal-isobaric flash computations can be applied for the modeling of multistage processes.

As in the modeling of single stage separation processes, the following phase equilibrium and stability relations for stage j can be derived :

$$\mathbf{x}_{ikj} = K_{ikj} \mathbf{x}_{irj} e^{\theta_{kj}}$$
 (i = 1,...,N; k = 1,...,\pi; k \neq r) (6.8)

and

$$\alpha_{kj} \theta_{kj} = 0$$
 $(k = 1,...,\pi; k \neq r)$ (6.9)

subject to,

$$\alpha_{kj} \ge 0 \quad \text{and} \quad \theta_{kj} \ge 0 .$$
(6.10)

In Equations (6.9) and (6.10), α_{ki} is the phase fraction of the phase k,

given by

$$\alpha_{kj} = \sum_{i=1}^{N} n_{ikj} / \sum_{l=1}^{\pi} \sum_{i=1}^{N} n_{ilj}, \qquad (6.11)$$

and K_{ikj} are the equilibrium ratios and they are given by

$$\mathbf{K}_{i\mathbf{k}j} = \phi_{i\mathbf{r}j} / \phi_{i\mathbf{k}j}. \tag{6.12}$$

The moles of component i leaving stage j, m_{ii} , are given by

$$m_{ij} = \sum_{k=1}^{\pi} n_{ikj}.$$
 (6.13)

The total moles leaving stage j are given by

٠

$$\mathbf{m}_{tj} = \sum_{i=1}^{N} \mathbf{m}_{ij} = \sum_{i=1}^{N} \sum_{k=1}^{\pi} \mathbf{n}_{ikj}.$$
 (6.14)

The number of moles of a component i in phase k on a stage j, n_{ikj} , can then be written in terms of the phase compositions, phase fractions (defined by Equation 6.11) and the total moles leaving stage j as

$$\mathbf{n}_{ikj} = \mathbf{x}_{ikj} \alpha_{kj} \mathbf{m}_{tj}$$
 (i = 1,...,N; k = 1,..., π). (6.15)

Substituting Equation (6.8) in Equation (6.15), we get

$$n_{ikj} = K_{ikj} x_{irj} e^{\theta_{kj}} \alpha_{kj} m_{tj}$$
 (i = 1,...,N; k = 1,...,\pi). (6.16)

Equations (6.13) and (6.16) give

$$\mathbf{m}_{ij} - \mathbf{m}_{ij} \mathbf{x}_{irj} \sum_{k=1}^{\pi} \mathbf{K}_{ikj} e^{\theta_{kj}} \alpha_{kj}$$
(6.17)

or,

$$\mathbf{x}_{irj} = \frac{\mathbf{m}_{ij}}{\mathbf{m}_{ij} \sum_{\mathbf{k}=1}^{\pi} \mathbf{K}_{ikj} e^{\theta_{kj}} \alpha_{kj}}.$$
 (6.18)

For the reference phase, the equilibrium ratios, K_{irj} , are equal to one and the stability variable, θ_{rj} , are equal to zero. Using this and the the phase summation equation,

$$\sum_{k=1}^{\pi} \alpha_{kj} = 1, \qquad (6.19)$$

Equation (6.18) reduces to

$$\mathbf{x}_{irj} = \mathbf{m}_{ij} / (\mathbf{m}_{ij} \mathbf{D}_{ij})$$
 (i = 1,...,N), (6.20)

where,

$$D_{ij} = 1 + \sum_{\substack{k=1\\k \neq r}}^{\pi} (K_{ikj} e^{\theta_{kj}} - 1) \alpha_{kj}.$$
 (6.21)

The component material balance equations (Equations 6.2) and the enthalpy balance equations (Equations 6.3) can now be written in terms of m_{ij} . Substituting Equations (6.13), (6.16) and (6.20) in the component material balance equation (Equation 6.2) we obtain,

$$M_{ij} = -m_{ij} + z_{ij} + (1 - wr_{ij+1}) K_{i1j+1} e^{\theta_{1j+1}} \alpha_{ij+1} m_{ij+1} / D_{ij+1}$$

$$+ \sum_{k=2}^{\pi} (1 - wr_{kj-1}) K_{ikj-1} e^{\theta_{kj-1}} \alpha_{kj-1} m_{ij-1} / D_{ij-1}$$

= 0. (6.22)

Similarly, substituting Equations (6.13), (6.16) and (6.20) in the energy balance equation (Equation 6.4) yields,

$$\mathbf{E}_{j} = -\sum_{k=1}^{\pi} \sum_{i=1}^{N} \mathbf{K}_{ikj} \mathbf{e}^{\theta_{kj}} \alpha_{kj} \mathbf{m}_{ij} \mathbf{h}_{ikj} / \mathbf{D}_{ij} + \mathbf{H}_{f}$$

+
$$Q_j$$
 + $(1 - wr_{ij+1}) \alpha_{ij+1} \sum_{i=1}^{N} K_{i1j+1} e^{\theta_{1j+1}} m_{ij+1} h_{i1j+1}/D_{ij+1}$

$$+ \sum_{k=2}^{\pi} (1 - wr_{kj-1}) \alpha_{kj-1} \sum_{i=1}^{N} K_{i k j - 1} e^{\theta_{k j - 1}} m_{i j - 1} h_{i k j - 1} / D_{i j - 1}$$

= 0. (6.23)

It should be noted that for a single stage process, the moles of a component leaving a stage, m_{ij} , will be equal to the moles of the component fed in, z_{ij} . The above set of equations for multistage processes will reduce exactly to those for single stage processes.

The above set of equations extends the simultaneous phase stability and equilibrium formulation for a single stage process to multistage separation processes. All the equations, required for the computations of multistage multiphase separation processes, are summarized in the next section.

6.4 GOVERNING EQUATIONS

For a multistage multiphase separation process, the set of equations, that describes the simultaneous equilibrium and stability calculations for the stage j is written as follows : Component Material Balance :

$$M_{ij} = -m_{ij} + z_{ij} + (1 - wr_{ij+1}) K_{i1j+1} e^{\theta_{1j+1}} \alpha_{ij+1} m_{ij+1} / D_{ij+1}$$
$$+ \sum_{k=2}^{\pi} (1 - wr_{kj-1}) K_{ikj-1} e^{\theta_{kj-1}} \alpha_{kj-1} m_{ij-1} / D_{ij-1}$$
$$= 0. \qquad (i=1,...,N) \qquad (6.24)$$

•

Energy Balance :

$$\mathbf{E}_{j} = -\sum_{k=1}^{\pi} \sum_{i=1}^{N} \mathbf{K}_{ikj} e^{\theta_{kj}} \alpha_{kj} \mathbf{m}_{ij} \mathbf{h}_{ikj} / \mathbf{D}_{ij} + \mathbf{H}_{f}$$

+
$$Q_j$$
 + (1 - wr_{ij+1}) $\alpha_{ij+1} \sum_{i=1}^{N} K_{i1j+1} e^{\theta_{1j+1}} m_{ij+1} h_{i1j+1}/D_{ij+1}$

$$+ \sum_{k=2}^{\pi} (1 - wr_{kj-1}) \alpha_{kj-1} \sum_{i=1}^{N} K_{i k j - 1} e^{\theta_{k j - 1}} m_{i j - 1} h_{i k j - 1} / D_{i j - 1}$$

(6.25)

Phase Fraction Summation :

$$\sum_{k=1}^{\pi} \alpha_{kj} = 1. \tag{6.26}$$

Mole Fraction Summation :

$$S_{kj} = \sum_{i=1}^{N} (K_{ikj} e^{\theta_{kj}} - 1) x_{irj} = 0 \qquad (k = 1, ..., \pi; k \neq r)$$
(6.27)

.

with

$$\mathbf{x}_{irj} = \mathbf{m}_{ij} / (\mathbf{m}_{ij} \mathbf{D}_{ij})$$
 (i = 1,...,N), (6.28)

where,

$$m_{tj} = \sum_{i=1}^{N} m_{ij},$$
 (6.29)

$$D_{ij} = 1 + \sum_{\substack{k=1\\k \neq r}}^{\pi} (K_{ikj} e^{\theta_{kj}} - 1) \alpha_{kj}, \qquad (6.30)$$

and

$$\mathbf{K}_{\mathbf{i}\mathbf{k}\mathbf{j}} = \boldsymbol{\phi}_{\mathbf{i}\mathbf{r}\mathbf{j}} / \boldsymbol{\phi}_{\mathbf{i}\mathbf{k}\mathbf{j}}. \tag{6.31}$$

Phase Equilibrium and Stability Relations :

$$\mathbf{x}_{ikj} - \mathbf{K}_{ikj} \mathbf{x}_{irj} \mathbf{e}^{\theta_{kj}}$$
 (i = 1,...,N; k = 1,..., π ; k \neq r) (6.32)

and

$$\alpha_{kj} \theta_{kj} = 0$$
 (k - 1,..., π ; k \neq r) (6.33)

subject to,

$$\alpha_{kj} \ge 0$$
 and $\theta_{kj} \ge 0$. (6.34)

For a stage in a multistage multiphase separation problem, the above $(\pi(N+2)+N)$ equations, namely (N) component material balance equations,

(1) energy balance, (1) phase fraction summation equation, $(\pi$ -1) mole (N) fraction summation equations, reference phase mole fraction equations (Equation 6.28) and $((N+1),(\pi-1))$ phase equilibrium and stability equations (Equations 6.32 and 6.33) are to be solved. The $(\pi(N+2)+N)$ unknowns are (N) m_{ij} 's, (1) T_{j} 's, (π) α_{kj} 's, ((π -1)) θ_{kj} 's and $(N.\pi) \propto_{ikj}$'s. It is noted that the θ corresponding to the reference phase r is always zero.

6.5 SPECIFICATION EQUATIONS

The formulation for the multistage multiphase separation processes, presented above, assumed that the following variables have been specified for the column :

- 1. the number of stages in the column
- 2. the location, temperature and the moles of each component in all the feed streams
- 3. the location and the withdrawal ratios of all the side streams
- 4. the pressure profile of the column
- 5. any external heat supplied or removed from a stage

The specification of the above set of variables, called the design variables, are the most convenient for absorbers. However, in the case of reboiled absorbers, generally, the bottom rate (or equivalently the top product rate) is specified and the reboiler duty (Q_S) is calculated. In the case of distillation towers, however, the bottom rate and the reflux ratios are specified while both the reboiler and the condenser duties $(Q_S and Q_1)$ are calculated.

For the reboiler,

$$S_{reb} = \sum_{k=2}^{\pi} \sum_{i=1}^{N} n_{ikS} - B = 0,$$
 (6.35)

where B is the specified bottom flow rate and S_{reb} is the residual to be driven to zero. Substituting Equations (6.20) and (6.16) in Equation (6.35), yields

$$S_{reb} = \sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ikS} e^{\theta_k S} \alpha_{kS} m_{iS} / D_{iS} - B = 0. \quad (6.36)$$

We will call Equations (6.35) or (6.36) as the reboiler specification equation.

For the partial condenser in a distillation column,

$$S_{\text{pcond}} = \sum_{k=2}^{\pi} \sum_{i=1}^{N} n_{ik1} - R_{1} \sum_{i=1}^{N} n_{i11} = 0, \qquad (6.37)$$

where S_{pcond} is the residual to be driven to zero, phase index 1 denotes the vapor phase and R_1 is the specified reflux ratio. It is to be noted that R_1 is defined as the ratio of the moles of liquid formed or liquid returned to the moles of vapor withdrawn from stage 1. Substituting Equations (6.20) and (6.16) in Equation (6.37), yields

$$S_{\text{pcond}} = \sum_{k=2}^{n} \sum_{i=1}^{N} K_{ik1} e^{\theta_{k1}} \alpha_{k1} m_{i1} / D_{i1} - R_{1} \sum_{i=1}^{N} K_{i11} e^{\theta_{11}} \alpha_{11} m_{i1} / D_{i1} - 0.$$

$$(6.38)$$

We will call Equations (6.37) or (6.38) as the partial condenser specification equation.

For a total condenser, the phase fraction of the vapor phase on

stage 1 is zero and the specification equation is

$$S_{t cond} = \alpha_{11} = 0.$$
 (6.39)

In the case of total condenser, $(\pi-1)$ reflux ratios corresponding to $(\pi-1)$ liquid phases on stage 1 are calculated from the specified withdrawal ratios. The relationship between the withdrawal ratio and the reflux ratio is given by

$$wr_{L_1} = 1 / (1+R_L), \quad (k = 2,...,\pi).$$
 (6.40)

Alternatively, the reflux ratios may be specified and the withdrawal ratios on stage 1 may be calculated from the above equation. In this study, the reflux ratios are used to calculate the withdrawal ratios for these phases on stage 1. Note that this sort of specification for the liquid phases is frequently useful when one wishes to specify that a particular liquid phase should not be refluxed. Furthermore, note that when a liquid is not formed in the condenser the terms corresponding to that particular liquid phase in the component and energy balances have to be made zero. This can conveniently be done by setting the withdrawal ratio for the phase to unity.

The specification equations corresponding to the reboiler and the condenser replace the energy balance equations in the set of equations to be solved. That is, for the reboiler (Sth stage) Equation (6.36) is solved instead of Equation (6.25) (E_S) while for the condenser (1st stage) Equation (6.38) or Equation (6.39) is solved instead of the energy balance equation, Equation (6.25) (E_1). Once the solution is obtained, the energy balance equations are used to calculate the condenser and the reboiler duties.

6.6 ADVANTAGES OF THE PROPOSED FORMULATION

The proposed formulation extends the simultaneous phase stability and equilibrium formulation for single stage isobaric isothermal processes to multistage multiphase separation processes. For multistage processes, the total moles of a component leaving a stage are defined as independent variables. All the describing equations are then written in terms of these new variables.

The advantages of the proposed formulation are :

- (1) It provides a unified set of simultaneous equations to describe the phase equilibrium and stability computations in single and multistage separation processes.
- (2) It is able to handle the three and two phase distillation problems, absorption and the liquid-liquid extraction problems using the same set of equations.
- (3) As in single stage processes, the formulation can easily handle the appearance and the disappearance of a phase during computations.
- (4) In the case of reacting systems, the proposed formulation can easily be modified to include the reactions.

An efficient method for the solution of the above equations for the simulation of two and three phase multistage separation processes will be presented in the next chapter. Furthermore, the usefulness of the proposed formulation for simulating a three phase distillation tower will be illustrated.

6.7 SUMMARY

A formulation for the simultaneous stability and equilibrium computations for multistage separation processes has been presented. It permits the simulation of two and three phase distillation processes, absorbers and reboiled absorbers with the same set of equations.

CHAPTER 7

A METHOD FOR THE SIMULATION OF MULTISTAGE MULTIPHASE SEPARATION PROCESSES

A Newton-Raphson method for the solution of coupled nonlinear algebraic equations derived in the previous chapter for multistage multiphase separation processes is presented in this Chapter. The method is applied to simulate two phase absorbers, reboiled absorbers and two and three phase distillation columns. The computational effort required by the proposed algorithm is compared with three other solution methods.

7.1 TWO PHASE SEPARATION COLUMNS

7.1.1 Proposed Algorithm

The proposed solution method for the simulation of two phase multistage separation process is similar to the solution procedure presented in Chapter 5 for a single stage multiphase flash computations. It partitions the system of S(3N+4) equations into two groups, The S(N+4) equations comprising of the component material balances, enthalpy balances, summation and the stability equations and the specification equations are solved simultaneously in an inner loop. Subsequently using the remaining S(2N) equations the component mole fractions are obtained in an outer loop.

In the inner loop of the algorithm the component material balances (Equation 6.24), energy balances (Equation 6.25), phase fraction summations (Equation 6.26), mole summation equations (Equation 6.27), stability equations (Equation 6.33) and the specification equations

(Equations 6.36, 6.38, 6.39) are solved for the moles of a component leaving a stage, m_{ij} , stage temperatures, T_{j} , phase fractions, α_{kj} , and the stability variables, θ_{i} . These equations for all the stages are solved simultaneously. The Newton-Raphson procedure with analytical derivatives (given in Appendix D) is utilized for this purpose. The arranged stagewise, resulting in block tridiagonal equations are a structure of the Jacobian matrix. For simplicity and efficiency, as in Chapter 5 for isenthalpic flash computations, approximate thermodynamic the equilibrium ratios, K_{iki} , and models for the partial molar enthalpies, h_{ikj} , are used in the inner loop. For a stage j, they are given by

$$\ln (K_{ikj}/K_{ikj}^{b}) = B_{ikj}(T_{j} - T_{j}^{b})/(T_{j}T_{j}^{b})$$
(7.1)

and

$$\mathbf{h}_{ikj} = \mathbf{h}_{ikj}^{b} + (\partial \mathbf{h}_{ikj}^{b} / \partial \mathbf{T})_{\mathbf{T}_{j}^{b}} (\mathbf{T}_{j}^{b} - \mathbf{T}_{j}^{b}).$$
 (7.2)

The details of these models are given in Appendix E.

The inner loop of the algorithm is considered to be converged when the sum of squares of the residuals defined by

$$\mathbb{R} = \sum_{j=1}^{N} \left\{ \left(\frac{\sum_{i=1}^{N} M_{ij}}{m_{ij}} \right)^2 + \left(\frac{E_j}{H_{sj}} \right)^2 + \left(\frac{\sum_{i=1}^{\pi} S_{ii}}{H_{sij}} \right)^2 + \left(\sum_{k=1}^{\pi} S_{kj} \right)^2 \right\} / (S^*(N+\pi))$$
(7.3)

are less than a predefined tolerance, ε . However, for each outer loop iteration only one inner loop iteration is performed and the inner loop

is not converged fully (i.e. it is not necessary that the sum of squares of the residuals in the inner loop are less than ε). In the inner loop it is ensured that the residuals when the loop is exited are less than those at the start of the inner loop i.e.

$$\mathbb{R}(\mathbf{u}^{(\boldsymbol{U}+1)}) < \mathbb{R}(\mathbf{u}^{(\boldsymbol{U})})$$
(7.4)

where, u is the unknown vector. This is done by utilizing the optimal step size policy of Kalogerakis and Luus (1983). The policy limits the amount of change in the variables by introducing a stepping parameter λ ($0 < \lambda \leq 1$) so the vector of change in the next iteration is

$$\mathbf{u}^{(\boldsymbol{\nu}+1)} = \mathbf{u}^{(\boldsymbol{\nu})} + \lambda \, \Delta \mathbf{u}^{(\boldsymbol{\nu}+1)}. \tag{7.5}$$

The value of the stepping parameter is obtained by choosing $\lambda = 1$ and halving it until the sum of squares of the residuals decreases i.e.

$$\mathbb{R}(\mathbf{u}^{(\boldsymbol{\mathcal{V}})} + \lambda \Delta \mathbf{u}^{(\boldsymbol{\mathcal{V}}+1)}) < \mathbb{R}(\mathbf{u}^{(\boldsymbol{\mathcal{V}})}).$$
(7.6)

In the outer loop of the proposed algorithm, using Equations (6.28) and (6.32), all the component mole fractions are obtained. Subsequently in the outer loop the equilibrium ratios, the partial molar enthalpies and their temperature derivatives are evaluated rigorously using the thermodynamic model employed. The outer loop is considered to be converged when the errors in the mole fractions and the stage temperatures are less than a predefined tolerance. The mole fractions are considered to be converged when the error defined by

$$E = \sum_{j=1}^{S} \sum_{k=1}^{\pi} (x_{ikj}^{(U)} - x_{ikj}^{(U-1)}) / (S.\pi) < \varepsilon.$$
(7.7)

The algorithm is initialized by assuming a linear temperature profile between the first and the last stage and a zero value for the

stability variables. Subsequently, using the thermodynamic model equilibrium this employed. the ratios are generated at assumed temperature and the average mole fractions calculated from all the feeds to the column. The initial values of the phase fractions are obtained by assuming constant molal overflow in the column. The tridiagonal system of equations, formed by the component material balance equations, is subsequently solved to obtain the value of m... The composition in the vapor and the liquid phases is next calculated using Equations (6.28) (6.32). Thereafter, the equilibrium the and ratios, partial molar enthalpies and their temperature derivatives are evaluated using the thermodynamic model employed.

7.1.2 Evaluation of the Proposed Algorithm

The results of six multistage separation calculations are presented next. The examples presented include computations of an absorber, a reboiled absorber and distillation columns with partial and total condenser. The distillation examples include azeotropic and extractive cases. The performance of the proposed algorithm is compared with three other solution methods.

The Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1988) is utilized in evaluating the thermodynamic properties for the hydrocarbon mixtures (Problems 4-6). In the systems containing polar compounds (Problems 1-3), the activity coefficients in the liquid phase are calculated using the UNIQUAC activity coefficient model (Abrams and Prausnitz, 1975) with parameters obtained from Prausnitz et al. (1980) while the vapor phase is considered to be ideal gas.

Prob	lem Components	Feed	Column Specifications
(1)	Acetone, chloroform, z methanol	$F_5 = 100$, S.V. 2 : 0.45, 0.33, 0.22	Simple distillation s=10, $P=0.1MPa$, B=40, $R=3.0$, Total condenser
(2)	Methylcyclohexane, toluene, phenol	$F_{10} = 76.74, \text{ liquid, } 323\text{K}$ z : 0.0, 0.0, 1.0 $F_{15} = 23.26, \text{ liquid, } 333\text{K}$ z : 0.5, 0.5, 0.0	Extractive distillation s = 21, P = 0.1MPa, B = 86, R = 8.1, Total condenser
(3)	Toluene, 2-butanone, n-heptane	$F_8 = 197.0$, S.L. z : 0.2284, 0.4924, 0.2792 $F_{12} = 97.0$, S.L. z : 0.0, 1.0, 0.0	Azeotropic distillation s = 17, P = 0.1MPa, B = 45, R = 1.5, Partial condenser

Table 7.1a : Specifications of the Two Phase Multistage SeparationProblems

·

S.L. - Saturated Liquid; S.V. = Saturated Vapor

.

Problem Com	ponents	Feed	Column Specifications
(4)		E - 1500 0 S I	Simple distillation
n-Bu	tane,	$F_{10} = 1500.0, S.L.$	S = 20, P = 0.1MPa, P = 1200, 0, P = 3.242
n-per	itane,	0.3333	B = 1200.0, R = 5.545 Total condenser
(5)			Reboiled absorber
Ethai	ne,	$F_{1} = 50.0, S.L.$	s = 13, P = 1.7MPa,
i-but:	ane,	z : 0.93, 0.04,	B = 60.0
n-but	ane,	0.028, 0.002	
n-her	tane	$F_3 = 300.0, S.L.$	
		z : 0.8, 0.12, 0.07, 0.01	
(6)			Absorber
Ethai	ne,	$F_1 = 100.0$, liquid, 220K	s = 13, P = 1.7MPa,
propa	ine,	z : 0.0, 0.0, 0.05	B = 60.0
n-but	ane,	0.20, 0.75	
n-her	tane,	$F_{12} = 680.1, S.V.$	
n-dec	ane	z : 0.882, 0.074,	
		0.044, 0.0, 0.0	

Table 7.1b :	Specifications	for	the	Two	Phase	Multistage	Separation
	Problems						

S.L. - Saturated Liquid; S.V. - Saturated Vapor

Table 7.1 gives the description of all the sample problems considered. All the problems (except for Problem 4) are from Saeger and Bishnoi (1986). Problem 4 is a debutaniser described by Naphtali and Sandholm (1971). The required number of iterations, thermodynamic evaluations and the CPU time for the test problems are given in Table 7.2. The problems are considered to be converged when the errors in the inner loop and outer loop given by Equations (7.3) and (7.7) are less than 1.0 x 10^{-8} and 1.0 x 10^{-4} respectively. As seen from Table 7.2, all the problems converge within reasonable number of iterations and CPU time.

.

As mentioned previously, the inner loop of the algorithm is only converged partially. The effect of the partial and full convergence of the inner loop for Problem 2 is shown in Figure 7.1. The error in the outer loop of the algorithm is only slightly less when the inner loop is converged fully. In other words, the partial convergence of the inner loop *does not* effect the error in the outer loop significantly. However, in case the inner loop is converged fully the computational time increases dramatically (from 158 seconds to 238 seconds).

Tables 7.3a and 7.3b compare the computational efforts required by the proposed algorithm with the solution methods of Wu and Bishnoi (1986b) and Saeger and Bishnoi (1986). The required number of thermodynamic evaluations are compared in Table 7.3a. For the three problems considered, the proposed algorithm requires less number of thermodynamic evaluations than the algorithm proposed by Wu and Bishnoi (1986b). Problem 3 the proposed algorithm requires For less thermodynamic evaluations than the algorithm of Saeger and Bishnoi

Problem	Iterations	Thermodynamic Evaluations	CPU_time, sec*
1	9	300	79.0
2	9	630	158.0
3	10	561	143.0
4	4	600	86.0
5	9	780	172.0
6	6	504	86.0

Table7.2: Number of Iterations and Thermodynamic Evaluations
for the test problems

÷

* Zenith Z-386, Intel 80287 coprocessor, Microsoft C 4.0



Figure 7.1 : Approach to convergence for Problem 2 with Partial and Full Convergence of Inner Loop

Problem Method	1	2	3
Wu & Bishnoi (1986b)	401	1243	952
Saeger & Bishnoi (1986)			
Ideal Option	242	586	934
Non-Ideal Option	162	586	220
This Work	300	630	561

Table 7.3a:Number of Thermodynamic Evaluations required by various
Solution Procedures

Table 7.3b:Number of Inverse operations required by various SolutionProcedures

Problem Method	1	2	3
Wu & Bishnoi (1986b)	11	19	18
Saeger & Bishnoi [*] (1986)			
Ideal Option	79	325	1019
Non-Ideal Option	28	2080	78
This Work	9	9	10

* Only tridiagonal matrix operations required

.

Problem Method	1	2	3	
Wu & Bishnoi (1986b)	401	1243	952	
Saeger & Bishnoi (1986)				
Ideal Option	242	586	934	
Non-Ideal Option	162	586	220	
This Work	300	630	561	

1

.

Table 7.3a:Number of Thermodynamic Evaluations required by variousSolution Procedures

Table 7.3b:Number of Inverse operations required by various SolutionProcedures

Problem Method	1	1 2		
Wu & Bishnoi (1986b)	11	19	18	
Saeger & Bishnoi [•] (1986)				
Ideal Option	7 9	325	1019	
Non-Ideal Option	28	2080	78	
This Work	9	9	10	

* Only tridiagonal matrix operations required

(1986) with the ideal option. However, it requires more thermodynamic evaluations than the algorithm of Saeger and Bishnoi (1986) with the nonideal option for all three problems. The number of times the Jacobian matrix is inverted by the various solution algorithms are compared in Table 7.3b. Note that in this case the proposed algorithm can only be compared with the method proposed by Wu and Bishnoi (1986b) as both methods invert *block* tridiagonal system of matrices. The solution method proposed by Saeger and Bishnoi (1986) utilizes only tridiagonal matrix, and hence a direct comparison of the proposed solution method is not possible. As observed from Table 7.3b, the proposed algorithm requires substantially less matrix operations than the method proposed by Wu and Bishnoi (1986b).

7.2 THREE PHASE SEPARATION COLUMNS

The algorithm for the two phase separation columns presented earlier is extended for the simulation of a three phase distillation column.

7.2.1 Proposed Algorithm

solution method presented earlier Section 7.1 The in for the simulation of two phase distillation columns can easily be utilized for three phase distillation calculations. The S(4N+6)the system of equations are partitioned into two groups. In an inner loop S(N+6)equations are solved simultaneously for the moles of a component leaving a stage, m_{ij} , stage temperatures, T_{ij} , phase fractions, α_{kj} , and the stability variables, θ_{i} . Subsequently, the remaining S(3N) equations are utilized to calculate the component mole fractions in an outer loop.

The inner loop solves the component material balances (Equation 6.24), enthalpy balances (Equation 6.25), phase fraction summations

(Equation 6.26). summation equations (Equation 6.27). stability equations (Equation 6.33) and the specification equations (Equations 6.36, 6.38, 6.39) simultaneously using the Newton-Raphson procedure. The Jacobian matrix for this purpose is obtained analytically. The required derivatives are given in Appendix D. Approximate thermodynamic models, as given in Section 7.1.1, are utilized. As in the case of two phase column calculations, the optimal step size policy of Kalogerakis and Luus (1983) is used in the inner loop. This ensures that the residuals in the inner loop decreases in each iteration. The inner loop of the algorithm is considered to be converged when the sum of squares of the residuals are less than a predefined tolerance, ε .

In the outer loop of the proposed algorithm, Equations (6.28) and (6.32) are solved for the component mole fractions. Subsequently the rigorous thermodynamic model is employed to update the equilibrium ratios, the partial molar enthalpies and their temperature derivatives. The outer loop is considered to be converged when the errors in the mole fractions, defined by Equation (7.7), and the stage temperatures are less than a predefined tolerance.

The computations of the proposed three phase distillation algorithm are initialized by performing a few iterations of two phase distillation calculations, typically until stage temperatures between two iterations are within 1 K. Subsequently on each stage the liquid generated is flashed for two liquid phases. However, only one iteration is performed. The liquid-liquid flash calculation generates the values of the compositions of the two liquid phases. These compositions are utilized to calculate the equilibrium ratios, the partial molar enthalpies and their temperature derivatives for the two liquid phases.

A difference in the proposed algorithm for the two and three phase distillation calculations should be noted here. In the case of three phase distillation calculations, some of the stages may have the same values of the equilibrium ratios for the two liquid phases (so called "trivial solution"). This would lead to a singular Jacobian matrix in the inner loop of the proposed algorithm. In this case the two phases are collapsed. The second summation and stability equations are removed from the equation set and the corresponding phase fraction and stability variable are set to zero. Furthermore, note that the "trivial" liquid phase is not reinitialized in the proposed algorithm. However, once the three phase algorithm converges, a stability test could be performed on the stages with two liquid phases having the same compositions.

7.2.2 Evaluation of the Proposed Algorithm

The proposed algorithm for three phase distillation calculations is utilized to solve two distillation problems in which some of the stages could have three phases. Both the problems are from Block and Hegner (1976). Table 7.4 gives the specifications of the problems. The NRTL activity coefficient model (Renon and Prausnitz, 1968) is utilized to calculate the liquid phase activity coefficients while the vapor phase is considered to be ideal. The parameters for the NRTL activity coefficient model for Problem 1 are obtained from Block and Hegner (1976) while those reported by Mandhane and Heidemann (1973) are used for Problem 2. The iterative calculations are considered to be converged when the errors in the inner loop and the outer loop are less than 1×10^{-8} and 1×10^{-4} respectively.

Problem Components	Feed	Column Specifications
(1)		
Water,	$F_{5} = 50,$	s=13, P=0.1 MPa,
n-propanol,	$T_{f} = 363.35$, liquid	$B=21, R_1=3.0, R_2=3.0$
n-butanol	z : 0.65, 0.22, 0.13	Total condenser
(2)		
Water,	F ₂ =50, S.L.	s=7, P=0.1 MPa,
butylacetate,	z : 0.32, 0.46, 0.22	$B=34$, $R_1=1.0$, $R_2=0.0$
n-butanol		Total condenser

Table 7.4 : Specifications for the Three Phase MultistageSeparation Problems

.

Stage	Тетр	ærature,	Va	por	Liquid	1	Liquid	2
	°C		(mol/h)		(mol/h)	(mol/h))
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1	88.3	88.4	0.00	0.00	116.0	116.0		
2	88.8	88.9	116.00	116.00	87.0	87.1		
3	89.5	89.5	115.98	116.10	87.0	87.2		
4	90.1	90.1	115.98	116.22	87.0	87.3		
5	90.5	90.5	115.98	116.31	137.0	137.4		
6	91.0	90.9	115.99	116.43	137.0	137.6		
7	91.4	91.3	116.01	116.56	135.1	137.7	1.89	
8	91.8	91.7	116.00	116.66	123.9	128.5	13.05	9.25
9	92.1	92.0	115.98	116.73	115.2	118.9	21.72	18. 9 1
10	92.3	92.2	115.96	116.79	108.6	111.7	28.37	26.15
11	92.5	92.4	115.93	116.84	103.4	106.2	33.49	31.68
12	92.7	92.6	115.90	116.88	18.8	19.1	2.22	1.89
Reboil	er Dut	y (Watts)		1367	1392		
Conde	nser D	uty (Wa	tts)		1368	1393		

 Table 7.5 : Comparison of results for the mixture of Water, n-Propanol

 and n-Butanol

(1) This Work

.

(2) Block and Hegner (1976)

Stage	Phase	Water	n-Propanol	n-Butanol	Ref
1	v	59.8940	38.6853	1.4207	(1)
-	-	60.1846	38.3460	1.4694	(2)
	L1	61.7352	35.2117	3.0530	ā
		61.9607	34.9552	3.0840	$(\tilde{2})$
	L2	68.2500	29.2689	2.4810	(1)
2	v	61.7352	35.2117	3.0531	(1)
		61.9607	34.9552	3.0840	$(\tilde{2})$
	L1	64.6658	29.5234	5.8108	(1)
		64.7114	29.5123	5.7763	$(\tilde{2})$
	L2	74.1626	21.8008	4.0366	(1)
3	v	63.9330	30.9458	5.1212	(1)
•		64.0244	30.8718	5.1038	$(\tilde{2})$
	L1	67.4198	24.0166	8.5635	(ī)
	21	67 2762	24 2514	8 4724	(2)
	L2	80.2341	15.0709	4.6949	(1)
4	v	65.9984	26.8160	7.1856	(1)
-		65.9498	26.9224	7.1278	$(\tilde{2})$
	L1	69.3391	19.8062	10.8547	ā
	21	69 0801	20 1717	10 7482	
	L2	85.5540	10.1159	4.3301	(1)
5	v	67.4378	23.6584	8,9039	(1)
•	·	67.3049	23.8578	8.8372	$(\tilde{2})$
	L.1	69 1687	17 6698	13 1615	$(\tilde{1})$
	LI	68 9119	18 0495	13 0386	(2)
	L2	88.0846	7.7613	4.1541	(1)
6	v	69 1072	20 1891	10 70308	(1)
v	•	68 8604	20 5639	10 5757	(2)
	T 1	70 5401	14 7103	14 7406	(2)
		70.3401	15 1800	14 5868	(1)
	12	01 6853	5 1236	3 1010	(2)
	24	71.00 JJ	J.12JU	J.1710	(1)

Table 7.6a:Phase Compositions (mol %) for the mixture of Water,
n-Propanol and n-Butanol

V = Vapor; L1 = Liquid 1; L2 = Liquid 2

(1) This Work (2) Block and Hegner (1976)

Stage	Phase	Water	n-Propanol	n-Butanol	Ref
7	v	70.7268	16.7041	12.5691	(1)
		70.4093	17.1852	12.4055	(2)
	L1	71.2783	12.1781	16.5436	(1)
		71.2946	12.5485	16.1569	(2)
	L2	93.8159	3.5230	2.6612	(1)
8	v	71.9660	13.5619	14.4721	(1)
		71.6722	14.0677	14.2601	(2)
	L1	70.1275	10.4084	19.4641	(1)
		70.5573	10.6984	18.7443	(2)
	L2	94.9276	2.5844	2.4880	$(\overline{1})$
		94.7484	2.7422	2.5094	(2)
9	v	73.0303	10.7326	16.2371	(1)
		72.7187	11.2534	16.0279	$(\overline{2})$
	L1	68.9912	8.6648	22.3439	(1)
		69.3227	9.0254	21 6519	(2)
	L2	95 7554	1 8877	2 3569	(2)
	22	95.5993	2.0223	2.3784	(2)
10	v	73.9110	8.2845	17.8046	(1)
		73.5998	8.7754	17.6248	(2)
	L1	67.9510	7.0093	25.0397	(1)
		68.2274	7.3864	24.3862	$(\hat{2})$
	L2	96.3728	1.3688	2.2584	(1)
	22	96.2448	1.4782	2.2770	(2)
11	v	74.6243	6.2184	19,1573	(1)
	·	74 3236	6 6531	19 0233	(2)
	L1	67 0326	5 4870	27 4805	(1)
	21	67 2697	5 8475	26 8828'	(2)
	12	06 8373	0 0786	20.0020	(\mathbf{L})
		96.7358	1.0650	2.1992	(1) (2)
12	v	75,1965	4,4980	20.3055	(1)
	·	74,9110	4.8634	20.2257	(2)
	L1	66 2390	4 1183	29 6428	(1)
		66 4300	4 4416	20 1105	(1)
	12	07 1000	1.4410 0.6815	27.1175 2 127K	(2)
	L2	97.1128	0.7478	2.1276	(2)
		21.1120	0		(~)

Table 7.6b:Phase Compositions (mol %) for the mixture of Water,
n-Propanol and n-Butanol

.

V = Vapor; L1 = Liquid 1; L2 = Liquid 2

(1) This Work (2) Block and Hegner (1976)

A Mixture of Water, n-Propanol and n-Butanol

A three phase distillation problem described by Block and Hegner (1976) is solved by the proposed algorithm. Table 7.4 gives the problem specifications. Table 7.5 and Table 7.6 compares the results obtained using the proposed algorithm and those of Block and Hegner (1976). As seen, stage temperatures and stage flow rates are in good agreement. Furthermore, the reboiler and the condenser duties also compare well with those reported by them. The second liquid phase is predicted on stages 6 to 12 using the proposed algorithm. The calculated phase compositions for the three phases are compared with those reported by Block and Hegner (1976) in Tables 7.6a and 7.6b. As seen, the phase compositions are in good agreement. Furthermore, note that even when the water rich liquid (Liquid 2) is absent on a stage, its composition and the corresponding equilibrium ratios are calculated by the proposed algorithm.

The phase fractions and the stability variables calculated for the water rich liquid phase is shown in Figure 7.2. The stages with a zero value of the phase fraction, have a nonzero positive value for the stability variable. This implies that for these stages the water rich liquid is unstable and would not be present at equilibrium.

The changes in the phase fraction and the stability variables for the water rich liquid during the iterations is shown in Figures 7.3 and 7.4. In the beginning, the phase fraction for the water rich liquid is non-zero and the stability variable is zero for all the stages. In the 11th iteration the phase fraction of the water rich liquid for stage 1 becomes zero and the stability variable becomes non-zero. As the


Figure 7.2 : Water Rich Liquid Phase Fraction and Stability Variable for the Mixture of Water, n-Propanol and n-Butanol



Figure 7.3 : Phase Fraction of the Second Liquid Phase for the Mixture of Water, n-Propanol and n-Butanol



٠

Figure 7.4 : Stability Variable of the Second Liquid Phase for the Mixture of Water, n—Propanol and n—Butanol



Figure 7.5 : Approach to convergence for the Mixture of Water, n-Propanol and n-Butanol

computations proceed, the phase fraction of the water rich liquid becomes zero on stages 2, 3, 5, 4, 6 in iterations 11, 13, 16, 17, 19 and 22 respectively and the stability variable becomes non-zero. Finally a solution in which the phase fraction of the water rich liquid is zero on stages 1 to 6 and the stability variable is non-zero is obtained.

Figure 7.5 shows the convergence behavior of the algorithm. As seen, the error in the inner loop decreases uptil 9th iterations, fluctuates and then again decreases after the 23rd iteration. The error in the outer loop shows less fluctuations than that in the inner loop and decreases continuously. A converged solution is obtained in the 33 iterations and 488, seconds.

A Mixture of Water, Butylacetate and n-Butanol

The algorithm is utilized to study a three phase distillation problem of water, butylacetate and n-butanol. The specifications of the problem are given in Table 7.4. Note, that the problem specifies that all the second liquid formed (water rich liquid) on stage 1 should be withdrawn. Table 7.7 gives the stage temperatures and the stage flow rates. As seen, the second liquid phase is formed only on stage 1. This liquid is withdrawn totally.

Figure 7.6 shows the calculated values of the phase fractions and the stability variables for the second liquid for different stages. For stages 2 to 6 the value of the phase fraction is zero and the value of the stability variable is non-zero. The second liquid phase is present on stage 1 and the stability variable is zero. For stage 7, the composition of the second liquid phase converges to the composition of the first liquid phase and a solution in which both the phase fraction

Stage	°C	Vapor (mol/h)	Liquid 1 (mol/h)	Liquid 2 (mol/h)
1	90.89	0.00	8.79	11.61
2	91.08	20.40	54.43	
3	91.08	20.43	54.42	
4	91.11	20.43	54.42	
5	91.29	20.42	54.38	
6	92.61	20.38	54.23	
7	100.60	20.23	34.00	
Reboiler Duty (Watts)			261	
Condenser Duty (Watts)			235	

 Table 7.7 : The results for the mixture of Water, Butylacetate and n-Butanol

.

Stage	Phase	Water	Butylacetate	n-Butanol	
1	v	70.7902	19.9895	9.2204	
-	L1	33.1395	45.7819	21.0787	
	L2	98.6223	0.4945	0.8832	
2	v	70.4001	20.0126	9.5873	
	L1	32.1111	45.9676	21.9213	
	L2	98.5537	0.5073	0.9390	
3	v	70.3915	20.0133	9.5952	
-	L1	32.0894	45.9714	21.9392	
	L2	98.5522	0.5076	0.9402	
4	v	70.3361	20.0218	9.6422	
	L1	31.9435	46.0125	22.0440	
	L2	98.5427	0.5096	0.9477	
5	v	69.9597	20.1229	9.9174	
Ū	Ĺ1	30.9221	46.4442	22.6336	
	$\overline{L2}$	98.4820	0.5238	0.9942	
6	v	67 3023	21 2287	11 4690	
Ū	Ĺ1	24.7758	49.8793	25.3450	
	L2	98.0129	0.6545	1.3327	
7	v	51 1034	30.2443	18,6523	
'	Ľ1	9.1152	61.5588	29.3260	
	L2	9.1152	61.5588	29.3260	

Table 7.8 : Equilibrium Phase Compositions (mol %) for the

mixture of Water, Butylacetate and n-Butanol

V = Vapor; L1 = Liquid 1; L2 = Liquid 2

.



Figure 7.6 : Water Rich Liquid Phase Fraction and Stability Variable for the Mixture of Water, Butylacetate and n-Butanol



Figure 7.7 : Approach to convergence for the Mixture of Water, Butylacetate and n-Butanol

and the stability variable is zero is obtained.

Table 7.8 gives the calculated equilibrium phase compositions for the mixture. Note that even when the water rich liquid is absent on a stage, its composition and the corresponding equilibrium ratios are calculated.

The convergence behavior of the proposed algorithm for this problem is shown in Figure 7.7. The three phase distillation calculations are started after six iterations of two phase distillation computations have been performed. The error in the inner loop decreases during these six iterations, then increases and fluctuates until 23rd iterations and then again decreases. The error in the outer loop also shows a similar behavior. A converged solution is obtained in the 31 iterations and 284 CPU seconds.

It should be noted from Table 7.8, that the two liquid phases leaving stage 7 are of the same compositions. In this case, the two liquid phases are collapsed together (i.e. their phase fractions are added together) and further computations on this stage are done with only vapor and one liquid phase. As mentioned before, in the proposed algorithm once one of the liquid phase becomes trivial, it is *not* reinitialized.

7.3 DISCUSSION OF RESULTS

The proposed algorithm for the two and three phase multistage separation calculations has been applied to simulate an absorber column, a reboiled absorber and a number of distillation columns. The utility of the simultaneous calculation of the phase fractions and the stability variables in the simulation of three phase column computation has been demonstrated. As shown for the single stage processes in Chapter 5, the simultaneous calculation the phase fractions of and the stability variables enables handle logically us to the appearance and disappearance of phase in multiphase multistage separation a a calculations.

The proposed algorithm for two phase separation columns is utilized to solve azeotropic and extractive distillation problems. For the extractive distillation problem, the effect of the partial convergence of the inner loop on the error in the outer loop has been examined. The results show that the partial convergence of the inner loop *does not* in anyway hamper convergence in the outer loop and leads to a computational savings of 50%.

In the proposed algorithm the convergence in the outer loop is checked on the differences between the mole fractions between two successive iterations. Instead, as in the conventional flash algorithms, it is possible to check the convergence on the differences of logarithm of the equilibrium ratios between two successive iterations. The change in the convergence criterion in the outer loop did not alter the converged results. Hence, as in single stage processes, the differences between the mole fractions between two successive iterations is utilized as the convergence criterion in the outer loop of the proposed algorithm.

The number of thermodynamic evaluations and the matrix operations required by the proposed algorithm is compared with those required by the solution methods proposed by Wu and Bishnoi (1986b) and Saeger and Bishnoi (1986). The proposed algorithm requires less thermodynamic and matrix evaluations than the method proposed by Wu and Bishnoi (1986b). However, more thermodynamic evaluations are required than the nonideal method proposed by Saeger and Bishnoi (1986).

The proposed algorithm for three phase distillation calculations has been applied to solve two problems from the literature. The usefulness of simultaneously calculating the stability variables and the phase fractions is demonstrated. As pointed out before in Chapter 3, stability variables provides with of us а means following the appearance/disappearance of a phase during computations. The compositions and the equilibrium ratios of the phases which are not computations is calculated. This allows present during for the appearance/disappearance of a phase during computations. A separate liquid-liquid stability test, as required by most of the other three phase distillation algorithms, is not required by the proposed algorithm. This is expected to lead to a large computational savings in a three phase distillation algorithm.

In the proposed algorithm for three phase distillation calculations, some of the phases could become trivial (i.e. two phases could have the same values of the equilibrium ratios) on some of the stages during computations. In this case, for these stages the proposed algorithm collapses the two liquid phases together and further computations on these stages are done on the vapor and one liquid phase. In the proposed algorithm the trivial liquid phase is not reinitialized. However, once the three phase algorithm has converged, the liquid phase on these stages could be checked for stability.

The proposed solution algorithm for multistage multiphase separation

processes has been illustrated for non-reactive systems. However, as shown in Chapter 5 for single stage processes, the proposed method can easily be modified for reactive system. In this case, as in the case of single stage processes, it would not be necessary to converge the extent of the reactions first and then examine the stability of the system. The phase fractions. the stability variables and the extents of the reactions could all be calculated simultaneously.

Simultaneous computation of the phase fractions and stability variables on a stage in multiphase computations permits us to monitor the appearance/disappearance of a phase during computations.

7.4 SUMMARY

Algorithms for the simulation of three phase distillation columns and two phase multistage separation processes are presented. Α comparison of the computational effort required by the proposed algorithm for two phase separation calculations is made with three other existing algorithms. The effectiveness of the three phase distillation algorithm is illustrated by solving problems from the literature.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

The main thrust of this work has been to develop computational methods for the steady state simulation of single and multistage separation processes involving multiple phases. The conclusions of this study are :

1. An acceleration technique, based on the Dominant Eigenvalue Method of Orbach and Crowe (1971), can be utilized to accelerate the successive substitution method in single stage flash computations. The proposed technique is evaluated in a two phase flash algorithm in which liquid and vapor compositions are used as the iteration variables. The proposed acceleration exhibits during scheme а less oscillatory behavior convergence and requires less storage than the accelerated methods using the K-factors as the iteration variables. However, the number of thermodynamic evaluations is comparable with that of Mehra et al. (1983) and is more than that of Michelsen (1982, 1987).

2. An alternative development of the stability criterion for multiphase reacting/non-reacting systems is presented. This new development of the stability criterion has led to a formulation of a set of coupled nonlinear algebraic equations which describe both the stability and the isothermal-isobaric flash calculations of reacting and non-reacting systems.

3. An active set solution algorithm is developed for the simultaneous

solution of stability and multiphase flash calculations. The effectiveness and efficiency of the proposed algorithm are illustrated by solving a number of multiphase problems. For a test example it is shown that the computational savings of more than fifty percent over the conventional algorithm can be obtained. The application of the algorithm is illustrated by solving a number of typical phase equilibrium problems encountered in gas processing and petrochemical industries, in enhanced oil recovery schemes and in systems containing gas hydrates.

4. A solution method which is based on the Newton-Raphson procedure is presented for the computation of stability and multiphase equilibria in reacting/non-reacting systems. The method solves the stability and the summation equations for the phase fractions and the stability variables. using the Newton Raphson method. The stability equation has been transformed alleviate the problems associated with the to ill-conditioning and the singularity of the Jacobian near the phase boundaries. The appearance or disappearance of a phase during the computations is easily handled. The algorithm is found particularly effective for computations near phase boundaries and for multiphase reactive systems.

5. The Newton-Raphson solution procedure for the simultaneous computation of stability and flash calculations in multiphase systems is extended to handle the isenthalpic flash computations in non-reacting systems. The proposed algorithm is found to be effective for narrow boiling mixtures and it does not show any oscillations in temperature during iterations.

6. A new scheme for the initializing of multiphase flash computations

is proposed. The scheme utilizes the distance between the Gibbs free energy and the tangent hyperplane as a criterion to select the required equilibrium ratios for the $(\pi$ -1) phases. This technique is subsequently utilized to initialize all the multiphase computations performed in this study.

7. The formulation of simultaneous stability and flash calculations for single stage separation processes is extended for the simulation for multistage separation processes involving multiple phases. New variables which represent the total moles of a component leaving a stage are introduced and utilized in this formulation. The formulation describes the two and three phase distillation processes, absorbers and reboiled absorbers with the same set of equations.

8. An algorithm is presented for the solution of two phase distillation columns, reboiled absorbers and absorber columns. The method is based on the Newton-Raphson solution procedure and in principle is an extension of single stage flash algorithm. Furthermore, it utilizes a norm reduction policy and approximate thermodynamic models in the inner loop. The performance of the algorithm is compared with three existing two phase algorithms. It is found to be efficient.

9. An algorithm for the computations of three phase distillation calculations is presented. It utilizes the formulation of multiphase multistage separation processes developed in this work and extends the two phase multistage separation algorithm. The effectiveness of the proposed algorithm is illustrated by solving two problems from the literature.

10. A major obstacle of phase appearance and disappearance in multiphase

computations is removed.

8.2 RECOMMENDATIONS FOR FURTHER RESEARCH

In order to improve the efficiency of the proposed algorithms and to obtain better thermodynamic representations of the phase behavior of complex systems more research work is required. In addition, methods for decreasing the large storage requirements for multistage separation algorithms should be investigated.

In this work all the algorithms proposed for the simulation of single stage separation processes are based on a "two-tiered" approach. An inner loop is utilized in solving for the phase fractions and stability variables while in the outer loop the phase compositions are updated. An acceleration procedure is used for updating the compositions in single stage processes. Algorithms based on the simultaneous solution of *all* the model equations should be investigated and their performance should be compared with the algorithms proposed in this work.

The simultaneous solution of stability and equilibrium computations investigated for isothermal and has been isenthalpic flash computations can be extended for specifications. These the other specifications of the variables. In particular, computations of multiple bubble and dew point temperatures and phase envelopes should be undertaken.

For the simulation of multistage separation processes, an algorithm based on the Newton Raphson procedure is proposed. Unfortunately, the storage requirement of the algorithm is of the order of N^2 , where N is the number of components present. This sort of algorithm is well suited for the simulation of systems when the number of components present is small and there is large interaction between the variables. However, for hydrocarbon systems generally large number of components are present. Since in these systems there is less interactions between the variables, alternative algorithms that require less storage should be examined.

The algorithm for three phase distillation calculations can give a solution in which two phases are trivial on some of the stages. This problem is similar to the problem encountered in single stage flash processes where trivial solution can also be obtained. As in the case of single stage processes, in this case it is possible to reinitiate a trivial Methods circumvent this problem phase. to should be investigated.

Another area which requires further research work is the development of thermodynamic models which represent the phase behavior of the polar components in a consistent manner. These models are extremely important in the simulation of three phase distillation columns. Three phases occur due to nonidealities in the mixture and these nonidealities should be well represented by the thermodynamic model. Furthermore, in the multistage computations it is necessary that the thermodynamic model represents the phase behavior of the system in the whole range of compositions and temperatures. Thermodynamic models which are consistent and suitable for this purpose should be investigated.

REFERENCES

Abrams, D. S. and J. M. Prausnitz, "Thermodynamics of Liquid Mixtures", AICHE J., 21, 116, 1975.

Agarwal R. K., Li, R. K., Nghiem, L. X. and D. A. Coombe, "Multi-Phase Multi-Component Isenthalpic Flash Calculations with a Cubic Equation of State", presented at 39th Annual Technical Meeting of the Petroleum Society of CIM, Calgary, June, 1988.

Ammar, M. N. and H. Renon, "The Isothermal Flash Problem: New Methods for Phase Split Calculations", AIChE J., 33, 926-939, 1987.

Asselineau, L., Bogdanic, G. and J. Vidal, "A Versatile Algorithm for Calculating Vapor-liquid-Liquid Equilibria", Fluid Phase Equilibria 3, 273-290, 1979.

Baden, N. and M. L. Michelsen, "Computer Methods for Steady-State Simulation of Distillation Columns", I. Chem. E. Symposium Series No. 104, A425, 1988.

Baker, L. E., A. C. Pierce and K. D. Luks, "Gibbs Energy Analysis of Phase Equilibria", Soc. Pet. Eng. J., 22, 731-742, 1982.

Bishnoi, P. R., Gupta, A. K., Englezos, P. and N. Kalogerakis, "Multiphase Equilibrium Flash Calculations for Systems Containing Gas Hydrates". Fluid Phase Equil., 53: 97-104, 1989.

Boston, J. F., "Inside-Out Algorithms for Multicomponent Separation Process Calculations", ACS Symp. Ser. No. 124, 1980.

Block, U. and B. Hegner, "Development and application of a Simulation Model for Three-Phase Distillation", AIChE J., 22, 582-589, 1976.

Boston, J. F. and H. I. Britt, "A Radically Different Formulation and Solution of the Single-Stage Flash Problem", Comput. Chem. Eng. 2, 109-122, 1978. Boston, J. F. and V. B. Shah, "An Algorithm for Rigorous Distillation Calculation with Two Liquid Phases". Paper presented at the 86th National Meeting of the A.I.Ch.E., Houston, April 1979.

Boston, J. F. and S. L. Sullivan, "A New Class of Solution Methods for Multicomponent, Multistage Processes", Can. J. Chem. Eng., 52, 52 1974.

Broyden, C.G., "A Class of Methods for Solving Nonlinear Simultaneous Equations", Math. Comput., 19, 577, 1965.

Broyden, C.G., "The Convergence of an Algorithm for Solving Sparse Nonlinear Systems", Math. Comput., 25, 285, 1971.

Cairns, B. P. and I. A. Furzer, "Multicomponent Three-Phase Azeotropic Distillation. 2. Phase-Stability and Phase-Splitting Algorithms", Ind. Eng. Chem. Res., 29, 1364-1382, 1990.

Castier, M., Rasmussen, P. and A. Fredenslund, "Calculation of Simultaneous Chemical and Phase Equilibria in Nonideal Systems", *Chem. Eng. Sci.*, 44, 237-248, 1989.

Castillo, J. and I. E. Grossmann, "Computation of Phase and Chemical Equilibria", Comput. Chem. Eng., 5, 99-108, 1981.

Crowe, C. M. and M. Nishio, "Convergence Promotion in the Simulation of Chemical Processes- The General Dominant Eigenvalue Method", AIChE J. 21, 528-533, 1975.

Crowe, C. M., "On a Relationship between Quasi-Newton and Dominant Eigenvalue Methods for the Numerical Solution of Non-Linear Equations", Computers and Chemical Engineering, 8, 35-41, 1984.

Dahlquist, G. and A. Bjorck, "Numerical Methods", Prentice-Hall, Englewood Cliffs, NJ, 1974.

Englezos P., "Phase Equilibrium in Gas Hydrates forming Systems in the Presence of Electrolyte or Methanol, and Estimation of Interaction Parameters in Equation of State", Ph.D. Thesis, University of Calgary, Calgary, Canada, 1990.

Ferraris, G. B. and M. Morbidelli, "Distillation Models for Two Partially Immiscible Liquids", AIChE J., 27, 881-888, 1981.

Ferraris, G. B. and M. Morbidelli, "An Approxiamate Mathematical Model For Three-Phase Multistage Separators", AIChE J., 28, 49-55, 1982.

Fussel, L. T., "A Technique for Calculating Multiphase Equilibria", Society of Petroleum Engineers Journal, 8, 203-211, 1979.

Gautam, R. and W. D. Seider, "Computation of Phase and Chemical Equilibria", AIChE J., 25, 991-1051, 1979.

Gupta, A. K., P. R. Bishnoi and N. Kalogerakis, "An Accelerated Successive Substitution Method for Single Stage Flash Calculations", Can. J. Chem. Eng., 66, 291-296, 1988.

Gupta, A. K. and P.R. Bishnoi, "Applications of a New Algorithm for Multiphase Flash Calculations using Trebble-Bishnoi Equations of State". Recent Advances in Chemical Engineering (Proceedings of the International Conference on Advances in Chemical Engineering, Kanpur, India, Jan 4-6) ed. D. N. Saraf and D. Kunzru, Tata McGraw-Hill, New Delhi, 1989.

Gupta, A.K., P.R. Bishnoi and N. Kalogerakis, "A Method for the Simultaneous Phase Equilibria and Stability Calculations for Multiphase Reacting and Non-Reacting systems". Accepted for publication in *Fluid Phase Equilibria* (September 20), 1990a.

Gupta, A.K., P.R. Bishnoi and N. Kalogerakis, "Simultaneous Multiphase Isothermal/Isenthalpic Flash and Stability Calculations for Reacting/Non-Reacting Systems", presented at American Institute of Chemical Engineers 1990 Spring National Meeting, March 18-22, Orlando, 1990. Accepted for publication in Gas Separation æ **Purification** (August 24), 1990b.

Heidemann, R. A., "Three Phase Equilibria using Equations of State", AIChE J., 20, 847-855, 1974.

Heidemann, R. A., "Computation of High Pressure Phase Equilibria", Fluid Phase Equilibria 14, 55-78, 1983.

Henley, E. J. and E. M. Rosen, "Material and Energy Balance Computations", John Wiley, New York, 1969.

Hirose, Y., Kawase, Y. and M. Kudoh, "General Flash Calculation by the Newton-Raphson method", J.Chem.Eng.Jpn. 11, 150-152, 1978.

Ishii, Y. and F. Otto, "A General Algorithm for Multistage Multicomponent Separation Calculations", Can. J. Chem. Eng., 51, 601-606, 1973.

Joulia, X., P. Maggiochi, B. Koehret, H. Paradowski and J. J. Bartuel, "Hybrid Method for Phase Equilibrium Flash Calculations", Fluid Phase Equilibria 26, 15-36, 1986.

Kalogerakis, N. and R. Luus, "Improvement of Gauss-Newton Method for Parameter Estimation through the use of Information Index", IEC Fundamentals, 22, 436-445, 1983.

Kinoshita, M. and T. Takamatsu, "A Powerful Solution Algorithm for Single-Stage Flash Problems", Comput. Chem. Eng. 10, 353-360, 1986.

Kinoshita, M., Hashimoto, I. and T. Takamatsu, "A New Simulation Procedure for Multicomponent Distillation Columns Processing Non-Ideal Solutions or Reactive Solutions", J. Chem. Eng. Japan., 16, 370-377, 1983a.

Kinoshita, M., Hashimoto, I. and T. Takamatsu, "A Simulation Procedure for Multicomponent Distillation Column within which Three Phases of Vapor and Two Partially Immiscible Liquids are present", J. Chem. Eng. Japan., 16, 513-516, 1983b. Lantagne, G., Marcos, R. and B. Cayrol, "Computation of Complex Equilibria by Nonlinear Optimization", Comput. Chem. Eng., 12, 589-599, 1988.

Mauri, C., "Unified Procedure for Solving Multiphase-Multicomponent Vapor-Liquid Equilibrium Calculation", Ind. Eng. Chem. Process Des. Dev., 19, 482-489, 1980.

Mandhane, J. M. and R. A. Heidemann, "NRTL Parameters for the Thernary System n-Butanol, n-Butylacetate and Water", Can. J. Chem. Eng. 51, 381-385, 1973.

Mehra, R. K., R. A. Heidemann and K. Aziz, "Computation of Multiphase Equilibrium for Compositional Simulation", Soc. Pet. Eng. J., 22, 61-68, 1982.

Mehra, R. K., R. A. Heidemann and K. Aziz, "An Accelerated Successive Substitution Algorithm", Can. J. Chem. Eng. 61, 590-596, 1983.

Michelsen, M. L.,"The isothermal flash problem. 1. Stability", Fluid Phase Equil., 9: 1-19, 1982a.

Michelsen, M. L., "The Isothermal Flash Problem. Part II. Phase-Split Calculations", Fluid Phase Equilibria 9, 21-40, 1982b.

Michelsen, M. L., "Multiphase Isenthalpic and Isoentropic Flash Algorithms", Fluid Phase Equilibria 33, 13-27, 1987.

Michelsen, M. L., "Calculation of Multiphase Ideal Solution Chemical Equilibrium", *Fluid Phase Equil.*, 53: 73-80, 1989.

Murray, W., "Second derivative methods". In W. Murray, (eds), Methods for Unconstrained Optimization, Academic Press, London, 1972.

Naphtali, L. M. and D. P. Sandholm, "Multicomponent Separation Calculations by Linearization", AICHE J., 17, 148-153, 1971.

Ng, N., Robinson, D. B. and A. Leu, "Critical Phenomena in a Mixture of Methane, Carbon dioxide and Hydrogen sulfide", *Fluid Phase Equil.*, 19, 273-286, 1985.

Nghiem, L.X. and Y. Li, "Computation of Multiphase Equilibrium Phenomena with an Equation of State", *Fluid Phase Equil.* 17, 77-95, 1984.

Nghiem, L.X. and R. A. Heidemann, "General Acceleration Procedure for Multistage Flash Calculations with Applications to Oil-Gas-Water Systems", Proceedings of the Second European Symposioum on Enhanced Oil Recovery, 1982.

Orbach, O. and C. M. Crowe, "Convergence Promotion in the Simulation of Chemical Processes with Recycle - the Dominant Eigenvalue Method", Can. J. Chem. Eng. 49, 509-513, 1971.

Peng, D. Y. and D. B. Robinson, "A New Two-Constant Equation of State", Ind. Eng. Chem. Fund. 15, 59-64, 1976.

Prausnitz, J. M., Anderson, T., Grens, E., Eckert, C., Hsieh, R. and J. O'Connell, "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria", Prentice-Hall, 1980.

Pucci, A., Mikitenko, P. and L. Asselineau, "Three-Phase Distillation. Simulation and Application to the Separation of Fermentation Products", Chem. Eng. Sci., 41, 485-494, 1986.

Rao, S. S., "Optimization : Theory and Application", John Wiley, New Delhi, 1984.

Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids", McGraw-Hill, New York, 1987.

Renon, H. and J. M. Prausnitz, "Local Composition in Thermodynamic Excess Functions for Liquid Mixtures", AICHE J., 14, 135, 1968.

Rijkers, M. P. W. and R. A. Heidemann, "Convergence Behavior of Single Stage Flash Calculations", in Equations of State- Theory and Applications ed. by K.C. Chao and R. L. Robinson, Am. Chem. Soc., Washington, 1986.

Risnes, R. and V. Dalen, "Equilibrium Calculations for Coexisting Liquid Phases", Soc. Pet. Eng., J. 24, 87-96, 1984.

Ross, B. A. and W. D. Seider, "Simulation of Three-Phase Distillation Towers", Comput. Chem. Eng., 5, 7-20, 1980.

Saeger, R. B. and P. R. Bishnoi, "A Modified 'Inside-Out' Algorithm for Simulation of Multistage Multicomponent Separation Processes Using the UNIFAC Group-Contribution Method", Can. J. Chem. Eng., 64, 759-767, 1986.

Schubert, L. K., 1970, "Modification of a Quasi-Newton for Non-Linear Equations with a Sparse Jacobian", Math. Comput., 25, 27-30, 1970.

Schuil, J. A. and K. K. Bool, "Three-Phase Flash and Distillation", Comput. Chem. Eng., 9, 295-300, 1985.

Shah, M. K. and P. R. Bishnoi, "Multistage Multicomponent Separation Calculations Using Thermodynamic Properties Evaluated by SRK/PR Equation of State", Can. J. Chem. Eng., 56, 478, 1978.

Shelton, J. C. and L. Yarborough, "Multiple Phase Behavior in Porous Media during CO₂ or Rich-gas Flooding", J. Petrol. Technol., 29, 1171-1178, 1977.

Smith, W. R., "The Computation of Chemical Equilibria in Complex Systems", Ind. Eng. Chem. Fundum., 19, 1-10, 1980.

Smith, W. R. and R. W. Missen, "Strategies for Solving the Chemical Equilibrium Problem and an Efficient Microcomputer-based Algorithm", *Can. J. Chem. Engg.*, 66, 591-598, 1988.

Soares, M. E., A. G. Medina, C. McDermott and N. Ashton, "Three Phase Flash Calculations using Free Energy Minimisation", Chem. Eng. Sci., 37, 521-528, 1982.

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State", Chem. Eng. Sci., 27, 1197-1203, 1972.

Soliman, M. A., "Quasi Newton Methods for Convergence Acceleration of Cyclic Systems", Can. J. Chem. Eng. 57, 643-647, 1979.

Sujata, A. D., "Absorber-Striper Calculations Made Easier", Petrol. Refiner., 40, No. 12, 137-140, 1961.

Swartz, C. L. and W. E. Stewart, "Finite-Element Steady State Simulation of Multiphase Distillation", AIChE J., 33, 1977-1985, 1987.

Thiele, E. W. and R. L. Geddes, "Computation of Distillation Apparatus for Hydrocarbon Mixtures", Ind. Eng. Chem., 25, 289-295, 1933.

Tomich, J. F., "A New Simulation Method for Equilibrium Stage Process", AICHE J., 16, 229-232, 1970.

Trangenstein, J. A., "Customized Minimization Techniques for Phase Equilibrium Computations in Reservoir Simulation", Chem. Eng. Sci., 42, 2847-2863, 1987.

Trebble, M. A. and P. R. Bishnoi, "Extension of the Trebble-Bishnoi Equation of State to Fluid Mixtures", Fluid Phase Equil., 40, 1-21, 1988.

van der Waals J.H., and J.C. Platteeuw, "Clathrate Solutions", Adv. Chem. Phys. 2: 1-57, 1959.

Wang, J. C. and G. E. Henke, "Tridiagonal Matrix for Distillation", Hydrocarbon Processing, 45, 155-163, 1966.

Wu, J. and P. R. Bishnoi, "An Algorithm for Three-phase Equilibrium Calculations", Comput. Chem. Eng., 10, 269-276, 1986a.

Wu, J. and P. R. Bishnoi, "A Method for Steady-state Simulation of Multistage Separation Columns involving Nonideal Systems", Comput. Chem. Eng., 10, 343-351, 1986b.

Zandijcke F. and L. Verhoeye, "The Vapor-liquid Equilibrium of Ternary Systems with Limited Miscibility at Atmospheric Pressure", J. Appl. Chem. Biotechnol. 24, 709, 1974.

Data Sources

Chappelow, C. C. and J. M. Prausnitz, "Solubility of Gases in High Boiling Hydrocarbon Solvents", AIChE J. 20, 1097, 1974.

DaSie, W., "An Evaluation of the Trebble-Bishnoi Equation-Of-State with respect to Prediction of Phase Equilibrium in Binary and Ternary Systems", MEng. Thesis, Univ. of Calgary, Calgary, Canada, 1988.

DiAndreth, J. R., Ritter, J. M. and M. E. Paulaitis, "Experimental Technique for Determining Mixture Compositions and Molar Volumes of Three or More Equilibrium Phases at Elevated Pressures", Ind. Eng. Res. 26, 337, 1987.

Fall, D.J., Fall, J. L. and K. D. Luks, "Liquid-Liquid-Vapor Immiscibility Limits in Carbon Dioxide + n-Paraffins Mixtures", J. Chem. Eng. Data 30, 82, 1985.

Fall, J. L. and K. D. Luks, "Effect of Additive Gases on the Liquid-Liquid-Vapor Immiscibility of the Carbon Dioxide + n-Nonadecane Mixture", J. Chem. Eng. Data 31, 332-336, 1986.

Gilbert, M. L. and M. E. Paulaitis, "Gas-Liquid Equilibrium for Ethanol-Water-Carbon dioxide Mixtures at Elevated Pressures", J. Chem. Eng. Data 31, 296, 1986.

Kidnay, A. J., Miller, R. C., Parrish, W. R. and M. J. Hiza, "Liquid-Vapor Phase Equilbria in the Nitrogen-Methane System from 130 to 180 K", Cryogenics 15, 531-540, 1975. Llave, F. M., Luks, K. D. and J. P. Kohn, "Three-Phase Liquid-Liquid-Vapor equilibria in the Binary Sytems Nitrogen + Ethane and Nitrogen + Propane", J. Chem. Eng. Data 30, 435, 1985.

Llave, F. M., Luks, K. D. and J. P. Kohn, "Three-Phase Liquid-Liquid-Vapor equilibria in the Nitrogen + Methane + Ethane and Nitrogen + Methane + Propane Systems", J. Chem. Eng. Data 32, 14-17, 1987.

Luks, K. D., Merrill, R. C. and J. P. Kohn, "Partial Miscibility behavior in Cryogenic Natural Gas Systems", Fluid Phase Equilb. 14, 193-201, 1983.

Makranczy, J., Megyery-Balog, K., Rusz, L. and L. Patyi, Hung. J. Ind. Chem. 2, 4, 1976 in IUPAC Solubility Data Series, 10, Pergamon Press, 146, 1982.

Merrill, R. C., Luks, K. D. and J. P. Kohn, "Three-Phase Liquid-Liquid-Vapor Equilibria in the Methane + n-Hexane + Nitrogen and Methane + n-Pentane + Nitrogen Systems", J. Chem. Eng. Data 29, 272-276, 1984.

Ng, S., Harris, H. G. and J. M. Prausnitz, "Henry's Constants for Methane, Ethane, Ethylene, Propane and Propylene in Octadecane, Eicosane, and Docosane", J. Chem. Eng. Data 14, 482, 1969.

Panagiotopoulos, A. Z. and R. C. Reid, "High-Pressure Phase Equilibria in Ternary Fluid Mixtures with a Supercritical Component", In Supercritical Fluids (Eds. Squires, T. G.; Paulaitis, M. E.) 115-129, 1987.

Paulaitis, M. E., Kander, R. G. and J. R. DiAndreth, "Phase Equibria Related to Supercritical-Fluid Solvent Extractions", Ber. Bunsenges. Phys. Chem. 88, 869, 1984.

Poston, R. S. and J. J. McKetta, "Vapor-Liquid Equibrium in the n-Hexane-Nitrogen System", J. Chem. Eng. Data 11, 364, 1966.

Radosz, M., "Vapor-Liquid Equibrium for 2-Proponol and Carbon Dioxide", J. Chem. Eng. Data 31, 43-45, 1986.

Shavarts, A. V. and G. D. Efremova, "Higher Order Critical Phenomena in the System of Ethanol-Water-Carbon dioxide", Russ. J. Phys. Chem. 44, 614-615, 1970.

Sultanov, R. G., Skripka, V. G. and A. Yu. Namiot, Gasov. Delov. 10, 43, 1972 in IUPAC Solubility Data Series, 10, Pergamon Press, 438, 1982.

Tremper, K. K. and J. M. Prausnitz, "Solubility of Inorganic Gases in High-Boiling Hydrocarbon Solvents", J. Chem. Eng. Data 21, 295, 1976.

Yorizane, M., Yoshimura, S., Masuoka, H., Mlyano, Y. and Y. Kakimoto, "New Procedure for Vapor-Liquid Equilibria. Nitrogen + Carbon Dioxide, Methane + Freon 22, and Methane + Freon 12", J. Chem. Eng. Data 30, 174-176, 1985.

Nelson, P. A., "Rapid Phase Determination in Multiple-phase Flash Calculations", Comput. Chem. Eng., 11, 581-591, 1987.

Related Reading

Elgin, J. C. and J. J. Weinstock, "Phase Equilibrium at Elevated Pressures in Ternary Systems of Ethylene and Water with Organic Liquids. Salting out with a Supercritical Gas", J. Chem. Eng. Data 4, 3, 1959.

Ellis, S. R. M. and R. D. Garbett, "A New Equilibrium Still for the Study of Partially Miscible Systems", Ind. Eng. Chem., 52, 385, 1960.

Fredenslund, A., Ghehling, J. and P. Rasmussen, "Vapor-Liquid Equilibria using UNIFAC, a Group-Contribution Method", Elsevier, 1977.

Kato, M., H. Konishi and H. Hirata, "New Apparatus for Isobaric Dew and Bubble Point Method", J. Chem. Eng. Data, 15, 435, 1970.

Nghiem, L.X. and K. Aziz, "A Robust Iterative Method for Flash Calculations Using the Soave-Redlich-Kwong or the Peng-Robinson Equation of State", paper SPE 8285, Paper presented at the 54th Annual Fall Meeting of SPE-AIME, Las Vegas, Nevada, September 23-26, 1979.

•

Ohanomah, M. O. and D. W. Thompson, "Computation of Multi-component Phase Equilibria-Part 3. Multi-phase equilibria", Comput. Chem. Eng., 8, 163-170, 1984.

Sampath, V. R. and S. Leipziger, "Vapor-liquid-liquid Equilibria Computations", Ind. Eng. Chem. Process Des. Dev., 24, 652-658, 1985.

Trebble, M. A. and P. R. Bishnoi, "Development of a New Four-Parameter Cubic Equation of State", Fluid Phase Equil., 35, 1-18, 1987.

4

APPENDIX A. An alternative derivation of the Stability Equations

Consider the problem of minimizing the Gibbs free energy, G, given by Equation (3.4),

$$\begin{array}{ccc}
\operatorname{Min} & \left\{ \begin{array}{c} \mathbf{G} \end{array} \right\}, \\
 (i = 1, \dots, N) \\
 (k = 1, \dots, \pi; \ k \neq r) \\
 (m = 1, \dots, R)
\end{array}$$
(3.6)

subject to the constraints

$$\alpha_{k} \geq 0$$
 (k = 1, ..., π ; k \neq r). (A.1)

The above inequality constraints can be converted to equality constraints by introducing slack variables, y_k^2 , to obtain

$$y_k^2 - \alpha_k = 0$$
 (k = 1, ..., π ; k \neq r). (A.2)

Defining the Lagrangian G[•],

$$G^* = G + \sum_{\substack{k=1\\k\neq r}}^{\pi} \lambda_k \left[y_k^2 - \alpha_k \right]$$
(A.3)

where λ_k are the Lagrange multipliers. Substitution of Equation (3.7) into Equation (A.3) yields

$$G^{*} = G + \sum_{\substack{k=1\\k\neq r}}^{\pi} \lambda_{k} \left[y_{k}^{2} - \sum_{\substack{i=1\\i\neq k}}^{N} n_{ik} / n_{t} \right].$$
(A.4)

The stationary point of Lagrangian G^{*} can be found by setting

$$\frac{\partial \mathbf{G}^{*}}{\partial \mathbf{n}_{ik}} = 0 \qquad (i = 1,...,N; k = 1,...,\pi; k \neq r), \quad (A.5)$$

$$\frac{\partial}{\partial} \frac{G}{\xi_{m}} = 0 \qquad (m = 1,...,R), \qquad (A.6)$$

$$\frac{\partial G^{*}}{\partial \lambda_{k}} = 0 \qquad (k = 1,...,\pi; k \neq r), \qquad (A.7)$$

and

$$\frac{\partial}{\partial} G^* = 0 \qquad (k = 1,...,\pi; k \neq r). \qquad (A.8)$$

Rearrangement of Equation (A.8) yields

$$y_{k} \lambda_{k} = 0.$$
 (9A)

Using Equation (A.2) to eliminate y_k from Equation (A.9) yields the stability equation,

$$\alpha_{k} \lambda_{k} = 0$$
 $(k = 1,...,\pi; k \neq r).$ (3.14)

Furthermore, the Lagrange multipliers, λ_k should satisfy (Rao, 1984)

$$\lambda_{k} \geq 0 \quad (k=1,...,\pi; k \neq r).$$
 (A.10)

Equations (A.5)-(A.8) and (3.14) together with the non-negativity conditions on α_k and λ_k (Equations A.1 and A.10) are known as the Kuhn-Tucker conditions (Rao, 1984) and λ_k are called the Kuhn-Tucker multipliers. Furthermore, Equation (3.14) is commonly referred to as the complementary slackness or orthogonality condition in the optimization literature.

APPENDIX B. Selection of the Equilibrium Ratios

The selection of the equilibrium ratios, to initiate the phase calculations, is based on the distance between the tangent plane and the surface of Gibbs energy of mixing. A vapor phase of component mole fractions, y, is generated using the Wilson equation for ideal equilibrium ratios. Let the phase fraction of this vapor phase be infinitesimal. Hence, the component mole fraction of the liquid phase generated would be z. Now, consider the N potential pure liquid phases, which may be formed from this liquid phase. The distance between the molar Gibbs energy of mixing and the tangent plane at z for the pure phase j, is given by (Baker, 1982; Michelsen, 1982a)

$$D_{j} (\mathbf{x}_{j} \rightarrow 1; \mathbf{x}_{i} \rightarrow 0; i \neq j) = D_{j}$$

$$= \lim_{\substack{j \\ \mathbf{x} \rightarrow 1}} \sum_{i=1}^{N} \mathbf{x}_{i} \ln [\mathbf{f}_{ii}(\mathbf{x})/\mathbf{f}_{ii}(\mathbf{z})] \qquad (B.1)$$

or,

$$D_{j} = \lim_{\substack{x_{j} \to 1 \\ j \to 1}} \ln [\phi_{jl}(x)/z_{j} \phi_{jl}(z)]$$
(B.2)

The liquid of component mole fraction, z, would be unstable with respect to the pure liquid phase j, if

$$D_{j} < 0 \tag{B.3}$$

or,

$$\lim_{\mathbf{x}_{j}^{-} \to 1} z_{j} \phi_{j1}(z) / \phi_{j1}(\mathbf{x}) > 1.0$$
(B.4)

Choosing vapor as the reference phase and considering phase j in the liquid state, Equation (4.11) gives,

$$\phi_{il}(\mathbf{x}) = \phi_{iv}(\mathbf{y}) / \mathbf{K}_{ii}$$
(B.5)

Substitution of Equation (B.5) in (B.4) yields

$$z_{j} K_{jj} \phi_{j1}(z) / \phi_{jv}(y) > 1.0$$
 (B.6)

The fugacity coefficient for the vapor phase may now be assumed to be weakly dependent on composition. Hence $\phi_{jv}(\mathbf{y})$ may be replaced by $\phi_{jv}(\mathbf{z})$ in the above equation to obtain,

$$z_{j} K_{jj} \phi_{jl}(z) / \phi_{jv}(z) > 1.0$$
 (B.7)

Thus, we can define

$$d_{j} = z_{j} K_{jj} \phi_{j1}(z) / \phi_{jv}(z)$$
 (B.8)

and the set equilibrium ratios which have the highest value of d_j will cause a phase split.

Moreover, in the selection of the equilibrium ratios, it is important to select those sets which are different from the equilibrium ratios for the phases which are already present. Hence for the selection for the equilibrium ratios for the phase m, d_i is modified to

$$\mathbf{d}_{j} = \frac{\mathbf{K}_{jj}}{\prod_{\mathbf{k}=1}^{\mathbf{m}-1} \mathbf{K}_{\mathbf{k}j}} \qquad \mathbf{z}_{j} \boldsymbol{\phi}_{j1}(\mathbf{z}) / \boldsymbol{\phi}_{jv}(\mathbf{z}) \qquad (4.12)$$

and the set equilibrium ratios which have the highest value of d_j may be selected to initiate the phase calculations.

APPENDIX C. Derivatives for the Single - Stage Flash

٠

The required derivatives for the Newton Raphson procedure in Chapters 4 and 5 are summarized in this Appendix. Derivatives of Summation Equation (3.25) :

$$S_{k} = \sum_{i=1}^{N} (K_{ik} e^{\theta_{k}} - 1) n_{i} / (n_{t} D_{i}) = 0$$

$$(k=1,...,\pi; k \neq r)$$
 (3.25)

where,

$$\mathbf{n}_{i} = \mathbf{z}_{i} + \sum_{m=1}^{R} \boldsymbol{v}_{im} \boldsymbol{\xi}_{m} \qquad (i = 1,...,N), \quad (3.27)$$
$$\mathbf{n}_{t} = \sum_{i=1}^{N} \mathbf{n}_{i}, \qquad (3.28)$$

and

$$D_{i} = 1 + \sum_{\substack{j=1\\ j \neq r}}^{\pi} (K_{ij} e^{\theta_{j}} - 1) \alpha_{j}. \qquad (3.29)$$

The derivatives are :

$$\frac{\partial S_{\mathbf{k}}}{\partial \alpha_{\mathbf{j}}} = -\sum_{i=1}^{N} \left(K_{\mathbf{i}\mathbf{k}} \frac{\theta_{\mathbf{k}}}{e^{\mathbf{k}}} - 1 \right) \frac{\mathbf{n}_{\mathbf{i}}}{\mathbf{n}_{\mathbf{i}}} \left((\mathbf{n}_{\mathbf{i}} \mathbf{D}_{\mathbf{i}}^{2}) \frac{\partial D_{\mathbf{i}}}{\partial \alpha_{\mathbf{j}}} \right), \quad (C.1)$$

$$\frac{\partial \mathbf{S}_{\mathbf{k}}}{\partial \theta_{\mathbf{j}}} = -\sum_{i=1}^{N} \left(\mathbf{K}_{i\mathbf{k}} \mathbf{e}^{\mathbf{\theta}_{\mathbf{k}}} - 1 \right) \mathbf{n}_{i} / \left(\mathbf{n}_{t} \mathbf{D}_{i}^{2}\right) \frac{\partial \mathbf{D}_{i}}{\partial \theta_{\mathbf{j}}}$$

$$+ \delta_{kj} \sum_{i=1}^{N} (K_{ik} e^{\theta_{k}}) n_{i} / (n_{t} D_{i}), \qquad (C.2)$$

•

$$\frac{\partial S_{k}}{\partial T} = -\sum_{i=1}^{N} (K_{ik} e^{\theta_{k}} - 1) n_{i} / (n_{t} D_{i}^{2}) \frac{\partial D_{i}}{\partial T}$$

+
$$\sum_{i=1}^{N} e^{\theta_{k}} n_{i} / (n_{t}D_{i}) \frac{\partial K_{ik}}{\partial T}$$
, (C.3)

$$\frac{\partial S_{k}}{\partial \xi_{s}} = -\sum_{i=1}^{N} (K_{ik} e^{\theta_{k}} - 1) n_{i} / (n_{t}^{2} D_{i}) \frac{\partial n_{t}}{\partial \xi_{s}}$$

+
$$\sum_{i=1}^{N} (K_{ik} e^{\theta_{k}} - 1) v_{is} (n_{t} D_{i}),$$
 (C.4)

where

$$\frac{\partial D_{i}}{\partial \alpha_{j}} = (K_{ij} e^{j} - 1), \qquad (C.5)$$

$$\frac{\partial D_{i}}{\partial \theta_{j}} = K_{ij} e^{\theta_{j}} \alpha_{j}, \qquad (C.6)$$

$$\frac{\partial \mathbf{D}_{i}}{\partial \mathbf{T}} = \sum_{\substack{j=1\\ j \neq r}}^{\pi} \mathbf{e}^{\mathbf{\theta}_{j}} \alpha_{j} \frac{\partial \mathbf{K}_{i}}{\partial \mathbf{T}}^{j}$$
(C.7)

and
$$\frac{\partial \mathbf{n}_{t}}{\partial \boldsymbol{\xi}_{s}} = \sum_{i=1}^{N} \boldsymbol{v}_{is} \boldsymbol{\xi}_{s}.$$
(C.8)

·

Derivatives of Stability Equation (5.2) :

$$\mathbb{T}_{\mathbf{k}} = \frac{\alpha_{\mathbf{k}} \theta_{\mathbf{k}}}{\alpha_{\mathbf{k}} + \theta_{\mathbf{k}}} = 0$$
(5.2)

$$\frac{\partial \mathbb{T}_{k}}{\partial \alpha_{j}} = \delta_{kj} \frac{\theta_{k}^{2}}{(\alpha_{k} + \theta_{k})^{2}}$$
(C.9)

$$\frac{\partial \mathbb{T}_{k}}{\partial \theta_{j}} = \delta_{kj} \frac{\alpha_{k}^{2}}{(\alpha_{k} + \theta_{k})^{2}}$$
(C.10)

Derivatives of Phase Summation Equation (3.24) :

$$\mathbb{P} = \sum_{k=1}^{n} \alpha_{k} - 1.0 \tag{3.24}$$

$$\frac{\partial \mathbb{P}_{k}}{\partial \alpha_{j}} = 1 \tag{C.11}$$

Derivatives of Chemical Equilibrium Relations (3.34):

$$\mathbb{C}_{m} = \sum_{i=1}^{N} v_{im} \ln \left[(z_{i} + \sum_{s=1}^{R} v_{is} \xi_{s}) \phi_{ir} P / (n_{t} D_{i}) \right] - \ln K_{am} \quad (m = 1, ..., R)$$
(3.34)

$$\frac{\partial \mathbb{C}}{\partial \alpha_{j}} = -\sum_{i=1}^{N} v_{im} / D_{i} \quad \frac{\partial D_{i}}{\partial \alpha_{j}}, \qquad (C.12)$$

$$\frac{\partial c_{m}}{\partial \theta_{j}} = -\sum_{i=1}^{N} v_{im} / D_{i} \frac{\partial D_{i}}{\partial \theta_{j}}, \qquad (C.13)$$

$$\frac{\partial \mathbb{C}_{\underline{m}}}{\partial \xi_{p}} = \sum_{i=1}^{N} v_{im} \left[v_{ip} / (z_{i} + \sum_{s=1}^{R} v_{is} \xi_{s}) - 1/n_{t} \frac{\partial n_{t}}{\partial \xi_{p}} \right]$$
(C.14)

Derivatives of Energy Balance Equation (5.5) :

$$E = n_{t} \sum_{k=1}^{\pi} \sum_{i=1}^{N} \alpha_{k} K_{ik} x_{ir} e^{\theta_{k}} h_{ik} - H_{spec} = 0, \qquad (5.5)$$

which using Equation (3.26) gives

$$E = \sum_{k=1}^{\pi} \sum_{i=1}^{N} \alpha_{k} K_{ik} e^{\theta_{k}} h_{ik} n_{i} / D_{i} - H_{spec} = 0, \qquad (C.15)$$

Equation (C.15) can be written as

$$E = \sum_{i=1}^{N} n_i h_{ir} / D_i + \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} \alpha_k (K_{ik} e^{\theta_k} h_{ik} - h_{ir}) n_i / D_i$$

- $H_{spec} = 0.$ (C.16)

The derivatives of Equation (5.5b) are :

$$\frac{\partial \mathbf{E}}{\partial \alpha_{j}} = -\sum_{i=1}^{N} \mathbf{n}_{i} \mathbf{h}_{ir} / \mathbf{D}_{i}^{2} \frac{\partial \mathbf{D}_{i}}{\partial \alpha_{j}} - \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} \alpha_{k} (\mathbf{K}_{ik} \mathbf{e}^{k} \mathbf{h}_{ik} - \mathbf{h}_{ir}) \mathbf{n}_{i} / \mathbf{D}_{i}^{2} \mathbf{x}$$

$$\frac{\partial D_i}{\partial \alpha_j} + \sum_{i=1}^{N} \alpha_j (K_{ij} e^{\theta_j} h_{ij} - h_{ir}) n_i / D_i$$
(C.17)

$$\frac{\partial \mathbf{E}}{\partial \theta_{j}} = -\sum_{i=1}^{N} \mathbf{n}_{i} \mathbf{h}_{ir} / \mathbf{D}_{i}^{2} \frac{\partial \mathbf{D}_{i}}{\partial \theta_{j}} - \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} \alpha_{k} (\mathbf{K}_{ik} \mathbf{e}^{k} \mathbf{h}_{ik} - \mathbf{h}_{ir}) \mathbf{n}_{i} / \mathbf{D}_{i}^{2} \mathbf{x}$$

$$\frac{\partial \mathbf{D}_{i}}{\partial \theta_{j}} + \sum_{i=1}^{N} \alpha_{j} \mathbf{K}_{ij} \mathbf{e}^{j} \mathbf{h}_{ij} \mathbf{n}_{i} / \mathbf{D}_{i}$$
(C.18)

$$\frac{\partial \mathbf{E}}{\partial \mathbf{T}} = -\sum_{i=1}^{N} \mathbf{n}_{i} \mathbf{h}_{ir} / \mathbf{D}_{i}^{2} \frac{\partial \mathbf{D}_{i}}{\partial \mathbf{T}} + \sum_{i=1}^{N} \mathbf{n}_{i} / \mathbf{D}_{i} \frac{\partial \mathbf{h}_{ir}}{\partial \mathbf{T}} - \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} \alpha_{k} (\mathbf{K}_{ik})$$

$$e^{\theta_{k}} \mathbf{h}_{ik} - \mathbf{h}_{ir} \mathbf{n}_{i} / \mathbf{D}_{i}^{2} \frac{\partial \mathbf{D}_{i}}{\partial \mathbf{T}} + \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} \alpha_{k} \mathbf{n}_{i} / \mathbf{D}_{i} (e^{\theta_{k}} \mathbf{h}_{ik})$$

$$\frac{\partial K_{ik}}{\partial T} + e^{\theta_{k}} K_{ik} \frac{\partial h_{ik}}{\partial T} - \frac{\partial h_{ir}}{\partial T}$$
(C.19)

APPENDIX D Derivatives for the Multistage Separation Processes

The required derivatives for the Newton Raphson procedure in Chapters 7 for two and three phase multistage computations are summarized in this Appendix. Note that in these equations π is 2 for two phase columns and is 3 for three phase columns. Furthermore, in obtaining these derivatives the reference phase is chosen to be the second phase on each stage.

Derivatives of Component Material Balance (6.24):

$$M_{ij} = -m_{ij} + z_{ij} + (1 - wr_{1j+1}) K_{i1j+1} e^{\theta_{1j+1}} \alpha_{ij+1} m_{ij+1} / D_{ij+1}$$

$$+ \sum_{k=2}^{\pi} (1 - wr_{kj-1}) K_{ikj-1} e^{\theta_{kj-1}} \alpha_{kj-1} m_{ij-1} / D_{ij-1}$$

$$= 0. \qquad (6.24)$$

$$\frac{\partial M_{ij}}{\partial m_{ij}} = -1$$
 (D.1)

$$\frac{\partial M_{ij}}{\partial m_{ij+1}} - (1 - wr_{1j+1}) K_{i1j+1} e^{\theta_{1j+1}} \alpha_{1j+1} m_{ij+1} / D_{ij+1}$$
(D.2)

$$\frac{\partial M_{ij}}{\partial m_{ij-1}} = \sum_{k=2}^{\pi} (1 - wr_{kj-1}) K_{ikj-1} e^{\theta_{kj-1}} \alpha_{kj-1} m_{ij-1} / D_{ij-1}$$
(D.3)

$$\frac{\partial M_{ij}}{\partial T_j} = 0 \tag{D.4}$$

+

$$\frac{\partial \mathbf{M}_{ij}}{\partial \mathbf{T}_{j+1}} = (1 - \mathbf{w}\mathbf{r}_{ij+1}) \mathbf{e}^{\theta_{1j+1}} \alpha_{ij+1} \mathbf{m}_{ij+1} / \mathbf{D}_{ij+1}\mathbf{x}$$

$$\left(\frac{\partial K_{i^{1}j+1}}{\partial T_{j+1}} - \frac{K_{i1j+1}}{\partial T_{j+1}} - \frac{\partial D_{i^{j}j+1}}{\partial T_{j+1}} / D_{i^{j}j+1}\right)$$
(D.5)

$$\frac{\partial M_{i_{j-1}}}{\partial T_{j-1}} = \sum_{k=2}^{\pi} (1 - wr_{k_{j-1}}) e^{\theta_{k_{j-1}}} \alpha_{k_{j-1}} m_{i_{j-1}} / D_{i_{j-1}} x$$

$$\left(\frac{\partial K_{ikj-1}}{\partial T_{j-1}} - \frac{K_{ikj-1}}{\partial T_{j-1}} - \frac{\partial D_{ij-1}}{\partial T_{j-1}} / D_{ij-1}\right)$$
(D.6)

$$\frac{\partial M_{ij}}{\partial \alpha_{kj}} = 0 \qquad (k = 1,...,3) \qquad (D.7)$$

$$\frac{\partial \mathbf{M}_{ij}}{\partial \alpha_{1j+1}} = (1 - \mathbf{wr}_{1j+1}) \mathbf{K}_{i1j+1} \mathbf{e}^{\theta_{1j+1}} \mathbf{m}_{ij+1} / \mathbf{D}_{ij+1} \mathbf{x}$$

$$(1 - \alpha_{i1j+1}, \frac{\partial D_{ij+1}}{\partial \alpha_{1j+1}} / D_{ij+1})$$
(D.8)

$$\frac{\partial M_{ij}}{\partial \alpha_{2j+1}} = 0 \tag{D.9}$$

٠

$$\frac{\partial \mathbf{M}_{ij}}{\partial \alpha_{3j+1}} = (1 - \mathbf{w}\mathbf{r}_{1j+1}) \mathbf{K}_{i1j+1} \mathbf{e}^{\theta_{1j+1}} \mathbf{m}_{ij+1} / \mathbf{D}_{ij+1} \mathbf{x}$$

•

$$(-1 - \alpha_{i1j+1} - \frac{\partial}{\partial} \frac{D_{ij+1}}{\alpha_{3j+1}} / D_{ij+1})$$
(D.10)

$$\frac{\partial M_{ij}}{\partial \alpha_{1j-1}} = -\sum_{k=2}^{\pi} (1 - wr_{kj-1}) K_{ikj-1} e^{\theta_{kj-1}} \alpha_{kj-1} m_{ij-1} / D_{ij-1}^2 x$$

.

$$\frac{\partial D_{ij-1}}{\partial \alpha_{1j-1}} - (1 - wr_{2j-1}) K_{i2j-1} e^{\theta_{2j-1}} m_{ij-1} / D_{ij-1}$$
(D.11)

$$\frac{\partial M_{ij}}{\partial \alpha_{2j-1}} = 0$$
 (D.12)

$$\frac{\partial M_{ij}}{\partial \alpha_{3j-1}} = -\sum_{k=2}^{\pi} (1 - wr_{kj-1}) K_{ikj-1} e^{\theta_{kj-1}} \alpha_{kj-1} m_{ij-1} / D_{ij-1}^2 x$$

$$\frac{\partial D_{i_{j-1}}}{\partial \alpha_{3j-1}} - (1 - wr_{2j-1}) K_{i_{2j-1}} e^{\theta_{2j-1}} m_{i_{j-1}} / D_{i_{j-1}}$$

+
$$(1 - wr_{3j-1}) K_{i3j-1} e^{\theta_{3j-1}} m_{ij-1} / D_{ij-1}$$
 (D.13)

$$\frac{\partial \mathbf{M}_{i}}{\partial \theta_{kj}} = 0 \qquad (k = 1,...,3) \qquad (D.14)$$

$$\frac{\partial \mathbf{M}_{i}}{\partial \theta_{1j+1}} = (1 - \mathbf{w}\mathbf{r}_{1j+1}) \mathbf{K}_{i1j+1} \mathbf{e}^{\theta_{1j+1}} \alpha_{1j+1} \mathbf{m}_{ij+1} / \mathbf{D}_{ij+1} \mathbf{x}$$

$$(1 - \frac{\partial D_{ij+1}}{\partial \theta_{ij+1}} / D_{ij+1})$$
(D.15)

$$\frac{\partial M_{i_{j}}}{\partial \theta_{k_{j}+1}} = -(1 - wr_{1j+1}) K_{i_{1}i_{j}+1} e^{\theta_{1}i_{j}+1} \alpha_{1j+1} m_{i_{j}+1} / D_{i_{j}+1}^{2} x$$

$$\frac{\partial D_{ij+1}}{\partial \theta_{kj+1}} \qquad (k = 2,3) \tag{D.16}$$

$$\frac{\partial M_{ij}}{\partial \theta_{1j-1}} = -\sum_{k=2}^{\pi} (1 - wr_{kj-1}) K_{ikj-1} e^{\theta_{kj-1}} \alpha_{kj-1} m_{ij-1} / D_{ij-1}^2 x$$

$$\frac{\partial \mathbf{D}_{i}}{\partial \theta_{1j-1}}$$
(D.17)

$$\frac{\partial \mathbf{M}_{i}}{\partial \theta_{kj-1}} = (1 - wr_{kj-1}) \mathbf{K}_{i k j - 1} \mathbf{e}^{\theta_{kj-1}} \alpha_{kj-1} \mathbf{m}_{ij-1} / \mathbf{D}_{ij-1} \mathbf{x}$$

$$(1 - \frac{\partial D_{ij-1}}{\partial \theta_{kj-1}} / D_{ij-1}) \quad (k = 2,3) \tag{D.18}$$

Derivatives of Energy Balance Equation (6.25) :

$$\mathbf{E}_{j} = \sum_{k=1}^{\pi} \sum_{i=1}^{N} \mathbf{K}_{ikj} \mathbf{e}^{\theta_{kj}} \alpha_{kj} \mathbf{m}_{ij} \mathbf{h}_{ikj} / \mathbf{D}_{ij} - \mathbf{H}_{f}$$

$$- Q_{j} - (1 - wr_{1j+1}) \alpha_{1j+1} \sum_{i=1}^{N} K_{i1j+1} e^{\theta_{1j+1}} m_{ij+1} h_{i1j+1}/D_{ij+1}$$

$$-\sum_{k=2}^{\pi} (1 - wr_{kj-1}) \alpha_{kj-1} \sum_{i=1}^{N} K_{i k j-1} e^{\theta_{k j-1}} m_{i j-1} h_{i k j-1} / D_{i j-1}$$

= 0. (6.25)

$$\frac{\partial \mathbf{E}_{j}}{\partial \mathbf{m}_{ij}} = \sum_{k=1}^{\pi} \mathbf{K}_{ikj} \mathbf{e}^{\mathbf{\theta}_{kj}} \alpha_{kj} \mathbf{h}_{ikj} / \mathbf{D}_{ij}$$
(D.19)

$$\frac{\partial E_{j}}{\partial m_{ij+1}} = -(1 - wr_{1j+1}) \alpha_{1j+1} K_{i1j+1} e^{\theta_{1j+1}} h_{i1j+1}/D_{ij+1}$$
(D.20)

$$\frac{\partial E_{j}}{\partial m_{ij-1}} = -\sum_{k=2}^{\pi} (1 - wr_{kj-1}) \alpha_{kj-1} K_{ikj-1} e^{\theta_{kj-1}} h_{ikj-1}/D_{ij-1}$$
(D.21)

$$\frac{\partial \mathbf{E}_{j}}{\partial \mathbf{T}_{j}} = -\sum_{i=1}^{N} \mathbf{m}_{ij} \mathbf{h}_{irj} / D_{ij}^{2} \frac{\partial \mathbf{D}_{ij}}{\partial \mathbf{T}_{j}} + \sum_{i=1}^{N} \mathbf{m}_{ij} / D_{ij} \frac{\partial \mathbf{h}_{irj}}{\partial \mathbf{T}_{j}}$$

$$- \sum_{\substack{k=1 \ k=1 \ k=1}}^{\pi} \sum_{\substack{i=1 \ k\neq r}}^{N} \alpha_{kj} (\mathbf{K}_{ikj} \mathbf{e}^{\theta_{kj}} \mathbf{h}_{ikj} - \mathbf{h}_{irj}) \mathbf{m}_{ij} / D_{ij}^{2} \frac{\partial \mathbf{D}_{ij}}{\partial \mathbf{T}_{j}}$$

$$+ \sum_{\substack{k=1 \ k\neq r}}^{\pi} \sum_{\substack{i=1 \ k\neq r}}^{N} \alpha_{kj} \mathbf{m}_{ij} / D_{ij} (\mathbf{e}^{\theta_{kj}} \mathbf{h}_{ikj} \frac{\partial \mathbf{K}_{ikj}}{\partial \mathbf{T}_{j}} + \mathbf{e}^{\theta_{kj}} \mathbf{K}_{ikj} \frac{\partial \mathbf{h}_{ikj}}{\partial \mathbf{T}_{j}}$$

$$- \frac{\partial \mathbf{h}_{irj}}{\partial \mathbf{T}_{j}} (\mathbf{D}.22)$$

$$\frac{\partial \mathbf{E}_{j}}{\partial \mathbf{T}_{j+1}} = -(1 - \mathbf{wr}_{1j+1}) \alpha_{1j+1} \mathbf{e}^{\theta_{1j+1}} \sum_{i=1}^{N} \mathbf{m}_{ij+1} / \mathbf{D}_{ij+1} \mathbf{x}$$

$$(\mathbf{h}_{i1j+1} \quad \frac{\partial \quad \mathbf{K}_{i1}}{\partial \quad \mathbf{T}_{j+1}} \quad + \quad \mathbf{K}_{i1j+1} \quad \frac{\partial \quad \mathbf{h}_{i1}}{\partial \quad \mathbf{T}_{j+1}} - \quad \mathbf{K}_{i1j+1} \mathbf{h}_{i1j+1} / \mathbf{D}_{ij+1} \quad \mathbf{x}_{ij+1} = \mathbf{K}_{i1j+1} \mathbf{h}_{i1j+1} / \mathbf{D}_{ij+1} = \mathbf{K}_{i1j+1} \mathbf{h}_{i1j+1} / \mathbf{D}_{ij+1} = \mathbf{K}_{i1j+1} + \mathbf{K}_{i1j+1}$$

$$\frac{\partial D_{ij}}{\partial T_{j+1}}$$
(D.23)

$$\frac{\partial \mathbf{E}_{j}}{\partial \mathbf{T}_{j-1}} \quad - \sum_{k=2}^{\pi} (1 - wr_{kj-1}) \alpha_{kj-1} \sum_{i=1}^{N} e^{\theta_{kj-1}} \mathbf{m}_{ij-1} / \mathbf{D}_{ij-1} \mathbf{x}$$

$$(\mathbf{h}_{\mathbf{i}\mathbf{k}\mathbf{j}-1} \quad \frac{\partial}{\partial} \frac{\mathbf{K}_{\mathbf{i}\mathbf{k}\mathbf{j}-1}}{\mathbf{T}_{\mathbf{j}-1}} + \mathbf{K}_{\mathbf{i}\mathbf{k}\mathbf{j}-1} \quad \frac{\partial}{\partial} \frac{\mathbf{h}_{\mathbf{i}\mathbf{k}\mathbf{j}-1}}{\mathbf{T}_{\mathbf{j}-1}} - \mathbf{K}_{\mathbf{i}\mathbf{k}\mathbf{j}-1} \mathbf{h}_{\mathbf{i}\mathbf{k}\mathbf{j}-1} / \mathbf{D}_{\mathbf{i}\mathbf{j}-1} \quad \mathbf{X}$$
$$\frac{\partial}{\partial} \frac{\mathbf{D}_{\mathbf{i}\mathbf{j}-1}}{\mathbf{T}_{\mathbf{j}-1}}$$
(D.24)

$$\frac{\partial \mathbf{E}_{j}}{\partial \alpha_{1j}} = -\sum_{i=1}^{N} \mathbf{m}_{ij} \mathbf{h}_{irj} / \mathbf{D}_{ij}^{2} \frac{\partial \mathbf{D}_{ij}}{\partial \alpha_{1j}} - \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} \alpha_{kj} (\mathbf{K}_{ikj} \mathbf{e}^{\theta_{kj}} \mathbf{h}_{ikj})$$
$$- \mathbf{h}_{irj} \mathbf{m}_{ij} / \mathbf{D}_{ij}^{2} \frac{\partial \mathbf{D}_{i}}{\partial \alpha_{1j}} + \sum_{i=1}^{N} \alpha_{1j} (\mathbf{K}_{i1j} \mathbf{e}^{\theta_{1j}} \mathbf{h}_{ilj})$$

$$-h_{irj}) m_{ij}/D_{ij}$$
 (D.25)

$$\frac{\partial E_{j}}{\partial \alpha_{2j}} = 0$$
 (D.26)

$$\frac{\partial \mathbf{E}_{j}}{\partial \alpha_{3j}} = -\sum_{i=1}^{N} \mathbf{m}_{ij} \mathbf{h}_{irj} / \mathbf{D}_{ij}^{2} \frac{\partial \mathbf{D}_{i}}{\partial \alpha_{3j}} - \sum_{\substack{k=1 \ k \neq r}}^{\pi} \sum_{i=1}^{N} \alpha_{kj} (\mathbf{K}_{ikj} \mathbf{e}^{\mathbf{h}_{kj}} \mathbf{h}_{ikj})$$
$$- \mathbf{h}_{irj} \mathbf{m}_{ij} / \mathbf{D}_{ij}^{2} \frac{\partial \mathbf{D}_{ij}}{\partial \alpha_{3j}} + \sum_{i=1}^{N} \alpha_{3j} (\mathbf{K}_{i3j} \mathbf{e}^{\mathbf{h}_{3j}} \mathbf{h}_{i3j})$$
$$- \mathbf{h}_{irj} \mathbf{m}_{ij} / \mathbf{D}_{ij} \qquad (D.27)$$

$$\frac{\partial \mathbf{E}_{j}}{\partial \alpha_{1j+1}} = -(1 - \mathbf{wr}_{1j+1}) \sum_{i=1}^{N} K_{i1j+1} e^{\theta_{1j+1}} \mathbf{m}_{ij+1} \mathbf{h}_{i1j+1} / \mathbf{D}_{ij+1} \mathbf{x}$$

.

$$(1 - \alpha_{ij+1} \frac{\partial D_{ij+1}}{\partial \alpha_{ij+1}} / D_{ij+1})$$
(D.28)

$$\frac{\partial \mathbf{E}_{j}}{\partial \alpha_{2j+1}} = 0 \tag{D.29}$$

$$\frac{\partial E_{j}}{\partial \alpha_{3j+1}} = (1 - wr_{1j+1}) \alpha_{1j+1} \sum_{i=1}^{N} K_{i1j+1} e^{\theta_{1j+1}} m_{ij+1} h_{i1j+1} / D_{ij+1}^{2} x$$

$$\frac{\partial D_{ij+1}}{\partial \alpha_{3j+1}}$$
(D.30)

$$\frac{\partial}{\partial} \frac{E_{j}}{\alpha_{1j-1}} = (1 - wr_{2j-1}) \sum_{i=1}^{N} K_{i2j-1} e^{\theta_{2j-1}} m_{ij-1} h_{i2j-1}/D_{ij-1} + \sum_{k=2}^{\pi} (1 - wr_{kj-1}) \alpha_{kj-1} \sum_{i=1}^{N} K_{ikj-1} e^{\theta_{kj-1}} m_{ij-1} h_{ikj-1}/D_{ij-1}^{2} x$$

$$\frac{\partial}{\partial} \frac{D_{ij-1}}{\alpha_{1j-1}} (D.31)$$

(D.31)

$$\frac{\partial}{\partial} \frac{\mathbf{E}_{j}}{\alpha_{2j-1}} = 0 \qquad (D.32)$$

$$\frac{\partial}{\partial} \frac{\mathbf{E}_{j}}{\alpha_{3j-1}} = -(1 - \mathbf{w}\mathbf{r}_{3j-1}) \sum_{i=1}^{N} \mathbf{K}_{i3j-1} e^{\theta_{3j-1}} \mathbf{m}_{ij-1} \mathbf{h}_{i3j-1} / \mathbf{D}_{ij-1}$$

$$+ (1 - \mathbf{w}\mathbf{r}_{2j-1}) \sum_{i=1}^{N} \mathbf{K}_{i2j-1} e^{\theta_{2j-1}} \mathbf{m}_{2j-1} \mathbf{h}_{i2j-1} / \mathbf{D}_{ij-1}$$

$$+ \sum_{k=2}^{\pi} (1 - \mathbf{w}\mathbf{r}_{kj-1}) \alpha_{kj-1} \sum_{i=1}^{N} \mathbf{K}_{ikj-1} e^{\theta_{kj-1}} \mathbf{m}_{ij-1} \mathbf{h}_{ikj-1} / \mathbf{D}_{ij-1}^{2} \mathbf{x}$$

$$\frac{\partial D_{ij-1}}{\partial \alpha_{3j-1}}$$
(D.33)

$$\frac{\partial \mathbf{E}_{j}}{\partial \theta_{1j}} = \sum_{i=1}^{N} \mathbf{K}_{i1j} \mathbf{e}^{\theta_{1j}} \alpha_{ij} \mathbf{m}_{ij} \mathbf{h}_{ilj} / \mathbf{D}_{ij} - \sum_{k=1}^{\pi} \sum_{i=1}^{N} \mathbf{K}_{ikj} \mathbf{e}^{\theta_{kj}} \alpha_{kj}$$
$$\mathbf{m}_{ij} \mathbf{h}_{ikj} / \mathbf{D}_{ij}^{2} \frac{\partial \mathbf{D}_{j}}{\partial \theta_{1j}} \quad (1=1,...,3) \quad (D.34)$$

$$\frac{\partial \mathbf{E}_{j}}{\partial \theta_{1j+1}} = - (1 - wr_{1j+1}) \alpha_{1j+1} \sum_{i=1}^{N} K_{i1j+1} e^{\theta_{1j+1}} m_{ij+1} h_{i1j+1} / D_{ij+1} x$$

$$(\delta_{11}^{-} \frac{\partial D_{ij+1}}{\partial \theta_{1j+1}})$$
 (1=1,...,3) (D.35)

$$\frac{\partial E_{j}}{\partial \theta_{1j-1}} = \sum_{k=2}^{\pi} (1 - wr_{kj-1}) \alpha_{kj-1} \sum_{i=1}^{N} K_{ikj-1} e^{\theta_{kj-1}} m_{ij-1} h_{ikj-1} / D_{ij-1}^{2} x$$

•

$$\frac{\partial D_{ij-1}}{\partial \theta_{1j-1}}$$
(D.36)

$$\frac{\partial \mathbf{E}}{\partial \theta_{1j-1}} = -(1 - \mathbf{wr}_{1j-1}) \alpha_{1j-1} \sum_{i=1}^{N} K_{i1j-1} e^{\theta_{1j-1}} \mathbf{m}_{ij-1} \mathbf{h}_{i1j-1} / \mathbf{D}_{ij-1}$$

$$+\sum_{k=2}^{\pi} (1 - wr_{kj-1}) \alpha_{kj-1} \sum_{i=1}^{N} K_{i k j - i} e^{\theta_{k j - 1}} m_{i j - 1} h_{i k j - 1} / D_{i j - 1}^{2} x$$

$$\frac{\partial D}{\partial \theta_{1j-1}} \qquad (1=2,3) \tag{D.37}$$

Derivatives of Mole Fraction Summation Equation (6.27):

$$S_{kj} = \sum_{i=1}^{N} (K_{ikj} e^{\theta_{kj}} - 1) m_{ij} / (m_{ij} D_{ij}) = 0$$

$$(k=1,...,\pi; k \neq r)$$
 (6.27)

where,

$$m_{ij} = \sum_{i=1}^{N} m_{ij},$$
 (6.29)

$$\frac{\partial S_{kj}}{\partial m_{1j}} = (K_{ilj} e^{\theta_{kj}} - 1) / (m_{ij} D_{1j}) - \sum_{i=1}^{N} (K_{ikj} e^{\theta_{kj}} - 1) x$$

$$m_{ij} / (m_{ij}^2 D_{ij}) \qquad (i=1,...,N) \qquad (D.38)$$

$$\frac{\partial S_{kj}}{\partial \alpha_{1j}} = -\sum_{i=1}^{N} (K_{ikj} e^{\theta_{kj}} - 1) m_{ij} / (m_{ij} D_{ij}^2) \frac{\partial D_{ij}}{\partial \alpha_{1j}}$$

$$(1=1,...,3; l \neq r)$$
 (D.39)

$$\frac{\partial S_{kj}}{\partial \theta_{1j}} = -\sum_{i=1}^{N} (K_{ikj} e^{\theta_{kj}} - 1) m_{ij} / (m_{ij} D_{ij}^2) \frac{\partial D_{ij}}{\partial \theta_{1j}} + \delta_{k1} \sum_{i=1}^{N} (K_{ikj} e^{\theta_{kj}}) m_{ij} / (m_{ij} D_{ij})$$

 $(1=1,...,3;1 \neq r)$ (D.40)

$$\frac{\partial S_{kj}}{\partial T_{j}} = -\sum_{i=1}^{N} (K_{ikj} e^{ikj} - 1) m_{ij} / (m_{ij} D_{ij}^{2}) \frac{\partial D_{ij}}{\partial T_{j}}$$

+
$$\sum_{i=1}^{N} e^{\theta_{kj}} m_{ij} / (m_{ij} D_{ij}) \frac{\partial K_{ikj}}{\partial T_{j}}, \qquad (D.41)$$

Derivatives of Stability Equation (6.33) :

$$\mathbb{T}_{kj} = \frac{\alpha_{kj} \theta_{kj}}{\alpha_{kj} + \theta_{kj}} = 0$$
(5.2)

$$\frac{\partial \mathbb{T}_{kj}}{\partial \alpha_{lj}} = \delta_{lk} \frac{\theta_{kj}^2}{(\alpha_{kj} + \theta_{kj})^2}$$
(D.42)

·

$$\frac{\partial \mathbb{T}_{kj}}{\partial \theta_{lj}} = \delta_{lk} \frac{\alpha_{kj}^2}{(\alpha_{kj} + \theta_{kj})^2}$$
(D.43)

Derivatives of Phase Summation Equation (6.26) :

$$\mathbb{P}_{j} = \sum_{k=1}^{n} \alpha_{kj} - 1.0 \tag{6.26}$$

$$\frac{\partial \mathbb{P}_{kj}}{\partial \alpha_{lj}} = 1 \tag{D.44}$$

Derivatives of Specification Equation for the reboiler(6.36) :

$$S_{reb} = \sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ikS} e^{\theta_{kS}} \alpha_{kS} m_{iS} / D_{iS} - B = 0.$$
(6.36)

$$\frac{\partial S_{reb}}{\partial m_{lS}} = \sum_{k=2}^{\pi} K_{1kS} e^{\theta_{kS}} \alpha_{kS} / D_{lS} \quad (i=,...,N)$$
(D.45)

$$\frac{\partial S_{reb}}{\partial \alpha_{1S}} = -\sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ikS} e^{\theta_{kS}} \alpha_{kS} m_{iS} / D_{iS}^{2} \frac{\partial D_{iS}}{\partial \alpha_{1S}}$$

$$-\sum_{i=1}^{N} K_{i2S} e^{\theta_{2S}} m_{iS} / D_{iS}$$
(D.46)

$$\frac{\partial}{\partial} \frac{S_{reb}}{\alpha_{2S}} = 0$$

$$\frac{\partial}{\partial} \frac{S_{reb}}{\alpha_{2S}} = -\sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ikS} e^{\theta_{kS}} \alpha_{kS} m_{iS} / D_{iS}^{2} \frac{\partial}{\partial} \frac{D_{iS}}{\alpha_{1S}}$$

$$+ \sum_{i=1}^{N} K_{i3S} e^{\theta_{3S}} m_{iS} / D_{iS}$$

$$- \sum_{i=1}^{N} K_{i2S} e^{\theta_{2S}} m_{iS} / D_{iS}$$
(D.48)

•

.

.

$$\frac{\partial S_{reb}}{\partial \theta_{1S}} = -\sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ikS} e^{\theta_{kS}} \alpha_{kS} m_{iS} / D_{iS}^{2} \frac{\partial D_{iS}}{\partial \theta_{1S}}$$
(D.49)

$$\frac{\partial S_{reb}}{\partial \theta_{1S}} = \sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ikS} e^{\theta_{kS}} \alpha_{kS} m_{iS} / D_{iS} x$$

$$(\delta_{k1} - \frac{\partial D_{iS}}{\partial \theta_{1S}} / D_{iS}) \quad (1=2,3) \quad (D.50)$$

$$\frac{\partial S_{r}}{\partial T_{S}} = \sum_{k=2}^{\pi} \sum_{i=1}^{N} e^{\theta_{k}S} \alpha_{kS} m_{iS} / D_{iS} x \left(\frac{\partial K_{ik}S}{\partial T_{S}} - K_{ik}S \frac{\partial D_{i}S}{\partial T_{S}} / D_{iS}\right)$$
(D.51)

Derivatives of Specification Equation for the partial condenser(6.38):

$$S_{\text{pcond}} = \sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ik1} e^{\theta_{k1}} \alpha_{k1} m_{i1} / D_{i1}$$
$$- R \sum_{k=1}^{N} K_{i11} e^{\theta_{11}} \alpha_{11} m_{i1} / D_{i1} = 0$$
(6.38)

.

The derivatives are :

i = 1

$$\frac{\partial S_{pcond}}{\partial m_{11}} = \sum_{k=2}^{\pi} K_{1k1} e^{\theta_{k1}} \alpha_{k1} / D_{11} - R K_{111} e^{\theta_{11}} \alpha_{11} / D_{11}$$
(1=,...,N) (D.52)

$$\frac{\partial S_{p^{\text{cond}}}}{\partial \alpha_{11}} = -R \sum_{i=1}^{N} K_{i11} e^{\theta_{11}} m_{i1} / D_{i1} \times (1 - \alpha_{11} \frac{\partial D_{i}}{\partial \alpha_{11}} / D_{i1})$$

+
$$\sum_{i=1}^{N} K_{i21} e^{\theta_{21}} m_{i1} / D_{i1} x (-1 - \alpha_{21} \frac{\partial D_{i1}}{\partial \alpha_{11}} / D_{i1}) (D.53)$$

$$\frac{\partial S_{p^{\text{cond}}}}{\partial \alpha_{21}} = 0 \tag{D.54}$$

$$\frac{\partial S_{pcond}}{\partial \alpha_{31}} = -\sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ik1} e^{\theta_{k1}} \alpha_{k1} m_{i1} / D_{i1}^{2} \frac{\partial D}{\partial \alpha_{31}}$$

+
$$\sum_{i=1}^{N} K_{i31} e^{\theta_{31}} m_{i1} / D_{i1}$$
 (D.55)

$$\frac{\partial \mathbf{S}_{\mathbf{p}^{\text{cond}}}}{\partial \theta_{11}} = -\mathbf{R} \sum_{i=1}^{N} \mathbf{K}_{i11} \mathbf{e}^{\theta_{11}} \alpha_{11} \mathbf{m}_{i1} / \mathbf{D}_{i1} \mathbf{x} (1 - \frac{\partial \mathbf{D}_{i1}}{\partial \theta_{11}} / \mathbf{D}_{i1}) (D.56)$$

·

$$\frac{\partial S_{\underline{p}^{cond}}}{\partial \theta_{11}} = -\sum_{k=2}^{\pi} \sum_{i=1}^{N} K_{ik1} e^{\theta_{k1}} \alpha_{k1} m_{i1} / D_{i1}^{2} \frac{\partial D_{i1}}{\partial \theta_{11}}$$

+
$$\sum_{i=1}^{N} K_{i11} e^{\theta_{11}} \alpha_{11} m_{i1} / D_{i1}$$
 (1=2,3) (D.57)

$$\frac{\partial S_{p^{cond}}}{\partial T_1} = \sum_{k=2}^{\pi} \sum_{i=1}^{N} e^{\theta_{k1}} \alpha_{k1} m_{i1} / D_{i1} \left(\frac{\partial K_{i^{k1}}}{\partial T_1} - K_{i^{k1}} \frac{\partial D}{\partial T_1} \right)$$

$$- \mathbf{R} \sum_{i=1}^{\mathbf{N}} \mathbf{e}^{\mathbf{\theta}_{11}} \alpha_{11} \mathbf{m}_{i1} / \mathbf{D}_{i1} \left(\frac{\partial \mathbf{K}_{i11}}{\partial \mathbf{T}_{1}} - \mathbf{K}_{i11} \frac{\partial \mathbf{D}_{i1}}{\partial \mathbf{T}_{1}} / \mathbf{D}_{i1} \right)$$

(D.58)

Derivatives of Specification Equation for the partial condenser(6.39):

$$S_{tcond} - \alpha_{11}$$
 (6.39)

$$\frac{\partial S_{t \text{ cond}}}{\partial \alpha_{11}} = 1.0 \tag{D.59}$$

APPENDIX E.Evaluations of the coefficients for the approximate thermodynamic model

Coefficients for the Equibrium Ratios :

The approximate thermodynamic model proposed by Boston (1980) is utilized for the equilibrium ratios. It is given by,

$$\ln K_{ij} = A_{ij} - B_{ij}(1/T - 1/T^{b}).$$
(E.1)

where T^b is the base temperature. The parameter B_{ij} in the above equation is determined from

$$\frac{\partial \ln K_{ij}}{\partial T} = B_{ij} / T^2$$
(E.2)

at temperature T^b in the outer loop (which is the temperature obtained in the inner loop) of the algorithm. Furthermore, the parameter A_{ij} is given by

$$\mathbf{A}_{ij} = \ln \mathbf{K}_{ij}^{\mathbf{b}} \tag{E.3}$$

Equations (E.1) and (E.2) give Equations (5.7) and (7.1)

$$\ln (K_{ij}/K_{ij}^{b}) = B_{ij} (T-T^{b})/(TT^{b}).$$
 (5.7)

Coefficients for the Partial molal enthalpy :

A linear thermodynamic model for the partial molal enthalpy is utilized in this work. The partial molal enthalpy of a component i in phase k is determined from

$$\mathbf{h}_{i\mathbf{k}} = \mathbf{h}_{i\mathbf{k}}^{\mathbf{b}} + (\partial \mathbf{h}_{i\mathbf{k}}^{\dagger} / \partial \mathbf{T})_{\mathbf{T}^{\mathbf{b}}} (\mathbf{T} - \mathbf{T}^{\mathbf{b}}).$$
(5.8)

The temperature derivative of the partial molal enthalpy, $(\partial h_{ik}/\partial T)$, is evaluated at the base temperature T^b in the outer loop. The derivative

 $(\partial h_{ik}/\partial T)$ is obtained by numerical perturbation of

$$\mathbf{h}_{ik} = \mathbf{h}_{i,ideal} - \mathbf{RT}^2 \ \partial \ln \ \phi_{ij} / \partial \mathbf{T} \qquad (E.4)$$

R.

where $h_{i,ideal}$ is the ideal gas enthalpy of component i.