Chapter I

Introduction

A multicomponent phase equilibrium involving three or more coexisting fluid phases is frequently encountered in liquefied natural gas processes such as CO_2+crude oil systems.In recent years the subject of three phases attention to understanding the occurrence of Liquid-Liquid-Vapor behavior in complex mixture and many algorithm of three phases flash have been developed. For process calculations particularly in petroleum and cryogenic technology,cubic equations of state have proved to be extremely useful.They are simple and can be solved with a straightforward algebraic procedure,so that they lead to robust computer programs for the predictive of thermodynamic data and to relatively short computing times.They contain only a small number of adaptable parameters which can easily be related to the critical properties,so that the equations lead themselves well for generalization and application to mixtures.

The Soave-Redlich-Kwong(SRK)equation yields a critical compressibility factor Z_c=0.333,whereas experimental compressibility factor Z_c range between 0.24 and 0.30.As a result,both the predicted densities of the saturated liquids and the critical volumes deviate noticeably from experimental values this shortcoming led various authors to suggest modified equations which give

reasonable predictions of both vapor pressure and liquid volume.Harmens & Knapp(1980)equation were chosen for the thermodynamic model,Harmens & Knapp three parameter cubic equation of state expressed the parameters of the equation in terms of critical parameters,including the critical compressibility and the accentric factor.For 831 data of pure substances.The HK equation had about half the error of the API-Soave equation. In the same time we presented the comparisons of experimental and calculation of equilibrium composition of three-phase flash and molar volume of individual phase for system of light hydrocarbon and heavy hydrocarbon mixtures which compute by Soave-Redlich-Kwong (SRK)(1972),Harmens & Knapp(HK)(1980),Peng & Robinson(PR) (1976),modified SRK by Graboski & Daubert(G&D)(1978).Pascal program and algorithm which use for calculation in this work be presented.In addition,the flash equations are formulated in such a way as to given insight into those characteristics which make for easy solution by the Newton-Raphson method.

Objective of Work

1. To study the accuracy of equations of state in computation of liquid molar volume, vapor molar volume and phase equilibrium compositions of light gases and heavy hydrocarbon mixtures of Liquid-Liquid-Vapor system under a variety of temperature and pressure.

2. To study the criteria for initial estimate of phase compositions in the iterative solution of Liquid-Liquid-Vapor system.

Scope of Work

1. Construct Pascal program for test criteria method of initial estimate phase compositions of Liquid-Liquid-Vapor system.

2. Construct Pascal program for three-phase(Liquid-Liquid-Vapor)flash calculation by Soave-Redlich-Kwong,Harmens and Knapp,Peng and Robinson,modified Soave-Redlich-Kwong (Graboski and Daubert) equations of state.

3. Comparisons of experimental and predicted liquid molar volume,vapor molar volume and phase compositions of Methane+Ethane+n-Docosane mixture at 298.15,303.15 K and variety of pressure.

4. Comparisons of experimental and predicted liquid molar volume,vapor molar volume and phase compositions of Carbon dioxide+Nitrogen+n-Nonadecane mixture at 294.15,297.15 and 301.15 K and variety of pressure.

Literature survey

Early work by Osborne(1964) Illustrated a simple method for calculating three-phases flash (two liquid phases and a vapor phase)and develope algorithm for calculating three-phase flashes which can applicable whether the two liquid phases and slightly or appreciably soluble in each other for every component in a three-phase system there will exist two sets of liquid-vapor equilibrium data;one is association with each liquid phase and composition of the liquid phase may be calculated.

Deam and Maddox(1969)suggested a technique by which Newton-Raphson method could be applied to accelerate convergence. Wu and Bishnoi(1986) proposed new algorithm used for liquid-liquid equilibrium,three-phase bubble-point and three-phase equilibrium flash calculations.Material-balance and equilibrium equations are rearranged suitably and solved by the Newton-Raphson method.A procedure for producing initial values of the variables required in three-phase equilibrium flash is proposed.

George,Brown,Farmer,Buthod and Manning(1976) presented algorithm for calculated multiphase mixtures by minimizing the Gibbs free energy.The Fortran program converts the Gibbs free energy of the mixture into a novel unconstrained form,then minimizes using Powell's method.

Mauri(1980)proposed a general procedure for

calculating multiphase-multicomponent vapor-liquid equilibrium has been developed.The proposed procedure has been considered satisfactory since it always converges with good results on the number of phases and their compositions about 1000 points of liquid-vapor,liquid-liquid and liquid-liquid-vapor equilibrium without a resulting trivial solution.

Ohanomah and Thompson(1984) proposed the algorithm for isothermal multicomposition phase equilibrium computation involving up to one vapor phase,two liquid phases and a solid phase.A number of algorithm have been developed for multiphase equilibria.The algorithm have been designed to effect a phase elimination without restarting the computation and they have been implemented to handle solid-liquid-liquid-vapor equilibria or any algorithms have been applied to a number of systems and their performance,based on iteration requirements,have been compared.

The traditional algorithm is derived from the thermodynamic condition that fugacity be matched for each component in each phase.More recently Gratum and Seider(1979) proposed flash algorithm based on Gibbs free energy minimization. Soares and Medina(1982)presented an algorithm for flash calculations in which partially miscible systems are involved is described.The algorithm is based on the principle of minimisation of the system Gibbs free energy.The minimisation procedure is based on a Newton-Raphson algorithm.

Schuil and Bool(1985)presented mixed K-value model

allows existing computer programs for the simulation of vapor-liquid equilibrium stage to be used for three-phase vapor-liquid-liquid systems.They concluded that the mixed K-value model can successfully simulate vapor-liquid-liquid equilibrium in existing flash and distillation algorithms.

Nelson(1987) described the method for determination of the number of phases actually present,based on a multi-phase generalization of the well-know bubble and dew-point criteria,S-R-K equation of state be used for calculated K-values in each phase and the algorithms documented this paper were installed in the Shell Process engineering calculation system in 1973.Since that time they have repeatedly proven to be fast,reliable and good citizens of a modular flowsheeting environment.

Diandreth and Paulaitis(1989)used Peng-Robinson equation of state for studied phase behavior of ternary mixture of CO_2+HO_2+Isopropanol(IPA) Liquid-Liquid-Vapor equilibrium at temperatures and pressures near the critical point of CO_2. The calculated results show that this equation of state can describe several unique features of phase diagram.These features include tricritical points, secondary critical endpoints. Wong and Sandler(1984)used the two constant cubic equation of state of Peng and Robinson and generalized three parameter corresponding states principle developed by Wong et al.(1984) and the three-constant cubic equation of state proposed by Teja and Patel(1982).