Flash Computation and EoS Modelling for Compositional Thermal Simulation of Flow in Porous Media



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I would like to dedicate this thesis to my parents.

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Abstract

The production of heavy oil is gradually becoming more viable, as both the price of production decreases and the price of oil (over the long term) increases. The reserves of heavy oil are far greater than the existing reserves of conventional oil, however it is often not economically desirable to extract. Heavy oil is characterised as a very viscous and dense substance, which flows very slowly under gravity at atmospheric temperature. As such it is often necessary to use steam to reduce the viscosity of the oil to enhance production. Novel production enhancement techniques can utilise a light hydrocarbon solvent to further increase recovery. The simulation of these reservoirs is not trivial, during production they undergo large changes in temperature and pressure depending upon the production strategy used. Furthermore the use of a light hydrocarbon solvent can lead to highly asymmetric mixtures and the appearance of a second oleic phase. However an accurate simulation is necessary due to the high cost of the production and the requirement for reliable predictions for new production enhancement strategies. In this work the thermodynamic models used to represent the fluid and the methods of flash calculation suitable for multiphase mixtures are studied. The final aim is to develop a reservoir simulator incorporating some of these elements.

To accurately represent the fluid phases in equilibrium in a heavy oil reservoir it is necessary to use an equation of state (EoS). There are a huge number of possible equations of state (EoS's) available. In this work, a number of these models are compared for heavy oil related binary systems to evaluate which are best suited. The accuracy of each model is compared and it is found that, if the interaction between the water and hydrocarbon phases is not considered to be important, then the commonly used cubic EoS's with the van der Waals mixing rules are suitable (optimally using two binary interaction parameters). If more complex interactions are considered important to the simulation then the cubic EoS's can be used with the Huron-Vidal type mixing rules (using the non-random two-liquid (NRTL) activity coefficient model). The more complex EoS's such as cubic plus association (CPA) or PC-SAFT can also be used and are generally as accurate as the Huron-Vidal type.

Another issue associated with thermal simulation is that it is necessary to add an energy balance to the system of PDEs used. It is common to use the temperature as an additional primary variable. The resulting isothermal flash specification can lead to some problems during transient simulation. The fluid in some of the grid-blocks may become narrow boiling. The enthalpy of a narrow boiling mixture changes rapidly due to very small changes in the temperature or pressure. This can lead to issues with convergence and potential oscillations during Newton steps. A related issue is when the solution requires more phases than components to meet the energy balance equation, this cannot be solved when using isothermal flash. This can often occur close to steam injection wells (where components other than water can be stripped away). An approach using the energy directly in the flash calculation (e.g. isobaric, isenthalpic flash) is explored in this work and an algorithm presented which takes only slightly more computational resources than the conventionally used isothermal flash. This is demonstrated to be robust for a number of mixtures, and an approach tailored for the flash calculation of mixtures containing water is described.

The issue of multiple co-existing equilibrium phases is also examined. The conventional isothermal flash framework is complex and cumbersome when dealing with more than two or three phases. A new method (modified RAND) is presented based on the related chemical equilibrium problem. This method is primarily examined for multiphase isothermal flash, with a robust implementation described. An extension to other state function based flash specifications is developed using the new proposed framework. Furthermore the conventional method of solving an EoS at a specified temperature and pressure is abandoned and a method which co-solves the EoS with the equilibrium equations is described (vol-RAND). A different approach to solving state function based flash specifications is also considered, where the EoS is solved at the given state function variables resulting in a minimisation without non-linear constraints. This proposed approach has not yet been tested.

Finally a thermal, EoS based reservoir simulator is developed from an isothermal simulator. The energy balance partial differential equation is added, and the temperature used as an additional primary variable. The EoS's compared for heavy oil related fluids are implemented in the simulator. A multiphase flash algorithm using modified RAND and stability analysis skipping is added to the simulator. Finally a test case is used to demonstrate that some of the more complex EoS models can be used and the multiphase flash algorithm is suitable. With the thermal reservoir simulation tool developed it is possible to carry out further comparisons and add more complexity in future work.

Resumé på Dansk Flash Computation og EoS Modellering for Termisk Kompositionssimulering af Strømning i Porøse Medier

Produktionen af tung olie bliver gradvist mere profitable, i takt med både produktionsprisen falder og oliepriserne (på lang sigt) stiger. Reserven af tung olie er langt større end de eksisterende reserver af konventionel olie, men det er ofte ikke økonomisk rentabelt at producere. Tung olie er karakteriseret som et meget viskøst stof og et stof med høj densitet, tung olie strømmer meget langsomt under tyngdekraften ved stuetemperature. Derfor er det ofte nødvendigt at bruge damp for at reducere viskositeten af olien for at forbedre produktionen. Nye produktionsforbedrings teknikker kan udnytte et let kulbrint opløsningsmiddel til yderligere at øge produktionen. Simulationen af disse reservoirer er ikke trivielt, under produktion er der store temperaturændringer og trykændringer afhængig af den anvendte produktionsstrategi. Brugen af et lys kulbrinteopløsningsmiddel kan desuden føre til stærkt asymmetriske blandinger og udseende lig et sekund oleisk fase. Men præcise simuleringer er nødvendige på grund af de høje omkostninger ved produktionen og på grund af kravet om pålidelige forudsigelser, i forbindelse med nye produktionsforbedringsstrategier. Heri arbejdet med de termodynamiske modeller, der bruges til at repræsentere væsken og studiet af metoder til flashberegninger egnet til flerfasede blandinger. Det endelige mål er at udvikle en reservoirsimulator der kan inkorporere nogle af disse elementer.

For nøjagtigt at repræsentere fluidfaserne i ligevægt, i et tungoliereservoir er det nødvendigt at bruge tilstandsligninger der er et stort udvalg af mulige tilstandsligninger, i dette projekt er en række af disse modeller blevet sammenlignet med tunge olierelaterede binære systemer til evaluering af hvilken var bedst egnet. Nøjagtigheden af hver model er sammenlignet og det er konstateret, at hvis interaktion mellem vand og kulbrinte faser ikke er vigtig, så er de almindelig brugte kubiske tilstandsligninger med van der Waals blandings regler egnede (optimalt ved brug af to binære interaktions parametre). Hvis mere komplekse interaktioner er anset for vigtige for simuleringen så kan den kubiske tilstandsligning bruges med Huron-Vidal blandingsregler (ved anvendelse af den ikke-tilfældige to-væske (NRTL) aktivitetskoefficientmodel). De mere komplekse tilstandsligninger såsom kubisk plus association (CPA) eller PC-SAFT kan også anvendes og er generelt lige så præcise som Huron-Vidal typen.

Et andet problem i forbindelse med termisk simulering er, at det er nødvendigt at tilføje en energi balance til det anvendte system af PDE'er. Det er almindeligt at bruge temperaturen som en ekstra primær variabel. Den resulterende isotermiske flash specifikation kan medføre nogle problemer under dynamisk simulering. Væsken i nogle af gitterblokkene kan blive smalkogende. Entalpien af en smal kogende blanding ændres hurtigt på grund af meget små ændringer i temperaturen eller tryk. Dette kan medføre til problemer med konvergens og potentielle svingninger under Newton iterationer. Et relateret problem er, når løsningen kræver flere faser end komponenter, der skal til for at løse energi balance ligningen, dette kan ikke løses, når der anvendes isothermal flash. Dette kan ofte forekomme tæt på dampinjektionsbrønde (hvor andre komponenter end vand kan fjernes). En tilgang ved hjælp af at bruge energien direkte i flashberegningen (fx. isobarisk, isenthalpisk flash) er udforsket i dette arbejde og en algoritme præsenteret, som kun bruger en smule mere computer ressourser end den traditionelt anvendte isotermiske flash. Dette er påvist at være robust for a række blandinger og en fremgangsmåde, der er skræddersyet til flashberegningen af blandinger der indeholder vand er beskrevet.

Spørgsmålet om flere samtidig sameksisterende ligevægts faser er også undersøgt. Den konventionelle isotermiske flash metoder er kompleks og besværlige, når de beskæftiger sig med flere end to eller tre faser. En ny metode (modificeret RAND) er præsenteret baseret på den relaterede kemiske ligevægt problem. Denne metode undersøges primært for multifase isotermisk flash med en robust implementering beskrevet. En udvidelse til andre tilstandsfunktion-baserede flashspecifikationer er udviklet ved hjælp af den nye foreslåede metode. Desuden er den konventionelle metode til løsning af tilstandsligning ved en bestemt temperatur og tryk udskiftet med en fremgangsmåde, som co-løser tilstandsligningen med ligevægtsligningerne er beskrevet (vol-RAND). En anden tilgang til løsning af tilstandsfunktions-baserede flashspecifikationer overvejes også, hvor tilstandsligning uden ikke-lineære begrænsninger. Denne foreslåede tilgang er endnu ikke blevet testet.

Endelig udvikles en termisk tilstandsligning baseret reservoirsimulator fra en isotermisk simulator. Energibalancens PDE tilsættes, og temperaturen bruges som en ekstra primær variabel. Tilstandsligninger sammenlignet med tunge olie relaterede væsker bliver implementeret i simulatoren. En multifase flash algoritme med modificeret RAND og stabilitetsanalyse undgåelse tilføjes til simulatoren. Endelig bruges en test sag til at demonstrere at nogle af de mere komplekse tilstandslignings modeller kan bruges, og flerfaset flash algoritme er egnet. Med det termiske reservoir simulerede værktøj udviklet er det muligt at gennemføre yderligere sammenligninger og tilføje mere kompleksitet i fremtidigt arbejde.

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List of symbols

Roman Symbols

D	Diagonal matrix with elements x_i
M	Inverse of m (equation 4.11)
m	Matrix defined in equation 4.11 or mass flow for reservoir simulation
q	Element for general state function RAND matrix, defined in equation 4.65
R	Matrix of column vectors of component densities ρ of each phase
\boldsymbol{s}_1	Element for general state function RAND matrix, defined in equation 4.65
s_2	Element for general state function RAND matrix, defined in equation 4.65
t	Element for general state function RAND matrix, defined in equation 4.65
X	Matrix of column vectors of component mole fractions x of each phase
Z	Diagonal matrix with elements z_i
\hat{H}	Positive definite matrix based on trust region type update of an indefinite Hessian
$\hat{m{R}}$	Matrix defined in equation 4.108
$\hat{m{w}}$	Defined in equation 4.36
\hat{a}	Conjugate intensive property of extensive property \tilde{b}
\hat{b}	Element mole amount
\hat{c}	Intensive variable

\hat{f}	Fugacity
\hat{g}	Parameter for NRTL equation
\hat{H}	Height of a grid cell
\hat{M}	General state function
\hat{m}	Parameter for the calculation of a
\hat{Q}	Parameter for MHV1 and MHV2 equations
\hat{u}	Eigenvector
\mathcal{A}	Formula matrix for chemical reaction equilibrium
L	Lagrangian
\tilde{b}	Independent extensive variable
$\widetilde{oldsymbol{Q}}$	Scaled Hessian of a phase Gibbs energy defined in equation 4.33
\widetilde{A}	Association site
\widetilde{B}	Association site
\widetilde{m}	Chain length for PC-SAFT EoS
A	Helmholtz energy or area
a	EoS energy parameter
В	Based on van der Waals mixing rules, defined in equation 1.18
b	EoS co-volume parameter
C	Number of components
c_1	Parameter for evaluation of α
$C_1 - C_5$	Parameters used for polynomial equations or other correlations
C_p	Isobaric heat capacity
C_v	Isochoric heat capacity

C_x	Defined in equation 4.63
C_{ji}	Energy parameter for NRTL equation
D	Based on van der Waals mixing rules, defined in equation 1.17
d	Factor used to ensure $\widetilde{oldsymbol{Q}}$ matrix is safely positive definite
E	Number of elements, or equation defined in 1.32
e	Reduced temperature derivative of the chemical potential, 4.13
F	Number of phases
f	General nonlinear function
G	Gibbs energy
g	Reduced molar Gibbs energy
g_n	Standard gravity
Н	Enthalpy or Hessian
h	Component enthalpy
J	Jacobian
K	Equilibrium K-factor
k	Permeability and factor used for procedure correction of RAND matrix
k_{ij}	Binary parameter for an EoS
kr	Relative permeability
l_{ij}	Binary parameter for an EoS
MM	Molecular weight of a component
Ν	Number of extensive variables \tilde{b}
n	molar amount of a component
NV	Number of control volumes reservoir is split into

Р	Pressure
p	Term for burden heat loss 5.31
Q	General function to be optimised
q	Source/sink term for reservoir grid block and term for burden heat loss 5.31
R	Universal gas constant
r	Term defined differently for each flash specification in table 4.2
S	Entropy or saturation
S	Trust region correction factor 4.47
Т	Temperature
t	Time
tm	A modified tangent plane distance function
tpd	The tangent plane distance function 1.29
U	Internal energy
u	Darcy velocity defined in equation 5.5
u_1 to u_4	RHS equations to be solved in RAND formulations
V	Volume
υ	Element to add to indefinite \boldsymbol{M} matrix defined as $v_i = \hat{u}_i \sqrt{x_i}$
W	Trial phase mole numbers
w	Trial phase composition
x	Molar composition
y	Component mole fraction or primary variable
Ζ	Compressibility factor

z Feed molar amount

Greek Symbols

α	Temperature dependent term for EoS
β	Phase molar amount (can also be phase mole fraction if there are no reactions)
ă	Step length modifier
χ	Component mass fraction
δ_1	Parameter for SRK or PR EoS
δ_2	Parameter for SRK or PR EoS
$\delta_{i,k}$	Kronecker delta function (where i, k can be replaced with other subscripts
ϵ	Infinitesimal amount
η	Term for burden heat loss 5.31
γ	Reduced pressure derivative of the chemical potential, 4.13
\hat{lpha}	Factor used in the procedure correction for modified RAND
$\hat{\epsilon}$	Energy of association
$\hat{\lambda}$	Equilibrium elemental potential, or chemical potential, or Lagrange multi- plier
$\hat{\mu}$	Viscosity
$\hat{\Psi}$	Set of system of equations solved in reservoir simulation
$\hat{\psi}$	Energy flux term
$\hat{ ho}$	Mass density
$\hat{ heta}$	Used to record previous time-step flash solution as initial estimate for next time step, equation 5.24
\hat{arphi}	Fugacity coefficient

$\hat{\xi}$	Specific mass enthalpy defined in equation 5.17
$\hat{\zeta}$	Energy accumulation term
κ	Thermal conductivity
λ	Reduced equilibrium elemental potential, reduced chemical potential, eigenvalue, or Lagrange multiplier
λ_{min}	Minimum absolute eigenvalue
μ	Chemical potential of a component
Ω	Defined in equation 4.63
ω	Pitzer's acentric factor
Φ	Potential due to gravity and pressure in equation 5.5
ϕ	Porosity
Ψ	Defined in equation 4.63
ψ	Mass flux term
ρ	Molar density
σ	Segment diameter for PC-SAFT EoS
au	Term for burden heat loss 5.31
Θ	Objective function for nonlinear regression, 2.20
θ	Deviation function for nonlinear regression
\widetilde{lpha}	NRTL non-randomness parameter
\widetilde{eta}	Volume of association
$\widetilde{\epsilon}$	Segment energy for PC-SAFT
ξ	Temperature derivative of the reduced chemical potential, 4.55
ζ	Mass accumulation term

Superscripts

*	Ideal gas property
0	Reference state property, or initial value
a	Aqueous phase
E	Excess property
eq	Equilibrium value
IG	Ideal gas property
l	Liquid phase
n	Iteration step or time step
r	Residual property
spec	Specified value
v	Vapour phase
Subscripts	

0	Ideal gas state
∞	Infinite pressure
С	Critical property
calc	Calculated value
exp	Experimental value
g	Gas phase
i	Component index
j	Phase Index
k	General index
kl	Interface between grid block k and l

L	Combined liquid phases property
l	General index
m	Phase index
max	Maximum limit
min	Minimum
mix	Mixture property
0	Index for Jacobian, or oil phase
old	Value from a previous time-step
r	Reduced property or rock property
ref	Reference state
w	Water component or phase
Acronyms / Abbreviations	
AARD	Absolute average relative deviation
BIP	Binary interaction parameter
CMG	Computer Modelling Group
CPA	Cubic plus association EoS [91] used here as the simplified version [89]
DIPPR	The Design Institute for Physical Properties, used for component proper- ties and correlations
DME	Di-methyl ether
EoS	Equation of state (note that EoS's refers to Equations of state)
HV	Huron-Vidal mixing rules [79]

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xxxvi
LBC	The Lorenz-Bray-Clark correlation [100]
LCVM	Linear combination of the Vidal and Michelsen mixing rules [16]
LLE	Liquid liquid equilibrium
MAD	Mean absolute deviation
MHV1	Linear modified Huron-Vidal mixing rule [113]
MHV2	Quadrating Modified Huron-Vidal mixing rule [44]
NRTL	Non-random two-liquid model [156]
NRTL _{HV}	Modified NRTL mixing rules of [79]
PC-SAFT	Perturbed chain SAFT of [67] used here as the simplified variant [192]
PR	Peng Robinson EoS [135]
PRSV	Peng Robinson Stryjek Vera model [177]
RAND	Research and development corporation, used here in reference to a chemi- cal equilibrium model [197]
SAFT	Satistical associating fluid theory Chapman et al. [25, 26]
SAFT-VR Mie	SAFT model with variable range using the Mei potential [94]
SAGD	Steam assisted gravity drainage (heavy oil recovery technique)
SRK	Soave Redlich Kwong EoS [175]
STARS	Thermal reservoir simulator from CMG
UNIFAC	UNIQUAC Functional-group Activity Coefficients [57]
UNIQUAC	Universal quasi-chemical equation [2]

- vdW1f Van der Waals one fluid mixing rules, combined with the classical combining rules
- VLE Vapour liquid equilibrium
- Vapour liquid liquid equilibrium VLLE

Chapter 1

Introduction

The international energy outlook [41] expects the energy demand worldwide will rise by 48% by 2040, with fossil fuels expected to contribute more than 75% in 2040. Petroleum and other liquid fuels are predicted to provide 30% of the total energy demand in 2040. To meet this demand it may be necessary to target new sources of fossil fuels.

The motivation for this work was to improve the description and simulation of the production of heavy oil in the presence of steam and a hydrocarbon solvent. Of the total known world oil reserves only 30% come from conventional sources while 70% are defined as heavy oil, extra heavy oil, oil sands and bitumen [53]. At present the cost of production is often close to the sale price of the oil. It is a desire of the oil industry in general to greatly reduce the cost of heavy oil production. A number of methods are used to enhance oil production which will be addressed in more detail in chapter 5. Field scale testing of enhanced production methods is often prohibitively expensive and may lead to unexpected results, hence it is desired to have suitable tools to accurately predict production for the reservoir engineer.

The focus of this work is on the thermodynamic description of the oil and how to carry out the phase split calculation when the temperature may not be known and there are up to four, or five phases present in equilibrium. A brief introduction to classical thermodynamics is given in section 1.1. A more detailed introduction to how equations of state (EoS's) are used to describe the thermodynamic properties of fluids is given in section 1.2. Variations of these EoS models will be tailored in chapter 2 to a number of heavy oil related systems. The phase equilibrium calculation will be introduced in section 1.3. A method to solve an energy based flash using the conventional approach to phase split calculations will be presented in chapter 3 and a new approach to solving the phase

split calculation will be presented in chapter 4. Finally oil reservoir simulation will be introduced in section 1.4 and in more detail with results presented in chapter 5.

1.1 Classical thermodynamics

Though a thorough review will not be given here there are many detailed books on the subject of the first and second law of thermodynamics and their applications. The description given here will focus on the major points of the book from Michelsen and Mollerup [117]. Here we will start with the description of the internal energy. The internal energy of an isolated system is a function of all of its extensive variables, in the context of this work we will ignore a number of contributions and focus only on:

$$U(S, V, \boldsymbol{n}) \tag{1.1}$$

where U is the internal energy, S is the entropy, V the volume and n the molar amount of each component present in the system. The extensive properties of a system are first order homogeneous functions, additive and proportional to the extent of the system. In contrast their conjugated intensive properties which are zero order homogeneous functions, non-additive and uniform throughout a homogeneous system at equilibrium. These are presented in table 1.1. Since the variables of the internal energy are homogeneous functions of degree one we can describe it as:

$$U = S\left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}} + V\left(\frac{\partial U}{\partial V}\right)_{S,\boldsymbol{n}} + \sum_{i=1}^{C} \left(\frac{\partial U}{\partial n_{i}}\right)_{S,V,n_{j}}$$
(1.2)

From table 1.1 this equation can be replaced with the more well known equation for the internal energy:

$$U = TS - PV + \sum_{n_i=1}^{C} \mu_i n_i \tag{1.3}$$

Table 1.1 Extensive and intensive properties of the internal energy

Ext	ensive properties	Conj	ugated intensive properties
S	Entropy	T	Temperature
V	Volume	-P	Pressure
n_i	Mole numbers	μ_i	Chemical potentials

Other contributions to the internal energy of a system are not relevant to this work. From this description of the internal energy it is possible to arrive at a number of other important state functions. How to arrive at each is not described here but each state function is presented in table 1.2 as described by Michelsen and Mollerup [117].

Table 1.2 Thermodynamic state functions and their properties

Property	$U(S, V, \boldsymbol{n})$	$H(S, P, \boldsymbol{n})$	$A(T, V, \boldsymbol{n})$	$G(T, P, \boldsymbol{n})$
S	-	-	$-\left(\frac{\partial A}{\partial T}\right)_{V,\boldsymbol{n}}$	$-\left(\frac{\partial G}{\partial T}\right)_{P,\boldsymbol{n}}$
V	-	$\left(\frac{\partial H}{\partial P}\right)_{S,\boldsymbol{n}}$	-	$\left(\frac{\partial G}{\partial P}\right)_{P,\boldsymbol{n}}$
T	$\left(rac{\partial U}{\partial S} ight)_{V,oldsymbol{n}}$	$\left(\frac{\partial H}{\partial S}\right)_{P,\boldsymbol{n}}$	-	-
P	$-\left(rac{\partial U}{\partial V} ight)_{S,oldsymbol{n}}$	-	$-\left(\frac{\partial A}{\partial V} ight)_{T,oldsymbol{n}}$	-
μ_i	$\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}$	$\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j}$	$\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$	$\left(\frac{\partial G}{\partial n_i}\right)_{T,P}$

A number of useful relations can be arrived at from this table which will be used in chapter 4. Compared with U, S, and H, A and G are functions directly of measurable quantities, (T, V, \mathbf{n}) and (T, P, \mathbf{n}) respectively. Most EoS's are pressure explicit functions using (T, V, \mathbf{n}) as variables, which avoids multiplicity in V at a given (T, P, \mathbf{n}) . For this reason, Helmholtz energy is more useful in terms of EoS related derivations.

A residual quantity (\hat{M}^r) is the difference between the property of a real mixture (\hat{M}) and that of an ideal gas (\hat{M}^*) at the same pressure, temperature. Depending on whether the ideal gas reference state is selected at the system pressure or volume, two different residual properties can be obtained.

$$\hat{M}(T, P, n) = \hat{M}^{*}(T, P, n) + \hat{M}^{r}(T, P, n)$$
 (1.4)

$$\hat{M}(T, V, \boldsymbol{n}) = \hat{M}^{*}(T, V, \boldsymbol{n}) + \hat{M}^{r}(T, V, \boldsymbol{n})$$
(1.5)

At an ideal gas state of (P_0, V_0, n) the two sets of properties become the same, $\hat{M}(T, V_0, n) = \hat{M}(T, P_0, n)$. At a real gas state they are not identical. For the Helmholtz energy if we integrate it from the ideal gas state to the real gas state we can find the difference between the two states:

$$A^{*}(T, V, \boldsymbol{n}) - A^{*}(T, P, \boldsymbol{n}) = \int_{V_{0}}^{V} \left(\frac{\partial A^{*}}{\partial V}\right)_{T}, \boldsymbol{n} dV - \int_{P_{0}}^{P} \left(\frac{\partial A^{*}}{\partial P}\right)_{T, \boldsymbol{n}} dP$$
$$= -nRT \ln \frac{V}{V_{0}} - nRT \ln \frac{P}{P_{0}}$$
$$= -nRT \ln Z$$
(1.6)

Here we use the relation

$$\left(\frac{\partial A^*}{\partial P}\right)_{T,\boldsymbol{n}} = P\left(\frac{\partial V}{\partial P}\right)_{T,\boldsymbol{n}}$$

to arrive at this result.

For a pure component the change in the chemical potential of an ideal gas from an arbitrary pressure P_0 is

$$\mu^*(T, P) - \mu^*(T, P_0) = RT \ln \frac{P}{P_0}$$
(1.7)

This can be generalised to a real gas by defining a property, the fugacity, which equals P for an ideal gas

$$RT\ln\frac{f(T,P)}{P_0} = \mu(T,P) - \mu^*(T,P_0)$$
(1.8)

By subtracting equation 1.7 from 1.8 we can replace P_0 by P and obtain the fugacity coefficient $\hat{\varphi} = \hat{f}/P$:

$$nRT \ln \hat{\varphi}(T, P) = nRT \ln \frac{\hat{f}(T, P)}{P} = \mu(T, P) - \mu^*(T, P)$$
(1.9)

Similarly for a mixture where the pure component chemical potential of an ideal gas is

$$\mu_i^*(T, P, \mathbf{n}) = \mu_i^*(T, P) + RT \ln x_i$$
(1.10)

which can be generalised again for a real fluid to:

$$RT \ln \frac{\hat{f}_i(T, P, \boldsymbol{n})}{P_0} = \mu_i(T, P, \boldsymbol{n}) - \mu_i^*(T, P_0)$$
(1.11)

where in this case the fugacity is defined as $\hat{f}_i = Px_i$ for an ideal gas. The fugacity coefficient for a component in a mixture is then found as:

$$RT \ln \hat{\varphi}(T, P, \mathbf{n}) = RT \ln \frac{\hat{f}_i(T, P, \mathbf{n})}{Px_i}$$

= $\mu_i(T, P, \mathbf{n}) - \mu_i^*(T, P, \mathbf{n})$ (1.12)
= $\left(\frac{\partial A^r}{\partial n_i}\right)_{T,V} - RT \ln Z$

The fugacity coefficient defined here is used to solve many different phase equilibrium problems. It is readily accessible from a pressure-explicit EoS, or one expressed in terms of the Helmholtz energy.

1.2 Equations of state

For this section we will assume that the EoS is pressure explicit, or expressed in terms of the Helmholtz energy. This assumption is true for the most commonly used EoS's in the oil and gas industry and therefore for those applicable to this work. The fugacity coefficient was introduced in equation 1.12 and it is shown to be related to the derivative of the residual Helmholtz energy.

We know the difference between the ideal gas at a given volume and pressure from equation 1.6, this is used to find

$$RT\ln\hat{\varphi}_i(T, P, \boldsymbol{n}) = \mu_i(T, V, \boldsymbol{n}) - \mu_i^*(T, V, \boldsymbol{n}) - RT\ln Z$$
(1.13)

since $\mu_i(T, V, \mathbf{n}) = \mu_i(T, P, \mathbf{n})$. The fugacity coefficient is found from an equation for the Helmholtz energy as

$$RT \ln \hat{\varphi}_i(T, P, \mathbf{n}) = \left(\frac{\partial A^r(T, V, \mathbf{n})}{\partial n_i}\right)_{T, V, n_j} - RT \ln Z$$

$$= -\frac{\partial}{\partial n_i} \left(\int_{\infty}^V \left(P - \frac{nRT}{V}\right) dV\right) - RT \ln Z$$
(1.14)

The residual Helmholtz energy is obtained by integrating a pressure equation P(V, T, n) at constant temperature. All other properties are then obtained from the equation through differentiation.

Four EoS's are considered in this work: SRK [175], PR [135], CPA [91] and PC-SAFT [67], using the simplified PC-SAFT of von Solms et al. [192] and the simplified CPA of Kontogeorgis et al. [89]. The first two are cubic EoS's, CPA is SRK with the addition of the Wertheim association term from SAFT, while PC-SAFT is a more complex representation of a fluid based on a perturbed chain representation of the statistical associating fluid theory derived by Chapman et al. [25, 26].

A full description of each of the models will be left to chapter 2 however a brief description of the framework used to solve these EoS's at a given pressure and evaluate their derivatives will be given here. The PR and SRK EoS's can be given by a generalised cubic EoS:

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V + \delta_1 b)(v + \delta_2 b)}$$
(1.15)

where for the SRK EoS $\delta_1 = 1$ and $\delta_2 = 0$ and the PR EoS $\delta_1 = 1 + \sqrt{2}$ and $\delta_2 = 1 - \sqrt{2}$. For the SRK and PR EoS the *a* and *b* parameter are fitted to match the critical pressure and temperature of each component, this leaves an additional term for the temperature dependence of the *a* term.

$$a(T) = a_c \alpha(T_r, \omega) \tag{1.16}$$

The acentric factor ω is often used to find the value of α using a suitable correlation. There are many different correlations used for this temperature dependence as is discussed in more detail in chapter 2.

For a mixture, each component has its own a_i and b_i term related to its critical properties and acentric factor (and temperature). To find the residual Helmholtz energy of the mixture we must first define how we mix the component parameters to a mixture parameter. Many different mixing and combining rules have been attempted and used in modern simulations, an overview is given by Kontogeorgis and Folas [88]. For example if we assume we use the van der Waals one-fluid (vdW1f) mixing rules:

$$D = n^2 a_{mix} = \sum_{i=1}^{C} n_i \sum_{k=1}^{C} n_k a_{ik}$$
(1.17)

and

$$nB = n^2 b_{mix} = \sum_{i=1}^{C} \sum_{k=1}^{C} n_k b_{ik}$$
(1.18)

then we can find the reduced residual Helmholtz energy from equation 1.14 as:

$$\frac{A^r(T,V,\boldsymbol{n})}{RT} = -n\ln\left(1-\frac{B}{V}\right) - \frac{D(T)}{RTB(\delta_1-\delta_2)}\ln\left(\frac{1+\delta_1B/V}{1+\delta_2B/V}\right)$$
(1.19)

The fugacity coefficient can then found from equation 1.14.

In general we do not specify the volume of a phase when carrying out phase equilibrium calculations, instead the pressure and temperature are often used. It is therefore necessary to first find the volume at a defined pressure, and then to find the relevant derivatives at a constant pressure (and with respect to pressure). A detailed description of the methods to do this from an EoS is given by Mollerup and Michelsen [120] and in the book Michelsen and Mollerup [117].

One important aspect of calculating the properties from a pressure explicit EoS is finding the volume of a phase at a given temperature, pressure and molar amount. Given a suitable mixing and combining rule neither the a_{mix} or b_{mix} terms are dependent on the volume. For a cubic EoS, such as that presented in equation 1.15, it is possible to explicitly calculate the possible volume roots (between one and three). Equation 1.15 can be rewritten as a cubic polynomial for the volume

$$V^3 + C_1 V^2 + C_2 V + C_3 = 0 (1.20)$$

and the cubic polynomial can be solved (e.g. using Cardano's method). However this method alone can result in round-off errors which may lead to errors during phase equilibrium calculations [121]. Therefore it is useful to further refine the explicit solution using Newton's method. This method is also not limited to any particular EoS and can be used for the more complex CPA or PC-SAFT EoS's used in this work.

Given an initial estimate for the volume V (e.g. the ideal gas volume) the pressure of a mixture at temperature T and molar amounts n is found from

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,n} \tag{1.21}$$

If we have a pressure specification P^{spec} then we can use Newton's method to refine our current estimate for the pressure. With the equation

$$f = P^{spec} + \left(\frac{\partial A}{\partial V}\right)_{T,n} = 0 \tag{1.22}$$

and its derivative

$$\frac{\mathrm{d}f}{\mathrm{d}V} = \left(\frac{\partial^2 A}{\partial^2 V}\right)_{T,n} \tag{1.23}$$

The Newton step is evaluated as

$$V^{n+1} = V^n - f / \frac{\mathrm{d}f}{\mathrm{d}V} \tag{1.24}$$

where V^n is the volume at the previous iteration. Using Newton's method, along with a suitable method to prevent unstable oscillation (such as bisection), the EoS is often solved very rapidly.

For the cubic EoS's the explicit solution is used followed by one Newton step to tighten the tolerance. For the more complex EoS's Newton's method is used with initial estimates of slightly greater than the co-volume and the ideal gas state. If there is more than one stable root, the root with the minimum Gibbs energy is selected. Only if either the vapour or liquid-like root are desired will they be used, this is sometimes useful to avoid initialising from both a liquid like trial and vapour like.

1.3 Phase equilibria calculation

Phase equilibrium problems are at the heart of process and reservoir simulation. Here we will introduce a few basic concepts of phase equilibria which will then be used in chapters 3 and 4. One description of a equilibrium state is that all of the intensive properties defined in table 1.1 are the same in all of the phases in equilibrium. For convenience we often use the component fugacities in place of the chemical potentials:

$$\ln f_{i,j} = \lambda_i, \quad i = 1, 2, ..., C, j = 1, 2, ..., F$$
(1.25a)

with λ_i used to denote the reduced equilibrium chemical potential.

$$P_j = P^{eq}, \quad j = 1, 2, ..., F$$
 (1.25b)

$$T_j = T^{eq}, \quad j = 1, 2, ..., F$$
 (1.25c)

The conventional phase equilibrium problem is isothermal flash, where we specify the temperature T^{eq} , pressure P^{eq} , and feed mole amounts z. Since we can solve an EoS at a specified temperature and pressure, as described in section 1.2, it is necessary that only the fugacity is equivalent in each phase at equilibrium.

One constraint on the isothermal flash problem is the extent of each of the phases is limited by the feed amount. This can be described by the material balance constraint

$$z_i - \sum_{j=1}^F n_{i,j} = 0, \quad i = 1, 2, ..., C$$
 (1.26)

How these equations are used to solve the phase equilibrium problem is the discussion of chapters 3 and 4. A brief summary of the current state of the art of the phase split and stability analysis will be given in this section.

One important problem associated with phase equilibrium problems is the trivial solution. The trivial solution is defined as two phases becoming identical in composition

and other properties

$$x_{i,j} = x_{i,l} \quad \forall i \tag{1.27}$$

Many of the methods used to solve phase equilibrium problems will fail if given a trivial solution. It occurs if poor initial estimates are used and is particularly problematic close to the critical point of a mixture. At a critical point the problem is degenerate, and two (or more) of the phases will have exactly the same composition. When close the critical point, in the critical region, great care must be taken to not remove a phase in error and high quality initial estimates are necessary.

It may also be noticed that the EoS used can be highly non-linear, and it may be possible for multiple equilibrium states, which satisfy equation 1.25a to exist. However only one of these equilibrium states will be completely stable. The only stable system is the one at the minimum energy. The energy used to describe a system at a given temperature and pressure is the Gibbs energy

$$G(\boldsymbol{n}, T, P) = \sum_{j=1}^{F} \sum_{i=1}^{C} n_{i,j} \mu_{i,j}$$
(1.28)

It is necessary that, given a stable phase distribution of F phases, G is at the local minimum in the Gibbs energy (i.e. the Hessian of equation 1.28 is positive definite). If the Gibbs energy of a phase is not at a local minimum then it is described as intrinsically unstable, and the current state will undergo spinodal decomposition (i.e. immediately split into another phase).

The Gibbs energy surface is generally not convex (when using an EoS to describe it). As such it is possible that a local minimum in the Gibbs energy can be identified which will correspond to a metastable state. The metastable region is of interest to some applications (e.g. hydrate formation). To define a phase as stable it is necessary to ensure that there is no possible mixture which can lead to a reduction in the Gibbs energy. One method to do so is to check the tangent plane distance function [9] at all possible trial phases:

$$tpd(\boldsymbol{w}) = \sum_{i=1}^{C} w_i (\ln \hat{f}_i(\boldsymbol{w}) - \ln \hat{f}_i(\boldsymbol{n}_j))$$
(1.29)

A necessary and sufficient condition for a given equilibrium mixture to be stable is for equation 1.29 to be non-negative at all possible trial compositions w. To check all possible trial compositions is prohibitively expensive for conventional calculations and as such the method of Michelsen [109] is often used.

Instead of the tangent plane distance function a modified tangent plane function is used:

$$tm(\mathbf{W}) = 1 + \sum_{i=1}^{C} W_i (\ln W_i + \ln \hat{\varphi}_i(\mathbf{W}) - \ln z_i - \ln \hat{\varphi}_I(\mathbf{z}) - 1)$$
(1.30)

where W_i are the mole numbers. It is possible to show that a minimum of equation 1.30 is also a minimum of equation 1.29 and that a negative value of tm will correspond to a negative tangent plane distance. It is therefore only necessary to find all of the minima of equation 1.30, if all are non-negative then the equilibrium mixture is stable. If any trial phase is found to be negative then a suitable initial estimate for a trial phase is immediately available as:

$$w_i = \frac{W_i}{\sum_{i=1}^C W_i} \quad \forall i$$

which, if introduced in an infinitesimal amount, will lead to a reduction in the Gibbs energy. Monitoring the Gibbs energy for a reduction at each iteration would then ensure that the trivial solution can be avoided. It is still necessary to select a suitably large number of initial estimates to not miss any minimum in the modified tangent plane function. The initial estimates used are tailored to each specific problem.

Once a suitable initial estimate of an incipient phase composition is found it is necessary to carry out a phase split calculation to find a local minimum in the Gibbs energy (to then be checked by stability analysis). One common approach is to use an ideal solution approximation. The fugacity coefficient is evaluated for each component in each phase from the selected EoS, then set as a constant while the equilibrium equation 1.25a is solved.

To solve the ideal solution problem for two phases the Rachford-Rice equations [147] are commonly used. For multiple phases it is often preferable to use a convex objective function which is at a minimum at the solution to the ideal solution problem. Such a function is described by [114]:

$$Q(\beta) = \sum_{j=1}^{F} \beta_j - \sum_{i=1}^{C} z_i \ln \hat{E}_i$$
 (1.31)

with

$$\hat{E}_i = \sum_{j=1}^F \frac{\beta_j}{\hat{\varphi}_{i,j}} \tag{1.32}$$

This function is convex with the variables of molar phase fractions β (when there are more components than phases). Newton's method with line search can be used to find the solution in a small number of iterations given any initial estimate.

Once the ideal solution problem is solved the fugacity coefficients can be updated and another iteration taken (successive substitution). This will be convergent in the vast majority of examples though divergent cases are possible [73]. Furthermore the rate of convergence can be intolerably slow for mixtures close to the critical point. As such second order methods are often desired. The conventional method to solve isothermal flash is given for two phases by Michelsen and Mollerup [117] and the for multiple phases by Michelsen [110]. Second order methods for multiphase flash will be described in more detail in chapter 4. In some cases the assumption that the temperature and pressure are known does not hold. This will be examined in chapters 3 and 4 with a detailed implementation for isenthalpic flash given in chapter 3.

1.4 Oil reservoir simulation

Transient simulations of oil reservoirs are carried out to predict future production from the reservoir, and in some cases to test ways of optimising the production. There are numerous ways to evaluate the performance of a reservoir with simulation gaining popularity as computers have become more powerful.

To carry out a reservoir simulation it is first necessary to define a physical model of the reservoir, based on the geology and geophysics of the rock formation. A mathematical description of the reservoir as a set of coupled time-dependent non-linear partial differential equations must then be developed. Third a numerical model incorporating the properties of the physical models and the mathematical model must be developed. The numerical model is then implemented in a computer and transient simulation carried out.

Once it is proven that a numerical reservoir simulator can accurately match historical data, it is then possible to make predictions for the behaviour of the reservoir in the future. Test cases can then be developed to plan optimal strategies for oil recovery.

Heavy oil reservoir simulation is an active area of research. It is often necessary to inject high temperature fluids into the reservoir to reduce the viscosity of the oil in place (e.g. using methods such as steam assisted gravity drainage, SAGD). As it is expensive to create and inject steam into an oil reservoir it is desired that, first the economics can be evaluated, and secondly that an optimal strategy can be developed (for example use of a solvent to enhance recover, e.g. solvent assisted SAGD).

The final aim of this thesis it is to develop an EoS based, thermal reservoir simulator. One important aspect of thermal reservoir simulation is the fluid description and the phase equilibrium calculations, where up to three hydrocarbon phases can co-exist (vapour, heavy liquid and light liquid) [92]. Furthermore the hydrocarbon solubility in the aqueous phase can increase at high temperatures (and pressures), as such it may be necessary to also accurately model the aqueous phase.

The simulator used is based on an existing Composition Simulator (COSI) which is a fully implicit isothermal simulator. A description of the existing simulator, and the features added to make it a thermal simulator are described in chapter 5. The simulator is also used for a brief comparison using some of the results from chapter 2. To test the multiphase flash methods presented in chapter 4 they will be applied to the reservoir simulator.

Chapter 2

Model Comparison for Phase Equilibrium in Heavy Oil/Steam/Solvent Related Systems

During reservoir simulation it is common to use an equation of state (EoS) to accurately model the fluid properties. One important property is which phases form and how the components split among the given phases (the phase equilibrium). In heavy oil recovery there is often a mixture of light and heavy hydrocarbons with water. It is common to use enhanced recovery techniques such as steam injection. It is therefore necessary to utilise an EoS which is accurate over a large temperature (and pressure) range.

For simple athermal, nearly symmetric mixtures it is often suitable to use pure component parameters with simple mixing and combining rules [88]. The cubic EoS is commonly employed for this purpose (equation 1.15). However if polar or associating components are present then it is necessary to use more complex models and mixing rules with binary interaction parameters. Even with binary parameters it is often difficult to capture the thermodynamic properties of mixtures exactly, and some derivative properties may show the wrong trends.

Instead a number of authors have used more complex and theoretically accurate models based on Wertheim's pertubation theory to accurately describe mixtures. The SAFT family of models [25, 26] was recently developed and there are numerous different implementations with a summary given by Kontogeorgis and Folas [88]. The association term from SAFT has been combined with the SRK EoS [175] to give the CPA EoS as described by Kontogeorgis et al. [91], in this work a simplified version is used [89].

This work aims to compare the cubic EoS's [135, 175], using one, two or three binary interaction parameters with more advanced EoS's. The models used with the cubic EoS's are: the van der Waals one fluid (vdW1f) mixing rules; the Huron-Vidal mixing rules [79]; the modified Huron-Vidal mixing rules MHV1 [113] and MHV2 [44]; HV, MHV1 and MHV2 use the NRTL activity coefficient model [156] or its variant NRTL_{HV} [79]. The cubics are compared with the advanced EoS's CPA [89, 91] and simplified PC-SAFT [67, 192]. A detailed description of each of the models used is given in section 2.1.

Though the use of temperature dependent binary interaction parameters can be justified theoretically [42] it can lead to problems outwith the temperature used for regression. There is often insufficient data to obtain reliable temperature dependent parameters over the range of temperature relevant to the thermal recovery of heavy oil (where temperature changes of >200K are possible). For these reasons, we have not introduced empirical temperature dependence into the binary interaction parameters in our comparison, though this option can be investigated in the future if further improvement is needed for specific systems.

There are a large number of articles, performing similar work (namely comparing EoS with the aim to demonstrate the capability of a new one, or highlight a deficiency of an existing one). All of the relevant articles cannot be given though some important and relevant works are highlighted. Boukouvalas et al. [16] gives a comparison of MHV2 with LCVM for asymmetric hydrocarbon pairs using UNIFAC, showing that MHV2 with UNIFAC is not well suited for this purpose. Knudsen et al. [86] compared the LCVM, WS and MHV2 EoS for binary and ternary mixtures of supercritical fluids, concluding that the MHV2 and LCVM models are the most promising. Orbey and Sandler [131] compared a number of models using UNIQUAQ model for asymmetric systems, and proposed a new model to overcome some of the drawbacks of the others. A number of group contribution models were compared by Ahlers et al. [4] who showed that a volume translated PR with a modified UNIFAC was best suited to the considered mixtures. Similarly the more modern models (PC-SAFT and CPA) have been compared numerous times. For example Voutsas et al. [193] compared the performance of CPA to PC-SAFT for a number of polar and associating mixtures. Yan et al. [199] compared SRK with HV with NRTL_{HV} to CPA for reservoir fluids with water, showing that both models were equally capable. Perez et al. [137] compared the cubic EoS to both PC-SAFT and SAFT VR-Mie with an interest for their application to carbon capture and storage modelling, concluding that the SAFT-VR Mie EoS is the most accurate for VLE and density data.

For heavy oil simulation it is necessary to determine if the simple cubic EoS's with the van der Waals mixing rules are sufficient, or if improved results are obtained using complex mixing rules or more advanced EoS's. To evaluate each model a number of binary test systems are investigated. In conventional compositional reservoir simulation the aqueous phase is modelled as a pure separate phase, however during the production of heavy oils it is possible to have mixtures where the composition of hydrocarbon components in the aqueous phase is non-negligible. Therefore the first system of interest for this work is mixtures of hydrocarbons with water.

Many oil reservoirs contain considerable amounts of carbon dioxide. Carbon dioxide is also a potential candidate for injection to enhance oil recovery (and is commonly used in this way). It is soluble in the liquid oleic phase. Injection can lead to near miscible fluids which are close to the critical conditions. Therefore its equilibrium in the reservoir is of interest and mixture of hydrocarbons with carbon dioxide are also investigated.

Finally new enhanced oil recovery techniques use a light hydrocarbon solvent such as ethane, propane or n-butane to further enhance recovery during steam injection. Such a solvent can lead to the production of two separate liquid hydrocarbon phases (i.e. one heavy hydrocarbon containing very long parafins and asphaltenes, and a separate lighter oleic phase containing smaller hydrocarbon components). Therefore we include a number of asymmetric hydrocarbons pairs in the model comparison. All of the experimental data used in this work is given in section 2.2.

The data collected for the model comparison is only the phase equilibrium data. The density of the mixtures and other mixture properties are not tested here. In practice, the Peneloux volume translation [134] is often employed to improve the density output from cubic EoS's. Either the absolute average relative deviation (AARD) or mean absolute deviation (MAD) is used depending upon the experimental data. This is described along with the regression method used in section 2.3.

The model comparison involves 17 models with 31 pure components, 45 binary pairs and over 6000 data points. Instead of presenting the overwhelming details for each system, we provide the tables with the optimal binary interaction parameters and corresponding deviations in appendix A. In section 2.4 a few representative systems are analysed and the conclusions based on all of the results are made. The parameters found are the optimum for the experimental data used however may not be suitable outwith the narrow range of the experimental conditions. This is particularly the case for the very flexible models using complex mixing rules with multiple binary parameters where the binary parameters should be used with care.

2.1 Models used

It is common to use the vdW1f mixing rules with a cubic EoS. The general cubic EoS (equation 1.15) was discussed in section 1.2, along with a brief mention of the vdW1f mixing rules. The vdW1f mixing rules give a quadratic composition dependency for both parameters:

$$a_{mix} = \sum_{i=1}^{C} x_i \sum_{j=1}^{C} x_j a_{ij}$$
(2.1a)

$$b_{mix} = \sum_{i=1}^{C} x_i \sum_{j=1}^{C} x_j b_{ij}$$
 (2.1b)

The vdW1f mixing rules are often combined with the classical combining rules, with the geometric mean rule for the cross-energy term and the arithmetic mean rule for the cross co-volume parameter:

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \tag{2.2a}$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \tag{2.2b}$$

where k_{ij} is the commonly used binary interaction parameter for the cross-energy binary pair and l_{ij} is the binary parameter for the cross co-volume. l_{ij} is not often used, but will be in this work.

For the PR and SRK EoS, the temperature dependence of equation 1.16 is defined as

$$a(T) = a_c (1 + \hat{m}(1 - \sqrt{T_r})^2)$$
(2.3)

based on the SRK EoS [175] where \hat{m} is found as

$$\hat{m}_{SRK} = 0.48 + 1.574\omega - 0.176\omega^2 \tag{2.4}$$

The PR78 EoS is based on the PR [135] but with a modified correlation for the temperature dependence as

if
$$\omega \le 0.491$$
, $\hat{m}_{PR} = 0.37464 + 1.54226\omega - 0.26992\omega^2$
if $\omega > 0.491$, $\hat{m}_{PR} = 0.379642 + 1.48503\omega - 1.64423\omega^2 + 0.016666\omega^3$
(2.5)

This correction is often necessary as the original formulation [135] is regressed to fit only the first 10 n-alkanes. Extrapolation outwith these components can lead to poor vapour pressure estimates [177]. This is not as necessary for SRK where the value of \hat{m} is

determined for the saturated vapour pressure at $T = 0.7T_c$ for acentric factors between 0 and 0.5 rather than fitting to experimental data and is better suited to extrapolation [117]. Improved correlations are available for both models (e.g. PRSV [177] for PR and the Mathias-Copeman temperature dependence [102] for SRK) however these are not used in this work.

Other mixing rules are possible and many have been attempted. A highly successful mixing rule is that given by Huron and Vidal [79]. The method uses the definition for the excess Gibbs energy from an EoS

$$g^{E}(T, P, \mathbf{z}) = \ln \hat{f}(T, P, \mathbf{z}) - \sum_{i=1}^{C} z_{i} \ln \hat{f}_{i}(T, P)$$
(2.6)

where for a cubic EoS, as given in equation 1.15, the mixture fugacity is defined by

$$\ln\left(\frac{\hat{f}b}{RT}\right) = \frac{PV}{RT} - 1 - \ln\left(\frac{V-b}{b}\right) - \frac{a}{RTb\left(\delta_2 - \delta_1\right)}\ln\left(\frac{V+\delta_2b}{V+\delta_1b}\right)$$
(2.7)

and similarly each of the pure component fugacities are:

$$\ln\left(\frac{\hat{f}_i b_i}{RT}\right) = \frac{PV_i}{RT} - 1 - \ln\left(\frac{V_i - b_i}{b_i}\right) - \frac{a_i}{RTb_i\left(\delta_2 - \delta_1\right)}\ln\left(\frac{V_i + \delta_2 b_i}{V_i + \delta_1 b_i}\right)$$
(2.8)

Using the excess Gibbs energy, Huron and Vidal [79] used the limit of infinite pressure to arrive at their new mixing rule (assuming a linear mixing rule on the cross co-volume parameter):

$$\lim_{P \to \infty} V = b, \quad V_i = b_i$$

$$\frac{a}{bRT} = \sum_{i=1}^C z_i \frac{a_i}{b_i RT} - \frac{\delta_2 - \delta_1}{\ln \frac{1 + \delta_2}{1 + \delta_1}} g_{\infty}^E$$
(2.9)

This allowed for any suitable model for the excess Gibbs energy at infinite pressure to be combined with a cubic EoS. One choice is the NRTL equation [156]:

$$g^{E} = \sum_{i=1}^{C} z_{i} \frac{\sum_{k=1}^{C} z_{j} \exp\left(-\widetilde{\alpha}_{ji} \frac{C_{ji}}{RT}\right) \frac{C_{ji}}{RT}}{\sum_{j=1}^{C} z_{j} \exp\left(-\widetilde{\alpha}_{ji} \frac{C_{ji}}{RT}\right)}$$
(2.10)

Or a modification thereof given by Huron and Vidal [79].

$$g^{E} = \sum_{i=1}^{C} z_{i} \frac{\sum_{j=1}^{C} z_{j} b_{j} \exp\left(-\widetilde{\alpha}_{ji} \frac{C_{ji}}{RT}\right) \frac{C_{ji}}{RT}}{\sum_{j=1}^{C} z_{j} b_{j} \exp\left(-\widetilde{\alpha}_{ji} \frac{C_{ji}}{RT}\right)}$$
(2.11)

Equation 2.11 is particularly useful as it can be reduced to the vdW1f mixing rules and the classical combining rules for the cross energy term by setting

$$\widetilde{\alpha}_{ij} = 0, \quad C_{ji} = \hat{g}_{ji} - \hat{g}_{ii}, \quad \hat{g}_{ii} = -\frac{a}{b} \frac{\delta_2 - \delta_1}{\ln \frac{1 + \delta_2}{1 + \delta_1}}$$

$$\hat{g}_{ji} = -2\sqrt{\frac{b_i b_j}{b_i + b_j}} \sqrt{\hat{g}_{ii} \hat{g}_{jj}} (1 - k_{ij})$$
(2.12)

This allows for the well known binary parameters for hydrocarbon pairs to be combined with mixtures containing highly non-ideal fluids. Note that this is equivalent to using binary interaction parameters with a temperature dependence described as

$$\frac{C_{j,i}}{RT} = C_{j,i}^1 + C_{j,i}^2 \sqrt{T} + C_{j,i}^3 T$$
(2.13)

This is the temperature dependence obtained from the $\sqrt{a_{ii}a_{jj}}$ term. Of course if the temperature dependence described in equation 2.13 is used then the HV NRTL_{HV} mixing rules can exactly replicate the vdW1f mixing rules for the *a* term.

An alternative formulation can be developed by using the limit of zero pressure. From this we find an excess Gibbs energy of

$$g_0^E + \sum_{i=1}^C z_i \ln \frac{b}{b_i} = \hat{Q} - \sum_{i=1}^C z_i \hat{Q}$$
(2.14)

where \hat{Q} is a function of $\hat{Q}(a/(bRT))$ only. \hat{Q} is only defined in the region where the cubic EoS has a liquid like root at zero pressure and as such it is common to approximate the value of the \hat{Q} -function with a straight line [113]:

$$\frac{a}{bRT} = \frac{1}{q_1} \left(g_0^E + \sum_{i=1}^C z_i \ln\left(\frac{b}{b_i}\right) \right) + \sum_{i=1}^C z_i \frac{a_i}{b_i RT}$$
(2.15)

which due to its similarities is referred to as the modified Huron Vidal mixing rule 1 (MHV1). A quadratic approximation is also possible [44] (MHV2):

$$q_1\left(\frac{a}{bRT} - \sum_{i=1}^C z_i \frac{a_i}{b_i RT}\right) + q_2\left(\left(\frac{a}{bRT}\right)^2 - \sum_{i=1}^C z_i \left(\frac{a_i}{b_i RT}\right)^2\right) = g_0^E + \sum_{i=1}^C z_i \ln\left(\frac{b}{b_i}\right)$$
(2.16)

The zero pressure limit does not put a restriction on the mixing rule used for the cross co-volume term, though for this work it is assumed to be linear.

For this study we use the classical combining rules with the vdW1f mixing rules, the NRTL equation with HV, MHV1 and MHV2, and the modified NRTL_{HV} with HV. All of these models used the pure component critical point and acentric factor to determine the pure component parameters for the EoS. The critical properties and acentric factor are reported in table 2.1.

Component name	Component ID	T_{c} (K)	P_c (bar)	$\mid \omega$	
Ethane	C ₂	305.32	48.72	0.0995	
Propane	C ₃	369.83	42.48	0.1523	
Butane	C ₄	425.1	37.96	0.2002	
Pentane	C ₅	369.83	33.7	0.2515	
Hexane	C ₆	507.6	30.25	0.3013	
Octane ^{<i>a</i>}	C ₈	568.7	24.9	0.3996	
Nonane	C ₉	594.6	22.9	0.4435	
Decane	C ₁₀	617.7	21.1	0.4923	
Undecane	C ₁₁	639	19.5	0.5303	
Dodecane	C ₁₂	658	18.2	0.5764	
Tetradecane	C ₁₄	693	15.7	0.643	
Pentadecane	C ₁₅	708	14.8	0.6863	
Hexadecane	C ₁₆	723	14	0.7174	
Eicosane	C ₂₀	768	11.6	0.9069	
Docosane	C ₂₂	787	10.6	0.973	
Tetracosane	C ₂₄	804	9.8	1.071	
Octacosane	C ₂₈	832	8.44	1.2375	
Dotriacontane	C ₃₂	855	7.5	1.377	
Continued on next page					

Table 2.1 Pure component critical parameters

Component name	Component ID	$T_{c}\left(\mathbf{K}\right)$	P_c (bar)	ω
Hexatriacontane	C ₃₆	874	6.8	1.526
Octatriacontane	C ₃₈	882	6.42	1.571
Tetracontane	C ₄₀	889.6	6.12	1.64
Tetratetracontane	C ₄₄	903.1	5.59	1.78
Hexatetracontane	C ₄₆	909.2	5.36	1.849
Tetrapentacontane	C ₅₄	929.5	4.6	2.128
Hexacontane	C ₆₀	941.8	4.16	2.337
Water	H ₂ O	647.13	220.55	0.3449
Carbon dioxide	CO_2	304.21	73.83	0.2236
Hydrogen sulphide	H_2S	373.53	89.629	0.0942
Benzene	Bz	562.16	48.98	0.21
Toluene	Tol	591.8	41.06	0.2621
Ethylbenzene	C_2Bz	617.2	36.06	0.3026

Table 2.1 – continued from previous page

The pure component data described in table 2.1 is taken from DIPPR for all components except hydrocarbons above C_{36} . For the components larger than C_{36} it was necessary to use a correlation to obtain the properties, the methodology described by Duarte et al. [51] was used in this work.

The classical combining rules and the excess Gibbs energy type mixing rules are compared with some more modern models. The first of these is simplified PC-SAFT [192], referred to herein as PC-SAFT. This model splits the contributions to the Helmholtz energy into contributions from the ideal gas, the hard sphere chain reference system, the dispersion, and the association

$$A = A^{IG} + A^{HC} + A^{Disp} + A^{Assoc}$$

$$(2.17)$$

The full details of the PC-SAFT EoS and its simplified variant are explained in the work of Gross and Sadowski [67] and von Solms et al. [192]. For this work we need to know the 3 pure component parameters for non-associating fluids: the chain length \tilde{m} ; the segment diameter σ ; and the segment energy $\tilde{\epsilon}$. The pure component parameters are reported in table 2.2.

Component ID	$\mid \widetilde{m}$	σ (Å)	$\widetilde{\epsilon}/R$ (K)		
C ₂	1.607	3.521	191.4		
C ₃	2.002	3.618	208.1		
C_4	2.332	3.709	222.9		
C ₅	2.690	3.773	231.2		
C_6	3.058	3.798	236.8		
C_8	3.818	3.837	242.8		
C ₉	4.208	3.845	244.5		
C_{10}	4.663	3.838	243.9		
C ₁₁	4.908	3.889	248.8		
C ₁₂	5.306	3.896	249.2		
C ₁₄	5.900	3.940	254.2		
C ₁₅	6.286	3.953	254.1		
C ₁₆	6.649	3.955	254.7		
C ₂₀	7.985	3.987	257.8		
C ₂₂	8.690	3.982	253.9		
C ₂₄	9.387	3.990	254.6		
C_{28}	10.782	4.002	255.7		
C ₃₂	12.176	4.011	256.5		
C ₃₆	13.571	4.019	257.1		
C ₃₈	14.268	4.022	257.4		
C ₄₀	14.965	4.025	257.7		
C ₄₄	16.359	4.030	258.1		
C ₄₆	17.057	4.032	258.3		
C ₅₄	19.845	4.039	258.9		
C ₆₀	21.937	4.043	259.3		
H ₂ O	2.0	2.345	171.7		
CO_2	2.073	2.785	169.2		
H_2S	1.684	3.027	227.7		
Bz	2.465	3.648	287.4		
Tol	2.815	3.717	285.7		
Continued on next page					

Table 2.2 PC-SAFT pure component parameters

Component ID	\widetilde{m}	σ (Å)	$\widetilde{\epsilon}/R$ (K)
C_2Bz	3.080	3.797	287.4

Table 2.2 PC-SAFT pure component parameters

The pure component properties for PC-SAFT were obtained from [181], including the correlation for the properties of components larger than C_{20} :

$$m = 0.0249MM + 0.9711 \tag{2.18a}$$

$$m\tilde{\epsilon} = 6.5446MM + 177.92$$
 (2.18b)

$$m\sigma^3 = 1.6947MM + 23.27 \tag{2.18c}$$

where MM is the molecular weight of the alkane component. For associating components two additional pure component parameters are necessary, the volume of association $\tilde{\beta}^{\tilde{A}_i\tilde{B}_i}$ and the energy of association $\hat{\epsilon}^{\tilde{A}_i\tilde{B}_i}$. Only water was considered as associating for PC-SAFT in this work. For the water component there are a large number of possible parameters sets when using PC-SAFT. A number of these are compared by Liang [99], the parameter set used here is from that work using the 4C scheme with a association energy of $\hat{\epsilon}/R = 1704.06K$ and a association volume of $\tilde{\beta} = 0.3048$.

For the regression it is necessary that there is a binary interaction parameter. For the PC-SAFT EoS the Lorentz-Bertholet combining rules are used with a single binary parameter on the segment energy:

$$\widetilde{\epsilon}_{ik} = \sqrt{\widetilde{\epsilon}_i \widetilde{\epsilon}_k} (1 - k_{ik}) \tag{2.19}$$

The combining rules for the other terms do not have an interaction parameter.

The association term used for the SAFT EoS can also be applied to the cubic EoS's. This was presented by Kontogeorgis et al. [91] as a cubic plus association (CPA) EoS and its simplified variant [89] is used here (referred to as only CPA in this work). One difference between CPA and SRK is that instead of determining the a_c and b_c from the critical point, and \hat{m} from the acentric factor, these terms are regressed to fit the saturated liquid density and vapour pressure. The pure component parameters are reported in table 2.3.

For CPA with H_2S two implementations are given (a and b). Scheme a has the hydrogen sulphide component defined with a 3B association scheme while scheme b has the hydrogen

Component ID	$a/(bR)(\mathbf{K})$	b(L/mol)	\hat{m}	$\widetilde{\epsilon}/R(\mathbf{K})$	$\widetilde{\beta}$
C ₁	959.028	0.0291	0.44718	N/A	N/A
C_2	1544.548	0.0429	0.58473	N/A	N/A
C_3	1896.453	0.057834	0.6307	N/A	N/A
C_4	2193.083	0.072081	0.70771	N/A	N/A
C_5	2405.105	0.091008	0.79858	N/A	N/A
C_6	2640.03	0.10789	0.8313	N/A	N/A
C_7	2799.762	0.12535	0.9137	N/A	N/A
C_8	2944.911	0.14244	0.99415	N/A	N/A
C_{10}	3190.542	0.17865	1.13243	N/A	N/A
C ₁₂	3471.038	0.21624	1.19531	N/A	N/A
Bz	2867.193	0.07499	0.7576	N/A	N/A
Tol	3051.36	0.09214	0.8037	N/A	N/A
C2Bz	3192.838	0.10872	0.8539	N/A	N/A
H_2O	1017.34	0.0145	0.6736	2003.25	0.0692
H_2S^a	1590.10	0.0292	0.5022	654.27	0.0583
H_2S^b	1878.15	0.0285	0.6027	N/A	N/A
CO_2	1551.22	0.0272	0.7602	N/A	N/A

Table 2.3 CPA pure component parameters from [188]

sulphide described as non-associating, though it is solvating into the water. A number of other components are described as solvating into water and the cross association volume of association is a given binary parameter (not regressed) from [188]. The values are reported in table A.4.

For CPA the vdW1f mixing rules are used with the classical combining rules with a single k_{ij} as in equation 2.2a. This is the only binary parameter used for the CPA EoS.

2.2 Experimental data

To compare the models it is first necessary to regress optimum binary interaction parameters. For models using NRTL three binary parameters are found for each pair ($\tilde{\alpha}_{ij}$, C_{ji} , and C_{ij}). For the cubic EoS the vdW1f mixing and classical combining rules both the l_{ij} and k_{ij} are fitted. For CPA and PC-SAFT only a single $k_{i,j}$ is fitted. To fit these binary parameters it is first necessary to select relevant binary pairs. Since this work is focused on the simulation of heavy oil recovery using steam and solvent it is desired to have asymmetric hydrocarbon pairs (similar to heavy oil and solvent) and pairs involving carbon dioxide with heavy hydrocarbons. Since steam is used binary data for water hydrocarbon pairs are also necessary. Many simulators do not include hydrocarbon solubility in the aqueous phase, however it may happen in relevant quantities at the conditions encountered in heavy oil recovery.

We focused only on the phase envelope calculations in this work (not density or derivative properties) and as such only saturation point data is used. The experiments to generate saturation point data are often carried out at the bubble point, in some cases the incipient vapour phase composition is also recorded. For water-hydrocarbon pairs it is more common to just measure the solubility of water in the hydrocarbon or the solubility of the hydrocarbon in the aqueous phase. Both of these are saturation point type data, though the type of objective function used can differ.

In table 2.4 the temperature and pressure range, and number of data points (both saturation and with incipient phase composition given), are given for binary pairs of ethane with a heavy hydrocarbon. Similar tables are given for pairs of propane with a heavy hydrocarbon (table 2.5) and carbon dioxide with a heavy hydrocarbon (table 2.6). The binary pairs including water (table 2.7) are split into two rows showing data where the composition of the aqueous phase is known, or the hydrocarbon phase is known (either liquid or vapour). Some of the experimental data is measured at conditions where neither phase is close to pure, these data points are described as bubble points and are given in brackets (with the number of points with the incipient phase reported given in brackets in the aqueous phase column).

For clarification the data is split into two types. Experimental data referred to as saturation point or bubble point (with incipient phase composition) is matched by setting the temperature and feed phase composition to a constant value and varying the pressure, while data referred to as compositional is matched by carrying out a flash calculation. Only binary pairs with water are occasionally treated as compositional all other pairs are treated as saturation point type.

Often data smoothing is used on experimental data to make the fitting of models simpler. However this is not done in this work. This meant that there is a significant error range in the experimental data used with different authors often showing very different results at the same conditions. This can lead to a more complex regression process as the data is not smooth and the derivative properties of the data are not smooth. Furthermore a lot of the experimental data used for some binary pairs is in the close to critical region or where the change in pressure with composition (P-xy line) is almost vertical. It was therefore necessary to use a robust regression method.

ID	T range (K)	P range (bar)	Sat data	& comp	references
C_{10}	277.6-510.9	3.4-117.2	249	125	20, 59, 151, 167, 202
C_{12}	273.2-373.15	3.6-62.8	145	0	96, 97, 105
C_{16}	262.3-453.15	5.4-163.2	233	0	46, 148, 167
C_{20}	264-450.7	5.05-168.5	305	0	60, 141, 167
C_{22}	294.95-367.9	1.7-99.1	119	0	142
C_{24}	300.8-368.7	8.4-144	134	0	140, 148
C_{28}	330-423.2	5.9-164.8	64	4	60, 76, 148, 167
C_{36}	350-573.3	3.68-224.3	79	0	60, 167, 184
C_{44}	373.2-423.2	3.9-29.8	15	0	60

Table 2.4 Experimental data for binary pairs with ethane

Table 2.5 Experimental data for binary pairs with propane

ID	T range (K)	P range (bar)	Sat data	& comp	references
C_{10}	277.6 - 510.9	1.7 - 68.9	103	51	80, 153
C_{12}	419.2 - 457.7	4.5 - 76.8	25	25	59
C_{14}	378 - 408	29.7 - 63.7	36	0	165
C_{20}	279.29 - 358.1	4.03 - 32.5	210	0	64
C_{32}	378.2 - 408.2	46 - 93.3	48	0	166
C_{36}	353.1 - 408.2	31.6 - 99.3	44	0	1, 164
C_{38}	378.2 - 408.2	46.2 - 100.8	45	0	164
C_{40}	322.8 - 434.7	20.7 - 133.1	122	0	1, 101, 164
C_{44}	378.2 - 408.2	52.7 - 114.9	48	0	164
C_{46}	378.2 - 408.2	40.3 - 116.3	57	0	164
C_{54}	378.2 - 408.2	74.6 - 136.7	33	0	164
C_{60}	351.7 - 431.3	13.4 - 142.6	114	0	139, 164

ID	T range (K)	P range (bar)	Sat data	& comp	references
C ₈	322.4 - 372.5	15.0 - 137.7	48	48	146, 196
C_9	315.1 - 418.8	20.3 - 167.7	44	44	22, 80
C_{10}	277.6 - 510.9	3.4 - 188.4	170	170	33, 123, 146, 152
C ₁₁	315 - 418.3	23.7 - 200.5	42	42	22
C_{12}	313.2 - 343.2	9.5 - 143	36	10	59, 126
C_{15}	293.2 - 353.2	5.1 - 105.3	85	77	168, 169, 179
C_{16}	297 - 323.2	4.3 - 168.4	32	0	126, 179
C_{20}	310.2 - 473.2	4.6 - 303.5	170	0	54, 61, 78, 126, 159, 162
C_{24}	329.7 - 573.2	9.4 - 301.6	63	10	126, 162, 185
C_{28}	338.5 - 573.5	8.07 - 289.5	80	5	61, 76, 126, 162
C ₃₆	344 - 573.3	5.2 - 289.8	65	0	61, 126, 184

Table 2.6 Experimental data for binary pairs with CO₂

Table 2.7 Experimental data for binary pairs with water

ID	T range (K)	P range (bar)	HC phase	aq phase	references
C_1	274.3 - 510.9	0.6 - 1000	179	54	28, 29, 43, 82, 128
					48, 98, 118, 158, 201
C_2	278.1 - 510.9	3.2 - 682	129	35	6, 27, 43, 84, 118, 150
C ₃	274.2 - 663.2	1.0 - 1872	53	464	7, 31, 36, 47, 87, 93
C_4	278.2 - 707	1.0 - 3101	120	233	12, 23, 154, 180, 200
					11, 36, 45, 95, 157, 195
C_5	273.2 - 625.2	1 - 678.9	4	55	63 [*] 12, 40
C_6	273.2 - 699	1 - 2270	103	18	63 [*] 129, 200
C ₁₀	293.2 - 613	0.1 - 251	45 (22)	17 (22)	56, 70, 163, 182, 194
C ₁₂	298.2 - 633	1 - 249.2	15 (23)	15 (23)	56, 163, 176, 182
Bz	273.2 - 573.2	0.04 - 810	100	155	63 [*] 8, 40, 125
Tol	273.2 - 583.2	0.015 - 461	72	113	63 [*] 40, 83, 125
C_2Bz	273.2 - 568.1	1.0 - 107	39	66	63 [*] 32, 132
CO_2	273.2 - 573.2	4.7 - 1200	243	342	19, 68, 85, 189
					10, 49, 50, 74, 160
					84, 106, 127, 161, 183
H_2S	273.2 - 444.3	0.3 - 344	153	188	21, 30, 35, 170, 198

* Reference to list of other references (with compiled data).

Numbers in brackets indicate the number of experimental data points treated as saturation points rather than compositional points.

2.3 Regression method

To evaluate which model is best suited, the experimental data is compared to the correlation from the model. To do this it is necessary to first fit the binary parameters. Some of the experimental data was difficult to reproduce for some of the models, or was in difficult to calculate areas such as the critical region. In some cases it was not possible for a data point to be reproduced with a model (i.e. experimental two phase data is in a region where the model predicts only a single phase). These issues lead to a complex objective function, where the derivative properties are often discontinuous. Since no initial estimates are used for the model binary parameters it is necessary to have a very robust regression method.

To regress the parameters, each data point is assigned to a deviation function. A data point is considered once for a saturation pressure, once for an incipient phase composition, and once for the composition of one phase at a given temperature and pressure. Therefore if the experimental data reported both the saturation point pressure and incipient phase composition, then two deviation functions are used. The objective function to minimise is taken as the l_2 norm of the system of equations defining the deviations:

$$\Theta = \sqrt{\sum_{k=1}^{NDat} \theta_k^2}$$
(2.20)

where if the experimental data point is treated as a saturation point then the pressure deviation is defined as a relative deviation:

$$\theta_k = \frac{P_{exp,i} - P_{calc,i}}{P_{exp,i}} \tag{2.21}$$

The pressure is calculated using a given thermodynamic model at a given temperature and bulk phase composition. If the incipient phase composition is also reported then an absolute deviation is used:

$$\theta_k = y_{exp,i} - y_{calc,i} \tag{2.22}$$

For data that is treated as compositional (both VLE and LLE), a relative error is used, ensuring the component present in a smaller amount is used on the denominator:

$$\theta_k = \frac{y_{exp,i} - y_{calc,i}}{\max(y_{exp,i}, 1 - y_{exp,i})}$$
(2.23)

The experimental composition is found by carrying out a flash calculation at a given temperature and pressure. As well as the objective function, the absolute average deviations

are evaluated based on the summations of the absolute of the deviations defined in equations 2.21, 2.22, and 2.23.

For some of the binary pairs much of the experimental data is located close to a critical point. This means that calculating the saturation point corresponding to this data is not simple. The approach given by Michelsen and Mollerup [117] to find a saturation point is used in this work as a first attempt. If the composition of the incipient phase is specified in the reference used then it is used as an initial estimate at the experimental pressure. Otherwise an initial estimate is generated from the Wilson K-factor approximation

$$\ln K_i = \ln \left(\frac{P_{c,i}}{P}\right) + 5.373 \left(1 + \omega_i\right) \left(1 - \frac{T_{c,i}}{T}\right)$$
(2.24)

where, at a bubble point, the initial incipient phase composition could be estimated from $y_i = K_i z_i$ for each component.

Following initialisation 10 steps are taken using an ideal solution approximation. As described in section 1.3, the ideal solution approximation assumes that the composition derivative of the fugacity coefficient is zero. At a bubble point Newton's method is used on:

$$f = \sum_{i=1}^{C} z_i K_i - 1 = 0$$
(2.25)

to find the saturation point based on the thermodynamic model used. One iteration of the method proceeds as

1. Evaluate the K-factors at the current pressure and composition

$$\ln K_i = \ln \hat{\varphi}_{i,l}(\boldsymbol{z}, P) - \ln \hat{\varphi}_{i,v}(\boldsymbol{y}, P)$$

2. Evaluate the equation 2.25.

$$f = \sum_{i=1}^{C} z_i K_i - 1 = 0$$

If suitably close to zero then output result.

3. Evaluate the pressure derivative of equation 2.25

$$\frac{\mathrm{d}f}{\mathrm{d}P} = \sum_{i=1}^{C} z_i K_i \left(\frac{\partial \ln \hat{\varphi}_{i,l}}{\partial P} - \frac{\partial \ln \hat{\varphi}_{i,v}}{\partial P} \right)$$

4. Take the Newton step

$$P^{n+1} = P^n - f / \frac{\mathrm{d}f}{\mathrm{d}P}$$

5. Update the incipient phase composition

$$y_i^{n+1} = z_i K_i P^{n+1}$$

6. Check if the result is trivial. If not trivial then another iteration can be taken.

Often for nearly ideal mixtures, or if the thermodynamic model is extremely close to the experimental data, then the result would be found without significant problems. However in many cases it is necessary to switch to a second order method to find the saturation point. The system of equations used is:

$$f_i = \ln K_i + \ln \hat{\varphi}_i(T, P, \boldsymbol{y}) - \ln \hat{\varphi}_i(T, P, \boldsymbol{z}) = 0, \quad \forall i$$
(2.26a)

$$f_{C+1} = \sum_{i=1}^{C} (y_i - x_i) = 0$$
(2.26b)

with $K_i = \ln(y_i/x_i)$. The full Jacobian is found based on this system of equations. Generally the solution is found within 5 second order iterations. After 10 second order iterations, or if the trivial solution is found then the method is abandoned. This was found to be common close to the critical region. As such a backup method was implemented.

Two further methods were attempted to find the the model saturation point at the same temperature as found experimentally. The first is to construct the whole phase envelope and interpolate to the experimental temperature. This starts from an easy initial point then generates extremely accurate initial estimates for other points on the phase envelope using a cubic polynomial extrapolation as described by Michelsen [108]. With the phase envelope constructed it is simple to interpolate and find the exact temperature and composition corresponding to any pressure. Unfortunately a number of issues with numerical precision were encountered when finding the vapour phase of mixtures containing a light hydrocarbon with a heavy hydrocarbon, as such this method was abandoned in favour of a more laborious search using stability analysis.

Stability analysis as described in equation 1.29 is carried out with a number of initial estimates. The method described by Michelsen [109] is used with the modified tangent plane function. As initial estimates for stability analysis, the pure component compositions are used along with an ideal gas based on the feed phase, and a liquid based on the Wilson

K-factors. If the incipient phase composition is specified with the experimental data then it is also used as an initial estimate. The objective function to minimise is the modified tangent plane

$$tm(\boldsymbol{W}) = 1 + \sum_{i=1}^{C} W_i \left(\ln W_i + \ln \hat{\varphi}(T, P, \boldsymbol{W}) - \ln z_i - \ln \hat{\varphi}_i(T, P, \boldsymbol{z}) \right)$$
(2.27)

the successive substitution method is used to obtain initial estimates

$$\ln W_i^{(k+1)} = \ln z_i + \ln \hat{\varphi}_i(T, P, \boldsymbol{z}) - \ln \hat{\varphi}_i\left(\boldsymbol{W}^{(k)}\right)$$
(2.28)

The successive substitution methods is used with two steps of acceleration using the dominant eigenvalue method [130]. A switch is then made to a second order minimiser. Newton's method is used with the ideally scaled Hessian and gradient described by Michelsen and Mollerup [117]. The restricted step method is used to ensure convergence to a minimum.

At the saturation point the minimum in the modified tangent plane distance is zero. As such if any of the trial phases found a negative tangent plane distance at one pressure and no negative solution is found at a different pressure, then bounds could be set on the problem and a method to guarantee convergence to the saturation point used (e.g. bisection), with the pressure the only variable. This is used until the solution is found to a suitable tolerance. Initial bounds are also set on the pressure defined as $P_{max} = 2 \times P_{exp}$ and $P_{min} = 0.5 \times P_{exp}$. If there is no phase transition within this range then the data point is described as a failed data point.

If instead of a saturation point, the experimental data is treated as a compositional point, then a flash is carried out at the specified temperature and pressure. Stability analysis is used to generate a trial phase and the Rachford-Rice equations solved for the phase fraction (and initial composition). The conventional second order two-phase flash method is then used [117]. Stability analysis is then tested again, if the two-phase mixture is found to be unstable then the multiphase Rachford-Rice equations are solved for the three phases (returning the solution to two-phase) and the conventional restricted step method is used for final two-phase convergence. If no trial phase could be identified then the input composition is changed. The trial for the input composition are first based on the composition data (i.e. at the halfway point between the two reported phases). Subsequent trials are then moved from an initial estimate of $z_1 = 0.5$ up and down by 0.1 at a time. Giving up to 12 initial estimates (including pure component and the first based on the

experimental data). If no two-phase solution is found then the point is considered to have failed.

To incorporate the failed data points into the objective function it is necessary to give them a set value. This is set at $\theta_k = 1.1$, to ensure that this is not better any of the successful data points where a maximum successful deviation of $\theta_k = 1$ is set.

2.4 **Results and Discussion**

Due to the large number of results it is not possible to present all of them. Instead the different systems will be viewed individually with the ethane and propane with large hydrocarbons in section 2.4.1. Binary pairs including carbon dioxide will be presented in section 2.4.2 and finally binary pairs involving water will be presented in section 2.4.3. For each system a few select examples will be used to demonstrate the results. The full tabulated binary parameters and deviations are given in appendix A

2.4.1 Asymmetric Hydrocarbons

The first set of systems investigated are mixtures of alkanes with ethane. The experimental data ranges and binary pairs investigated are presented in table 2.4. The optimum interaction parameters are presented in appendix A in table A.1.

The lightest pair considered is n-decane with ethane. Figure 2.1 presents the P-x envelope for this binary pair (along with experimental data) at 277.6K and 510.9K. At the lower temperature all of the models are reasonably accurate, though problems are immediately evident when using the zero pressure mixing rules (MHV1). At low temperatures there is no obvious difference between SRK and PR, however as the temperature is increased a small deviation at high pressures is noticeable. Temperature independent binary parameters do not allow for the high temperature bubble point curve to be matched accurately, except when using the PC-SAFT EoS.

The difficulty with the zero pressure limit models (MHV1 and MHV2), when combined with the NRTL gamma model, is further displayed in figure 2.2 between the binary of ethane with n-octacosane. For such a pair the zero pressure mixing rules are completely unsuitable at high ethane mole fractions, where a liquid liquid split is predicted at high temperatures. The results for MHV2 are similar to (and often worse than) MHV1. Similar problems are evident when the zero pressure mixing rules are combined with UNIFAC, with a number of models being developed in an attempt to overcome these issues (e.g.



Fig. 2.1 Plot showing the P-x projection of ethane with n-decane at 277.6K (solid lines, circles) and 510.9K (dashed lines, crosses). The models used are PR with k_{ij} (black), PR with MHV1 (red), PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Reamer and Sage [151]. The parameters used are given in table A.1.

LCVM [16] GCVM [39] or CHV [131] a more comprehensive list is given by Kontogeorgis and Folas [88]). It has been suggested that the poor results from the zero pressure models are due to the two combinatorial contributions (one from the cubic EoS and one from the activity coefficient model) being dissimilar in size [90]. NRTL has no combinatorial contribution and, even when using fitted parameters, it can be concluded that NRTL is not suitable for combination with MHV1 or MHV2 for representing asymmetric hydrocarbon pairs.

In figure 2.2 there are larger deviations between the models. Much of the experimental data is in the region very close to pure ethane (not that presented in the figure). The resulting phase envelope is therefore distorted as the models attempt to match the near critical data, often causing them to miss the data far from the critical point. The only model which matches the bubble point data accurately is PC-SAFT in the presented figure, the vdW1f mixing rules with an l_{ij} also match the bubble point data, though at the cost of accuracy in the near pure ethane region. PR and SRK with the vdW1f mixing and combining rules with two binary parameters are excellent for modelling these mixtures. The infinite pressure g^E mixing rules are acceptable though not excellent for this pair.



Fig. 2.2 Plot showing the P-x projection of ethane with nC_{28} at 473.3K (solid lines, circles) and 573.15K (dashed lines, crosses). The models used are PR with k_{ij} (black), PR with MHV1 (red), PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Huang et al. [76]. The parameters used are given in table A.1.

The average results for all of the pairs are reported in table 2.8. This table shows: the total number of failed data-points, the AARD in pressure over all of the experimental data points (from equation 2.21); the MAD over all data points (from equation 2.22); and the objective function for all data-points (from equation 2.20). Though the objective function has no real significance, it is useful to present which model is best suited to these binary pairs. This shows that the worst performing models on average, are the zero pressure type mixing rules. The vdW1f mixing rules are very accurate, particularly with an l_{ij} or two binary parameters. The three best models are vdW1f with 2 BIPs, HV with NRTL_{HV} and PC-SAFT.

Similar to ethane and n-decane the propane and n-decane binary pair can be modelled effectively by each of the models, as demonstrated on figure 2.3. In this figure we include PR with HV and NRTL, it is clear for this simple pair that this model is as good as the others. PC-SAFT is the best for modelling both the low temperature and high temperature data. The other models struggle without a temperature dependent binary interaction parameter. However PC-SAFT does slightly miss the critical region predicted by the other models.

A P-T projection is given in figure 2.4 instead of a P-x plot (this is because much of the experimental data is gathered at a constant composition rather than constant temperature).

Table 2.8 Result summary for binary pairs of ethane with a large n-alkane. Results for SRK not included in summary. Asterisk is used to highlight the recommended models.

Model	Failures	P deviation (%)	y deviation (×10 ²)	Objective function
$PR(k_{ij})$	5	8.38	0.88	5.65
$PR(l_{ij})$	4	5.85	0.87	3.79
PR 2 BIP*	2	3.66	0.88	2.69
PR MHV1	1	11.42	0.75	6.08
PR MHV2	2	31.96	0.79	15.14
PR HV	1	6.61	0.90	4.02
PR HV NRTL _{HV} *	1	5.00	0.85	2.87
PC-SAFT*	1	4.79	0.62	3.03



Fig. 2.3 Plot showing the P-x projection of propane with n-decane at 277.59K (solid lines, circles) and 510.93K (dashed lines, crosses). The models used are PR with k_{ij} (black), PR with HV using NRTL (red), PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Reamer and Sage [153]. The parameters used are given in table A.2.
It is noticeable that each of the models predicts significantly different high pressure, high temperature regions of the phase envelope. Though the experimental temperature is over a reasonably large range as described in table 2.5 (between 279.29K and 358.1K), it does not describe the high pressure and high temperature regions. In this instance the red line indicates the vdW1f mixing rules with only an l_{ij} . It is clear that it is as capable as the other models for this binary pair. PC-SAFT predicts a higher cricondenbar and cricondentherm than the other models at 25.4% propane, though without experimental data it is not clear if this is accurate or not. There is very little difference between SRK and PR.



Fig. 2.4 Plot showing the T-P projection of propane with nC_{20} at 94.97% propane (solid lines, circles) and 25.4% propane (dashed lines, crosses). The models used are PR with k_{ij} (black), PR with l_{ij} (red), PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Gregorowicz et al. [64]. The parameters used are given in table A.2.

Propane with both n-decane and n-eicosane are relatively simple pairs and can be adequately represented by all of the models (excluding the zero pressure excess Gibbs energy models). However more significant differences are found with more asymmetric pairs as shown by figure 2.5. In this figure the red line represents the HV model with NRTL. There are significant differences in this pair between the HV with NRTL model and the other models, it predicts much lower bubble point pressures than all of the other models. This may be due to the experimental data used being very close to the critical point of the mixture leading to poor representation at lower propane mole fractions. This is a risk when using the very flexible NRTL model with its 3 binary interaction parameters. Even

though the models for NRTL and NRTL_{HV} are similar, the results for HV with NRTH_{HV} are much closer to the other models and it is in fact the best at correlating the experimental data with an average deviation in pressure of less than 2 percent. The PC-SAFT model is not accurate for this binary pair, this is possibly due to poor correlation of the C_{36} pure component parameters for PC-SAFT.



Fig. 2.5 Plot showing the P-x projection of propane with nC_{36} at 378.2K (solid lines, circles) and 408.2K (dashed lines, crosses). The models used are PR with k_{ij} (black), PR with HV using NRTL (red), PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Schwarz and Nieuwoudt [164]. The parameters used are given in table A.2.

The other optimal models for each of the asymmetric binary pairs with experimental data close to the critical point are the vdW1f mixing rules with two binary interaction parameters. This is shown in figure 2.6 which is for the most asymmetric pair considered. For this mixture none of the models are excellent with large deviations for each. For this pair there is experimental data close to the critical point and some further from the critical point from Peters et al. [139]. The overall best model is the vdW1f mixing rules with two binary parameters. One interesting difference between SRK and PR is that SRK predicts a LLE region at a much lower pressure than PR. This is presented in figure 2.6 where a high pressure LLE region for SRK is found at less than 300 bar while for PR the region is above 300bar. The excess Gibbs energy mixing rules predict the region at much higher pressures. Without experimental data in this region it is not clear which model is more accurate.

However the LLE region is extremely sensitive to the binary interaction parameter used (with larger values of k_{ij} creating a larger LLE region).



Fig. 2.6 Plot showing the P-x projection of propane with nC_{60} at 378.2K (solid lines) and 408.2K (dashed lines). The models used are PR with k_{ij} (black), PR with k_{ij} and l_{ij} , PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Schwarz and Nieuwoudt [164]. The parameters used are given in table A.2.

The results for the binary pairs of propane with a large n-alkane are summarised in table 2.9. For the asymmetric hydrocarbon pairs, the models which are suitable are: the vdW1f mixing rules with two binary interaction parameters; the HV NRTL_{HV} model, often with the non-randomness parameter close to zero; and PC-SAFT in the region far from the critical point, but only for pairs where the pure component parameters are fitted to experimental data rather than an extrapolation.

2.4.2 Carbon Dioxide

Mixtures of carbon dioxide with alkanes are more dissimilar and exhibit LLE at much lower asymmetries and pressures than mixtures of ethane or propane with large alkanes. The quadrupolar moment of CO_2 is very large, models which take this quadrupolar term into account have been demonstrated to be well suited for modelling CO_2 [66]. However the addition of a quadrupolar term is not simple. Though adequate results are obtained the additional complexity is not necessarily desirable depending on the mixture being

Model	Failures	P deviation (%)	y deviation ($\times 10^2$)	Objective function
$PR(k_{ij})$	5	7.43	0.44	11.02
$PR(l_{ij})*$	1	4.58	0.46	6.61
PR 2 BIP*	1	3.07	0.40	5.26
PR MHV1	0	6.39	0.39	10.79
PR MHV2	6	24.23	0.53	28.05
PR HV	12	8.60	0.50	11.00
PR HV NRTL _{HV} *	1	3.58	0.46	6.88
PC-SAFT	0	7.65	0.62	9.52

Table 2.9 Result summary for binary pairs of propane with a large n-alkane. Results for SRK not included in summary. Asterisk is used to highlight the recommended models.

considered. It is possible to represent mixtures containing CO_2 without such complex models. For example the mixture of n-C₈ with CO_2 in figure 2.7 is adequately represented with most of the considered mixing rules.

Though the use of the vdW1f mixing rules with an l_{ij} alone is not suitable it is of use when combined with a k_{ij} . The best model for fitting this data is PC-SAFT with a k_{ij} . Using the zero pressure mixing rules (MHV1 or MHV2) can lead to an LLE region at low CO₂ compositions, though they are not shown in figure 2.7. For larger asymmetries a separate LLE is predicted at high pressures and high CO₂ concentrations by other mixing rules.

Figure 2.8 demonstrates the predicted CO_2 rich LLE region for the binary pair of CO_2 with n-decane. The region is predicted at much higher pressures by the excess Gibbs energy mixing rules. With the regressed binary parameter, the use of PR with the vdW1f mixing rules on the k_{ij} leads to the prediction of an LLE region which coincides with the VLE region for this mixture, this is very sensitive to the binary parameter used. When using two binary parameters this region is predicted at a higher pressure. There is no experimental data available for the LLE region and the prediction from PR with the vdW1f mixing rules is likely an error (though the given parameter fits the experimental data most accurately). There is a significant difference between SRK and PR, especially for the pressure expected for the LLE critical point. The use of the more complex HV with NRTL_{HV} leads to generally worse results than the simple vdW1f mixing rules. If the HV with NRTL_{HV} mixing rules used the temperature dependence describe in equation 2.13 then it could at least reproduce the results from the vdW1f mixing rules. More significant difference between the models can be found with more asymmetric pairs such as shown in figures 2.9 and 2.10.



Fig. 2.7 Plot showing the P-x projection of carbon dioxide with nC_8 at 313.2K (solid lines) and 372.5K (dashed lines). The models used are PR with k_{ij} (black), PR with k_{ij} and l_{ij} , PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Weng and Lee [196] (blue), and R. Jimenez-Gallegos and Elizalde-Solis [146] (red). The parameters used are given in table A.3.



Fig. 2.8 Plot showing the P-x projection of carbon dioxide with nC_{10} at 510.93K (solid lines) and 277.59K (dashed lines). The models used are PR with k_{ij} (black), PR with k_{ij} and l_{ij} , PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Reamer and Sage [152]. The parameters used are given in table A.3.



Fig. 2.9 Plot showing the P-x projection of carbon dioxide with nC_{20} at 373.2K (solid lines) and 310.2K (dashed lines). The models used are PR with k_{ij} (black), PR with k_{ij} and l_{ij} , PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Sato et al. [162] (blue), Gasem and Jr. [61] (red), and Huie et al. [78]. The parameters used are given in table A.3.

There are significant differences between the vdW1f mixing rules, PC-SAFT and the HV with NRTL_{HV} for both figures 2.9 and 2.10. The best model in general for both of these mixtures is the vdW1f mixing rules with two binary interaction parameters (though with only a k_{ij} the results are often excellent). PC-SAFT can struggle in some regions though it is excellent for much of the phase envelope as well.

The results are summarised in table 2.10. In general it is possible to conclude that for mixtures of CO_2 with hydrocarbons that the simple cubic EoS's with a single k_{ij} or two binary parameters with the vdW1f mixing rules are optimal. There are no significant advantages of using the HV with NRTL_{HV} mixing rule in spite of its three binary interaction parameters. PC-SAFT is generally accurate though there are some indications of problems for the mixture presented in figure 2.9. Additional pure component terms to account for the quadrupolar terms have not been investigated in this study.



Fig. 2.10 Plot showing the P-x projection of carbon dioxide with nC_{36} at 573.2K (solid lines) and 373.2K (dashed lines). The models used are PR with k_{ij} (black), PR with k_{ij} and l_{ij} , PR with HV using NRTL_{HV} (blue), PC SAFT with k_{ij} (green) and SRK with k_{ij} (cyan). The experimental data is from Tsai et al. [184] (blue) and [61] (green). The parameters used are given in table A.3.

Model	Failures	P deviation (%)	y deviation ($\times 10^3$)	Objective function
PR $(k_{ij})^*$	40	8.53	8.76	8.15
$PR(l_{ij})$	128	17.24	6.66	15.03
PR 2 BIP*	22	6.14	7.74	5.89
PR MHV1	31	24.53	10.31	11.78
PR MHV2	77	33.65	6.35	16.78
PR HV	7	19.20	12.90	8.30
PR HV NRTL _{HV} *	20	10.65	8.72	6.41
PC-SAFT	58	6.32	11.90	9.00

Table 2.10 Result summary for binary pairs of CO_2 with a large n-alkane. Results for SRK not included in summary. Asterisk is used to highlight the recommended models.

2.4.3 Water

Some more complex systems involving water are also investigated. In general the vdW1f type mixing rules are not considered to be suitable for these mixtures. To remedy these difficulties some complex models have been developed (e.g. CPA).

The first example considered is the mixture of carbon dioxide with water. This is presented in figure 2.11. For this mixture, the vdW1f mixing rules with only a single parameter is not suitable, however reasonable results (accurate to within an order of magnitude) are obtained when using two parameters.



Fig. 2.11 Plot showing the CO₂ in the aqueous phase (solid) and water in the CO₂ rich phase (dashed) at 298.15K. The models used are SRK with k_{ij} (black), SRK with k_{ij} and l_{ij} (red), SRK with HV and NRTL_{HV} (blue), CPA with k_{ij} (yellow), CPA with k_{ij} and solvation, $\beta = 0.1836$, (green) and PC-SAFT with k_{ij} (cyan). Experimental data from [68] (circles), [189] (crosses), [85] (diamonds), [74] (plus sign), and [84] (asterisk).

The most accurate models are the excess Gibbs energy mixing rules, both the MHV types and the HV type. For CPA two models are considered, the first with only the water considered as associating, the second with a fitted cross-association volume with CO_2 solvating into the water. The cross association energy is one half of the water association energy. For PC-SAFT only the water is considered associating. With only the water considered as associating, the model is inaccurate at representing the CO_2 rich phase. The use of solvation does improve the representation of the CO_2 rich phase but is still not as accurate as the excess Gibbs energy type models. PC-SAFT suffers from the same

drawback as CPA without solvation for the CO_2 and cannot adequately represent both liquid phases simultaneously.

The mixture of water with methane can be well represented by most of the models. This is demonstrated in figures 2.12 and 2.13. The vdW1f mixing and combining rules with a single parameter on the k_{ij} is capable of representing either the water in hydrocarbon rich phase or the hydrocarbon in the aqueous phase, but not both simultaneously. However using both a k_{ij} and l_{ij} , it is possible to adequately represent both phases at low temperature, although more significant deviations are encountered at high temperatures as shown in figure 2.13.



Fig. 2.12 Plot showing C_1 in the aqueous phase (solid line) and water in the C_1 rich phase (dashed) at 298K. The models used are SRK with k_{ij} (black), SRK with k_{ij} and l_{ij} (red), SRK with HV and NRTL_{HV} (blue), CPA with k_{ij} (green) and PC-SAFT with k_{ij} (cyan). Experimental data from [43] (circles), [29] (crosses), [28] (diamonds), [118] (plus sign), and [201] (asterisk).

The excess Gibbs energy type mixing rules are suitable at low pressures, however there are some small deviations at very high temperature (510.9K). The best model for methane with water is CPA or PC-SAFT, these model can represent the equilibrium at all conditions with only a single binary parameter. As the size of the hydrocarbon is increased from methane to n-butane, the simple vdW1f mixing rules become less suitable. For mixtures of water with butane the representation of both the aqueous and hydrocarbon rich phases simultaneously is not accurate using any of the models at all temperatures. This is shown in figures 2.14 and 2.15. The use of temperature dependent parameters leads to more



Fig. 2.13 Plot showing C_1 in the aqueous phase (solid line) and water in the C_1 rich phase (dashed) at 510.93K. The models used are SRK with k_{ij} (black), SRK with k_{ij} and l_{ij} (red), SRK with HV and NRTL_{HV} (blue), CPA with k_{ij} (green) and PC-SAFT with k_{ij} (cyan). Experimental data from Olds et al. [128]

accurate results, but is not considered here. In this instance the vdW1f mixing rules with a k_{ij} and l_{ij} is not suitable over a large temperature range, though can be accurate for a small temperature range at low pressures (P<100 bar).

The most accurate models are PC-SAFT, CPA and HV with $NRTL_{HV}$. Each of these is suitable without temperature dependent binary interaction parameters, though HV with $NRTL_{HV}$ does match the low temperature experimental data better at the cost of larger deviations at higher temperatures.

For mixtures of water with n-decane (shown in figure 2.16) there is a low pressure VLE and a high pressure LLE region (which are separate). There is not much data available at elevated temperatures on the water rich phase composition. However based on the data available MHV1 is the most accurate. Of the other models HV with NRTL_{HV} is the most accurate with CPA also suitable. The vdW1f mixing rules are extremely poor for this mixture. PC-SAFT has results similar to CPA.

More complex mixtures where solvation is possible include aromatics with water. The example of benzene with water is presented in a P-x diagram in figure 2.17. The results at very high temperature for CPA are not suitable. The best model for this binary are the excess Gibbs energy type mixing rules. At this temperature (573.2K) there is a low



Fig. 2.14 Plot showing C₄ in the aqueous phase (solid line) and water in the C₄ rich phase (dashed) at 310.9K. The models used are SRK with k_{ij} (black), SRK with k_{ij} and l_{ij} (red), SRK with HV and NRTL_{HV} (blue), CPA with k_{ij} (green) and PC-SAFT with k_{ij} (cyan). Experimental data from [154] (circles) and [95] (crosses)



Fig. 2.15 Plot showing C₄ in the aqueous phase (solid line) and water in the C₄ rich phase (dashed) at 510.9K. The models used are SRK with k_{ij} (black), SRK with k_{ij} and l_{ij} (red), SRK with HV and NRTL_{HV} (blue), CPA with k_{ij} (green) and PC-SAFT with k_{ij} (cyan). Experimental data from [154]



Fig. 2.16 Plot showing C_{10} in the aqueous phase (solid line) and water in the C_{10} rich phase (dashed) at 573.2K. The models used are SRK with k_{ij} (blue), SRK with k_{ij} and l_{ij} (green), SRK with MHV1 (cyan), SRK with HV and NRTL_{HV} (red), CPA with k_{ij} (black). Experimental data from [70] (circles) and [194] (diamonds)



Fig. 2.17 Plot showing the P-x projection of water with benzene at 573.2K. The models used are SRK with k_{ij} (blue), SRK with MHV1 (cyan), SRK with HV and NRTL_{HV} (red), CPA with k_{ij} (black). Experimental data from [40]

pressure VLE region and a high pressure LLE region. CPA and the vdW type models represent a continuous envelope, which differs from the excess Gibbs type mixing rules which can represent two distinct two-phase regions.

The final mixture of interest is the mixture of water with hydrogen sulphide. Both of these components can be considered as associating. Therefore they are generally very difficult to accurately model. The majority of the experimental data available is only at very low pressures, where most models can accurately predict the data (nearly ideal). However some high temperature, high pressure data is available. Figure 2.18 is a P-x projection at 444.26K.



Fig. 2.18 Plot showing the P-x projection of water with H_2S at 444.26K. The models used are SRK with k_{ij} (blue), SRK with MHV1 (cyan), SRK with HV and NRTL_{HV} (red), CPA with k_{ij} (black). Experimental data from [170] (circles) and [21] (crosses) at 443K.

None of the considered models can accurately match the experimental data. The flexible excess Gibbs energy type models are the most successful. The use of a single binary parameter with the vdW1f mixing rules can accurately correlate some of the data but is inaccurate at elevated pressures. The use of CPA with both water and hydrogen sulphide treated as associating components can accurately represent the low pressure data but is inaccurate at elevated pressures. The vdW1f mixing rules with two parameters is as accurate as the more complex models.

The summary of results for the water containing systems is reported in table 2.11. For CPA the results are shown for the model both with and without solvation. In the case of

Table 2.11 Result summary for binary pairs of water with hydrocarbons. The error are reported under each heading where Aq refers to the deviation in the calculation of hydrocarbon content in the aqueous phase, similarly for HC, DP refers to deviation in bubble point pressure and DY in incipient phase concentration. Results for SRK not included in summary. Asterisk is used to highlight the recommended models, note that MHV1 and MHV2 are not recommended due their problems with asymmetric alkane systems, though are suitable for water mixtures.

Model	Failures	Aq (%)	HC (%)	DP (%)	DY ($\times 10^2$)	Objective fun
$PR(k_{ij})$	45	78.41	31.85	10.04	14.86	41.49
PR 2 BIP	29	47.82	31.78	23.42	21.78	29.75
PR MHV1	55	31.76	31.56	30.17	28.36	25.27
PR MHV2	62	24.59	32.00	51.17	34.94	25.45
PR HV	72	34.13	44.03	32.41	25.53	28.15
PR HV NRTL _{HV} *	44	25.55	26.72	7.05	19.45	22.75
PC-SAFT*	17	29.75	29.24	15.74	27.05	26.87
CPA*	12	32.87	27.34	11.43	12.76	26.23
CPA Solv*	12	29.02	21.22	11.43	12.76	14.28

the model with solvation the results for the pairs without solvation are also included (e.g. water with methane). Because none of the hydrocarbons considered here is very large the zero pressure mixing rules are suitable. The most consistently accurate model is HV with NRTL_{HV}. However CPA with solvation for some pairs is also very accurate. PC-SAFT is accurate for some mixtures, however struggles without additional terms for solvation or a quadrupolar term for some mixtures.

2.5 Conclusion

A large number of models have been tested with a large number of systems. There are a number of conclusions which can be drawn from the results. The first is that it is not suitable to use the zero pressure models (MHV1 and MHV2) with NRTL for binary pairs of highly asymmetric hydrocarbons. Similar problems are encountered when using other activity coefficient models (e.g. UNIFAC).

It is suitable to have only a single binary parameter (k_{ij}) on only slightly asymmetric hydrocarbons using the vdW1f mixing rules. However on very asymmetric hydrocarbon mixtures it is necessary to include a binary parameter on the l_{ij} term. For mixtures containing CO₂ with a hydrocarbon, the vdW1f mixing rules are superior to all other tested mixing rules. With only a single parameter on the k_{ij} it is possible to obtain accurate results up to even n-C₃₆. A second parameter does not significantly improve the results. For mixtures of water with methane or ethane it is possible with the vdW1f mixing rules, when using two binary parameters, to represent both phases accurately at low- to moderate- pressures. As the length of the carbon chain increases to three or four, the use of a parameter on the l_{ij} term adds very little benefit and it is necessary to use more complex mixing rules to represent both phases simultaneously over a wide temperature range. The vdW1f mixing rules cannot represent both the CO₂ and water rich phases in the binary pair containing both. For mixtures of water with hydrogen sulphide, a single parameter leads to inaccurate results, however with two parameters the results are similar to the more complex models.

Two infinite pressure limit models are considered in this work. The first is the HV with the standard implementation of NRTL, the second is HV with a modified NRTL_{HV}. In almost all cases considered the second model is more successful, and it has the additional benefit of being reduced to the vdW1f mixing rules for hydrocarbon containing mixtures. For asymmetric hydrocarbon binary pairs, the models are suitable though there are a large number of parameter sets which produced similar accuracy in the results, but different phase envelopes. The use of three parameters allows the models to be very flexible, however this also requires a lot of experimental data to ensure the correct parameter set is used. The models are generally suitable for CO_2 with hydrocarbons although the results are often not as good as the simple vdW1f mixing rules.

For mixtures containing water and hydrocarbons the use of HV with NRTL_{HV} is capable of representing both phases simultaneously, although results at very high pressures are not as good as CPA. The model is the best for mixtures of water with CO_2 and water with H_2S . The energy terms do not need to be made temperature dependent (although temperature dependence will lead to more accurate results in the regressed region).

The CPA model was not considered for the hydrocarbon pairs. For non-associating components it is identical to SRK, although the pure component parameters $(a_i, b_i \text{ and } \hat{m}_i)$ are generally determined by fitting to the experimental vapour pressure and liquid density rather than from the critical point and acentric factor as is done for SRK. For mixtures of water with light hydrocarbons, CPA is very accurate using a single binary parameter. However it is not accurate at high temperatures for long chain hydrocarbons with only a single binary parameter. For mixtures of water with CO₂ solvation is necessary, and the results are often not as accurate as the excess Gibbs energy models. For mixture of water with H₂S where both components are associating, CPA is not as accurate as the excess Gibbs models, and is not much better than the vdW1f mixing rules with two binary parameters. As the number of associating components increases, the computational cost of

CPA increases significantly as the solution of the volume root requires a minimisation in an inner loop. Mixtures containing water and a solvating hydrocarbon can be accurately represented using CPA, however the results are normally not as good as HV with NRTL_{HV}.

PC-SAFT is tested on all binary pairs. For the asymmetric hydrocarbons it is accurate with only a single binary parameter. However for the binary pairs containing very large hydrocarbons some of the results are poor. It is suspected that this may be due to the linear extrapolation used to determine the pure component parameters for C_{20} +. For CO₂ the model is accurate with results similar to the vdW1f type mixing rules. When modelling water there is a large number of different pure component parameters available. In general the results are not as good as when CPA is used however are often much better than the vdW1f type mixing rules.

The best results for hydrocarbon pairs are obtained using the vdW1f mixing rules with a l_{ij} or PC-SAFT when accurate pure component data is available. For mixtures of CO₂ with hydrocarbons the vdW1f mixing rules with a k_{ij} are best. For mixtures of water with small hydrocarbons CPA and PC-SAFT are the most accurate. For all other mixtures the flexible HV with NRTL_{HV} mixing rules are the most accurate. For systems containing mixtures of water with short and long chain hydrocarbons with CO₂ and H₂S (commonly found in oil reservoirs) it would be best to use a model which uses the above recommended mixing rules for each pair. The most simple implementation would use the vdW1f type mixing rules for hydrocarbon pairs and pairs with CO₂ and a hydrocarbon, while using the more flexible HV with NRTL_{HV} when sufficient experimental data is available. CPA or PC-SAFT could also be used, though there are a number of issues with implementing these models in a reservoir simulation, including that they are much more computationally demanding.

Chapter 3

Multiphase Isenthalpic Flash using the Conventional Flash Framework

3.1 Introduction

The conventional equilibrium problem is the isothermal flash, with (T, P, z) specified. However in some cases the temperature is not known and instead an energy is specified. A related equilibrium problem is the isenthalpic flash, with (H, P, z) specified. The solution to the isenthalpic flash is the global maximum of the entropy. The same tangent plane stability analysis as discussed in section 1.3 can be used to check if a new phase can be introduced.

The isenthalpic flash problem is relevant to a number of industrially important processes. It can be used to describe adiabatic expansion processes and steady state flow. There is renewed interest in its applicability to the simulation of thermal recovery of heavy oil, e.g. using steam injection [72]. For this thermal simulation it is necessary to add an energy balance to the system of equations used to carry out transient reservoir simulation. An additional variable must also be added, this is often chosen as either the temperature or the internal energy. When specifying the temperature, problems can be encountered for narrow boiling mixtures, as the energy and volume can change dramatically due to a small change in the temperature. Instead it can be preferable to use internal energy as a variable leading to an energy based flash (often isenthalpic flash) [17].

Isenthalpic flash problem can be solved with general thermodynamic models like EoS's. They provide a consistent and accurate description of fluid phase behaviour over a wide temperature and pressure range. There is a desire to use EoS's to simulate the production from oil reservoirs using thermal recovery techniques, especially when solvents are used in combination with steam injection. However, flash calculation with an EoS is more complex than ideal solution models, and can become a bottleneck in the simulation speed. As a trade-off, one can limit the number of grid blocks in a simulation. Most commercial thermal reservoir simulators (e.g. CMG STARS) use temperature dependent K-value correlations instead of an EoS. In such a case it is common to use a correlation for the residual enthalpy of the phases, which is not always thermodynamically consistent with the employed K-value correlation. The system in such a situation reduces to an ideal solution where a simplified procedure can be used.

Most early work on the isenthalpic flash problem focused on calculations for two phases (e.g. [15]). The first fully multiphase implementation was described by Michelsen [111], where both a first order direct substitution approach and a second order approach were presented. The direct substitution algorithm has been investigated by a number of authors. Alternatives to the acceleration were suggested by Agarwal et al. [3] along with a combined approach using direct substitution and a nested isothermal flash. Carrying out simultaneous phase split and stability analysis calculations was presented by Gupta et al. [69] as an alternative to the sequential approach to the phase split calculation and stability analysis, this was further examined by Zhu and Okuno [204]. Narrow boiling fluids were investigated by Zhu and Okuno [203] who suggested using bisection for degenerate cases. Heidari et al. [72] used the negative flash to avoid stability analysis.

For nearly ideal mixtures direct substitution is rapidly convergent, however the rate of convergence is slow for non-ideal mixtures and may even become divergent. Large scale simulation may involve millions of separate flash calculations. The linear rate of convergence and lack of a guarantee of convergence can be problematic for simulation. A robust approach is required and a more rapid second order approach desired. One possible solution is the direct maximisation of the entropy. This was used by Brantferger et al. [17] for reservoir simulation with a robust implementation developed by Sun et al. [178] where the cost was compared to isothermal flash. Michelsen [115] demonstrated a general solution strategy for two-phase isenthalpic flash, as well as several other state function based flash specifications. He proposed to use a Newton approach for efficiency with a Q-function maximisation approach for robustness. The Q-function maximisation approach is essentially a nested loop approach with an isothermal flash in the inner loop and an outer loop maximising the Q-function to determine the temperature. The Q-function maximisation is used as a backup when direct solution of the equilibrium equations by the Newton approach fails.

In this work we extend the two-phase work of Michelsen [115] to the general multiphase isenthalpic flash. For the Q-function maximisation method, challenging cases will be highlighted and solutions proposed. A full algorithm will be described for the general solution of the multiphase isenthalpic flash problem, capable of dealing with narrow boiling and degenerate cases and dynamically adding and removing phases. For thermal recovery of heavy oil, the general algorithm is tailored by including a separate phase for initialisation and using the Rachford-Rice type equations to improve early steps in the partial Newton method with poor initial estimates. For commercial thermal recovery simulators, the temperature dependent K-factors and separate correlations for heat capacities are typically used as the thermodynamics model. For this ideal solution case, we propose a formulation as an extension of the isothermal flash formulation for ideal solutions [107]. It has one additional equation for the enthalpy balance and can be solved by the Newton approach in the majority of cases. A nested loop procedure with the outer loop searching for temperature is used as a fallback method. It should be noted that the ideal solution model employed in commercial simulators is not always thermodynamically consistent. If the correlations for K-factors and for heat capacities are consistent, the outer loop can be treated as a maximisation.

We first present how to solve the multiphase isenthalpic flash for K-factor based thermodynamics in section 3.2.1. How to solve the general multiphase isenthalpic flash using full thermodynamics is also presented, with partial Newton (3.2.3), Newton (3.2.2), and Q-function maximisation (3.2.4) methods described. How each of these methods can be tailored to thermal simulation of heavy oil production is described in section 3.2.5. A general implementation for each of the described methods is given in section 3.3. The presented methods are tested on seven isenthalpic flash examples, for both the ideal solution case and with general EoS based thermodynamics in section 3.4. Each example is tested over a wide pressure and molar enthalpy range so as to evaluate the robustness and efficiency of the proposed methods. The computational cost of the isenthalpic flash is compared with that of the isothermal flash at the same conditions (specified pressure and converged temperature), showing that the additional cost would not be prohibitive for reservoir simulation.

3.2 Isenthalpic flash

For a mixture of C components with molar amounts $\{z_i\}$ at pressure P^{spec} and enthalpy H^{spec} the aim of isenthalpic flash is to find the number of phases F, with phase fractions

 $\{\beta_j\}\$, the composition of each phase $\{x_{i,j}\}\$ and the equilibrium temperature T^{eq} . From table 1.2 and the (S, H, P, n) surface we know that the solution to the isenthalpic flash corresponds to the maximum in the entropy:

$$\max \frac{S(H, P, \boldsymbol{n})}{R} \tag{3.1a}$$

subject to the material balance constraints

$$\sum_{j=1}^{F} n_{i,j} - z_i = 0, \quad \forall i$$
(3.1b)

and non-negativity of any component in any phase

$$n_{i,j} \ge 0, \quad \forall i, j$$
 (3.1c)

Direct entropy maximisation was investigated by Brantferger et al. [17] and Sun et al. [178]. However thermodynamic models are commonly solved at a given (T, P, n) for each phase rather than (H, P, n). The enthalpy is then described as a constraint which is nonlinear in the variables. Most implementations of isenthalpic flash carry out some form of constrained maximisation, or simply solve for the equilibrium conditions, with the enthalpy specification met at the solution.

For any intermediate solution of F phases, stability analysis [109] can check if an additional phase should be introduced and provide an initial composition estimates for the new phase. A phase split step is subsequently performed to determine the new equilibrium distribution at the specified pressure and enthalpy. In this study we employ essentially the same stability analysis and mainly focus on the variations in the other parts of the flash procedure.

In many simulations a full EoS is not used. Instead correlations are used to evaluate both the K-values and the enthalpy of the liquid phases (or enthalpy of vaporisation). The solution procedure for these ideal solutions is simpler than when using full thermodynamics.

3.2.1 Ideal solution

In the ideal solution approximation it is assumed that the fugacity coefficient for each component in each phase is available as a function of temperature and pressure $\hat{\varphi}_{i,j}(T, P)$.

The residual enthalpy of the phases must also be available using a suitable correlation. Using the fugacity coefficients, the composition of each phase is found as:

$$x_{i,j} = \frac{z_i}{E_i \hat{\varphi}_{i,j}} \qquad E_i = \sum_{k=1}^F \frac{\beta_k}{\hat{\varphi}_{i,k}}$$
(3.2)

with temperature derivatives

$$\frac{\partial x_{i,j}}{\partial T} = x_{i,j} \left(-\frac{\partial \ln \hat{\varphi}_{i,j}}{\partial T} - \frac{\partial \ln E_i}{\partial T} \right)$$
(3.3)

$$\frac{\partial \ln E_i}{\partial T} = -\frac{\sum_k^F \beta_k x_{ik} \frac{\partial \ln \hat{\varphi}_{i,k}}{\partial T}}{z_i}$$
(3.4)

and phase fraction derivatives

$$\frac{\partial x_{i,j}}{\partial \beta_k} = -\frac{x_{ik}x_{ij}}{z_i} \tag{3.5}$$

The system of equations which must be satisfied at equilibrium is:

$$f_j = 1 - \sum_{i}^{C} x_{ij} \quad j = 1, 2, ..., F$$
 (3.6)

and

$$f_{F+1} = H - H^{spec} \tag{3.7}$$

The enthalpy is found from:

$$H = \sum_{j=1}^{F} \beta_j \sum_{i=1}^{C} x_{i,j} h_{i,j} = \sum_{j=1}^{F} \beta_j \sum_{i=1}^{C} x_{i,j} (h_{i,j}^{IG} + h_{i,j}^r)$$
(3.8)

The Jacobian for this system of equations is

$$J_{jk} = -\sum_{i=1}^{NC} \frac{\partial x_{i,j}}{\partial \beta_k}$$
(3.9)

$$J_{j,F+1} = -\sum_{i=1}^{C} \frac{\partial x_{i,j}}{\partial T}$$
(3.10)

$$J_{F+1,j} = \sum_{i=1}^{C} x_{i,j} h_{i,j} + \sum_{k=1}^{F} \beta_k \sum_{i=1}^{C} h_{i,k} \frac{\partial x_{i,k}}{\partial \beta_j}$$
(3.11)

the ideal gas terms cancel in the difference in equation 3.11 to leave:

$$J_{F+1,j} = \sum_{i=1}^{C} x_{i,j} h_{i,j}^{r} + \sum_{k=1}^{F} \beta_k \sum_{i=1}^{C} h_{i,k}^{r} \frac{\partial x_{i,k}}{\partial \beta_j}$$
(3.12)

and finally

$$J_{F+1,F+1} \approx \frac{1}{R} \sum_{j=1}^{F} \beta_j \left(C_{p,j} + \sum_{i=1}^{C} h_{ij} \frac{\partial x_{ij}}{\partial T} \right)$$
(3.13)

This approximation is exact at the solution. If the temperature derivatives of the component enthalpies are readily accessible from the equation used then it may be replaced with:

$$J_{F+1,F+1} = \sum_{i=1}^{C} \sum_{j=1}^{F} \left(n_{ij} \frac{\partial h_{i,j}}{\partial T} + \beta_j h_{i,j} \frac{\partial x_{ij}}{\partial T} \right)$$
(3.14)

If the thermodynamic model employed is consistent then the temperature derivative of the fugacity and the residual heat capacity are related through:

$$RT^2 \frac{\partial \ln \hat{\varphi}_{ij}}{\partial T} = -h_{i,j}^r \tag{3.15}$$

in which case equation 3.12 can be replaced by

$$J_{F+1,j} = RT^2 J_{j,F+1} ag{3.16}$$

Alternatively a symmetric system of equations can be arrived at by dividing equation 3.7 by RT^2 .

The presented system of equations and Jacobian will be convergent in the majority of cases. However in some cases it is necessary to nest the isothermal flash in an inner loop with the temperature updated in the outer loop.

3.2.2 Newton's method

When each phase is represented using an EoS the ideal solution may no longer be appropriate. Instead the fugacity coefficients are now also functions of composition $\hat{\varphi}_{i,j}(T, P, n_j)$. The equilibrium equations and enthalpy constraint can be solved directly using Newton's method. As in the conventional isothermal flash framework, for each component set its mole number in a certain phase as dependent through the material balance:

$$n_{i,J(i)} = z_i - \sum_{j \neq J(i)}^F n_{i,j} \quad \forall i$$
 (3.17)

where J(i) represents the phase for component *i* where the component is present in the greatest amount. The equilibrium equations are

$$f_{l} = \ln \hat{f}_{i,j} - \ln \hat{f}_{i,J(i)}, \quad l = 1, 2, ..., C(F - 1),$$

$$i = 1, 2, ..., C, j = 1, 2, ..., F, j \neq J(i)$$
(3.18)

and the enthalpy constraint

$$f_{C(F-1)+1} = \frac{H^{spec} - H}{RT}$$
(3.19)

These equations lead to a symmetric Jacobian with elements

$$J_{l,o} = (\delta_{j,m} - \delta_{j,J(k)}) \frac{\partial \ln \hat{f}_{i,j}}{\partial n_{k,m}} + (\delta_{J(i),J(k)} - \delta_{J(i),m}) \frac{\partial \ln \hat{f}_{i,J(i)}}{\partial n_{k,J(i)}},$$

$$l = 1, 2, ..., C(F-1), o = 1, 2, ..., C(F-1), i = 1, 2, ..., C, k = 1, 2, ..., C,$$

$$j = 1, 2, ..., F, m = 1, 2, ..., F, j \neq J(i), m \neq J(k) \quad (3.20)$$

with $\delta_{j,m}$ representing the Kronecker delta function. The derivative of the fugacity is:

$$\frac{\partial \ln \hat{f}_{i,j}}{\partial n_{k,j}} = \frac{\delta_{i,k}}{n_{i,j}} - \frac{1}{\beta_j} + \frac{\partial \ln \hat{\varphi}_{i,j}}{\partial n_{k,j}}$$

The remaining row and column are

$$J_{C(F-1)+1,l} = J_{l,C(F-1)+1} = T\left(\frac{\partial \ln \hat{f}_{i,j}}{\partial T} - \frac{\partial \ln \hat{f}_{i,J(i)}}{\partial T}\right)$$
(3.21)

with the final equation:

$$J_{C(F-1)+1,C(F-1)+1} = -\frac{C_p}{R}$$
(3.22)

The variables used for this Jacobian are Δn_j , $\Delta \ln T$. This is the extension of the implementation of Michelsen [115] to the multiphase case. Alternatively it is possible to use component yields $\theta_{i,j} = n_{i,j}/z_i$ in place of mole numbers as variables as shown by

Paterson et al. [133]. This may lead to a better conditioned Jacobian but the resulting convergence behaviour is similar.

3.2.3 Partial Newton

The full Newton method often requires an accurate initial estimate. For the isothermal flash successive substitution using the multiphase Rachford-Rice equations is commonly carried out for a small number of iterations. Similarly for isenthalpic flash it is possible to use direct substitution, this is similar to successive substitution but due to the temperature dependence of the fugacity coefficients, they must be updated at each iteration.

From the ideal solution equations given here it is possible to obtain the direct substitution equations by setting one phase fraction as dependent through the material balance

$$\beta_F = 1 - \sum_{j=1}^{F-1} \beta_j$$

and replacing equation 3.6 with:

$$f_j = \sum_{i=1}^{C} (x_{iF} - x_{ij}) \quad j = 1, 2, ..., F - 1$$
(3.23)

The Jacobian of equations 3.23 and 3.7 with one phase fraction set as dependent can be found and will be similar to that presented by Michelsen [111]. The direct substitution method is often useful for early iterations, and to remove phases from the system of equations when necessary.

An alternative partial Newton method is possible starting from the full Newton method. Making an ideal solution approximation, the composition derivative of the fugacity coefficient can be set to zero:

$$\frac{\partial \ln \hat{\varphi}_{i,j}}{\partial n_{k,j}} = 0 \tag{3.24}$$

Otherwise the system of equations and Jacobian is the same as presented for Newton's method in equations 3.20 to 3.22. This leads to a simple Jacobian where the explicit inverse is readily available for part of the matrix for the two-phase case, reducing the number of variables from C + 1 to 2. For the multiphase case a similar reduction in variables is possible though more complex. An alternative is presented in chapter 4.

The partial Newton method will be convergent when the mixture is not highly non-ideal [111]. However the rate of convergence can be intolerably slow, with a nested isothermal flash often outperforming the computational cost of the partial Newton method alone.

The update from the Newton-Raphson iteration is only convergent to the desired solution with a suitably close initial estimate. Often non-convergent updates can be encountered when more than one eigenvalue from the Newton update is negative. In these cases a small number of additional partial Newton steps can be useful, or a reduction of the impact of the composition derivatives of the fugacity coefficient using a suitable scaling factor can aid in convergence (i.e. instead of setting the derivatives to zero, equation 3.24, reduce them by a half). Doing so for a small number of iterations can help with the convergence while not significantly increasing the computational cost of the method. In practice it is often best to just switch to Q-function maximisation if convergence problems are encountered.

3.2.4 Q-function Maximisation

Michelsen [115] demonstrated that using a nested loop for (P, T) flash, the (P, H) flash problem could be posed as a maximisation of a suitable objective function:

$$Q = \frac{G_{\min}(T) - H^{spec}}{RT}$$
(3.25)

with the gradient

$$\frac{\partial Q}{\partial \frac{1}{T}} = \frac{H - H^{spec}}{R} \tag{3.26}$$

and the Hessian

$$\frac{\partial^2 Q}{\partial \left(\frac{1}{T}\right)^2} = -\frac{T^2 C_{p,min}}{R}$$
(3.27)

with

$$C_{p,min} = \sum_{j=1}^{F} \beta_j C_{p,j} + \sum_{i=1}^{C} \sum_{j=1}^{F} \left(\frac{\partial H_j}{\partial n_{i,j}} - \frac{\partial H_F}{\partial n_{i,F}} \right) \frac{\partial n_{i,j}}{\partial T}$$
(3.28)

where the first term is the pure phase heat capacity and the second is the heat capacity of phase change. The Hessian requires the solution to the flash equations and is always negative.

Instead of evaluating the Hessian directly, it is possible to use the Jacobian presented in equations 3.20 - 3.22 to evaluate the same temperature step. The step in the component amounts can be used as an initial estimate for the next nested isothermal flash iteration.

The convergence in the temperature is quadratic, and using a robust and efficient isothermal flash solver the Q-function maximisation is efficient.

3.2.5 Thermal simulation

In thermal simulation it is often the case that, close to the wellbore the number of phases can exceed the number of components (e.g. one component, two phases or two components in three phases).

The case where there are more phases than components is of obvious concern since it does not exist when using (P, T) flash. Therefore using temperature as a variable is not possible and variable substitution or isenthalpic flash must be used. Using a nested isothermal flash is susceptible to oscillations if F > C. Similarly at the solution when F > C the Gibbs energy of both stable roots to the EoS will be identical for one or more phases and may lead to the wrong root being chosen.

There are a number of possible solutions to deal with this problem. For Newton's method and the partial Newton methods, selecting the desired root to the EoS is possible in a manner proposed by Michelsen [111]. For Q-function maximisation it would be necessary to find the transition temperature then split the two oscillating phases to meet the enthalpy constraint and material balance. This will require a few additional iterations to find the transition temperature.

An alternative which will work with both Q-function maximisation and Newton's method (or a partial Newton method) is to introduce a tolerably small amount of an additional component (e.g. 10^{-8}). This will remove the discontinuity in the enthalpy though the use of Q-function maximisation may have issues due to the highly narrow boiling nature of the new mixture.

For initialisation of the vapour liquid equilibrium a simple K-value correlation is often used (for example [115] proposed the use of the Wilson K-factors). This can be used with a second correlation for the solubility of water in oil allowing for a three phase initialisation. The solubility of water in the oleic phase was modelled based on the correlation of [52], where the fugacity coefficient for each phase is calculated as:

$$\hat{\varphi}_i^v = 1 \forall i, \quad , \hat{\varphi}_i^l = K_i^{Wilson} \quad i \neq w, \quad \hat{\varphi}_w^a = K_w^{Wilson}$$
(3.29)

$$\hat{\varphi}_{w}^{l} = \exp\left(\ln K_{w}^{Wilson} + 21.263 - 0.0595T + 0.0000408T^{2}\right),$$

$$\hat{\varphi}_{i}^{a} = 10^{10}, \quad i \neq w$$
(3.30)

The residual enthalpy of each phase was evaluated using equation 3.15. The ideal solution method given above was used to solve this ideal solution problem. In general the initial estimates provide reasonably accurate temperature and phase composition estimates which can be used with Newton's method following only a small number of partial Newton steps. More complex correlations are possible for the solubility of components in the aqueous phase, though often their solubility is very small and a large constant value for the fugacity coefficient is suitable.

The stability analysis for such systems can also be simplified. Instead of using each pure component as an initial estimate it is generally sufficient to use the water component, lightest component, heaviest component and an intermediate, to initialise the stability analysis.

Though the initial estimate from the initialisation is often close to the solution temperature, the molar amount of some components in the aqueous phase may be far from the solution. When using the partial Newton method such deviations can lead to very slow rates of convergence, the direct substitution method directly calculates the composition of each phase based on the fugacity coefficients and does not run into such difficulties.

The partial Newton method can be improved in the early steps by using an update based on the Rachford-Rice equations. Once the partial Newton update is found $(\Delta n_j, \Delta T)$, the change in the dependent mole number of component *i* can be found as

$$\Delta n_{i,F} = -\sum_{j=1}^{F-1} \Delta n_{i,j}$$

and the update to the equilibrium K-factors evaluated:

$$\Delta \ln K_{i,j} = \frac{\Delta n_{i,j}}{n_{i,j}} + \frac{\sum_{i=1}^{C} \Delta n_{i,F}}{\beta_F} - \frac{\Delta n_{i,F}}{n_{i,F}} - \frac{\sum_{i=1}^{C} \Delta n_{i,j}}{\beta_j}$$
(3.31)

For each component where the fugacity difference between the phases is large (e.g. if $|\ln \hat{f}_{i,j} - \ln \hat{f}_{i,F}| > 1$), an estimate for the new molar amount can be evaluated from

$$n_{i,j} = \frac{\beta_j K_{i,j} z_i}{1 + \sum_{j=1}^{F-1} \beta_k \left(K_{i,k} - 1 \right)}$$
(3.32)

where the values for β_j have been updated as $\beta_j^{n+1} = \beta_j^n + \sum_{i=1}^C \Delta n_{i,j}$. For component *i* the dependent phase is found as

$$n_{i,F} = \frac{\beta_F z_i}{1 + \sum_{j=1}^{F-1} \beta_k \left(K_{i,k} - 1 \right)}$$
(3.33)

And the flow of component *i* is then rescaled by z_i .

$$n_{i,j} = \frac{z_i n_{i,j}}{\sum_{j=1}^F n_{i,j}}$$
(3.34)

This update ensures the poor initial estimate of the hydrocarbon components in the aqueous phase do not cause significant convergence issues. Though described for updating only the components in the aqueous phase the general method is sometimes useful following large temperature changes where the solubility of some components can change by one or more orders of magnitude (in either the full or partial Newton implementations).

The update can also provide an estimate for the composition of a phase which might be removed:

$$x_{i,j} = \frac{K_{i,j}z_i}{1 + \sum_{j=1}^{F-1} \beta_k \left(K_{i,k} - 1\right)}$$
(3.35)

This composition estimate can be useful either to attempt to re-introduce the phase or as an initial estimate for stability analysis. In simulation if the deleted phase is close to the phase boundary it will provide an excellent initial estimate to be stored for stability analysis skipping using the shadow phase method of [149].

3.3 Implementation

A number of different methods for isenthalpic flash have been presented. These can be split between those which use K-factor approximations (ideal solution) and full thermodynamics (Newton's method, partial Newton, and Q-function maximisation). For each of these a suitable implementation is necessary.

3.3.1 Ideal solution

Given an initial estimate with F phases at temperature T one iteration of the ideal solution procedure is carried out as:

1. For each phase evaluate the thermodynamic properties

$$\ln \hat{\varphi}_{i,j}, \quad \frac{\partial \ln \hat{\varphi}_{i,j}}{\partial T}, \quad h_{i,j}, \quad C_{p,j}$$

2. Calculate the composition of each phase

$$x_{i,j} = \frac{z_i}{E_i \hat{\varphi}_{i,j}} \qquad E_i = \sum_k^F \frac{\beta_k}{\hat{\varphi}_{i,k}}$$

and the temperature derivatives from equations 3.3 and 3.4.

- 3. Evaluate the gradient from equations 3.6 and 3.7 and the Jacobian from equations 3.9 3.13.
- 4. Factorise and solve the system of equations to find the update to the phase fractions and temperature

$$\left(\Delta\boldsymbol{\beta},\Delta T\right)^{T} = -\boldsymbol{J}^{-1}\boldsymbol{f}$$

- 5. Evaluate the new phase fractions $\beta^{n+1} = \beta^n + \check{\alpha}\Delta\beta$ and temperature $T^{n+1} = T^n + \check{\alpha}\Delta T$. If any phase fraction becomes negative then reduce the step length modifier so one phase is set to zero. Limiting the step in temperature may be necessary to avoid stepping outwith the bounds on the ideal gas heat capacity correlation, normally $\check{\alpha} = 1$.
- 6. If no phase has been deleted then check for convergence and output the result.
- 7. If a phase is removed then iterations can continue with the remaining phases. It can be checked if the deleted phase can be re-introduced. If $\Delta\beta > 0$ for the removed phase then it can be re-introduced and iterations continued.

The proposed method is useful for systems where the enthalpy and fugacity coefficients are represented using separate models. If the proposed method is not convergent for the ideal solution case, it is necessary to nest an isothermal flash. The isothermal flash problem can be solved using the gradient and Hessian (equations 3.6 and 3.9) of the equation

$$Q = \sum_{j=1}^{F} \beta_j - \sum_{i=1}^{C} z_i \ln E_i$$

using the algorithm described by Michelsen and Mollerup [117] chapter 11 for solving the multiphase ideal solution phase split of Michelsen [107].

One example of an ideal solution model is the Wilson K-factor approximation as given in equation 2.24. The vapour phase can be assumed to be an ideal gas $\hat{\varphi}_i^v = 1$ and the liquid phase fugacity is equal to the Wilson K-factor.

3.3.2 Partial Newton

Two partial Newton methods have been described. The first is direct substitution and the second is a partial Newton method based on the full Newton method with the composition derivatives of the fugacity coefficients set to zero. The implementation for direct substitution can follow the procedure described by Michelsen [111]. The partial Newton method described as a simplification of the full Newton method can be carried out as:

1. For each phase evaluate the thermodynamic properties

$$\ln \hat{\varphi}_{i,j}, \quad \frac{\partial \ln \hat{\varphi}_{i,j}}{\partial T}, \quad H_j, \quad C_{p,j}$$

- 2. Evaluate the gradient and Jacobian, then using the properties of the Jacobian solve for Δn , $\Delta \ln T$.
- 3. For each phase find $\Delta \beta_j = \sum_{i=1}^{C} \Delta n_{i,j}$. If for any phase $-\Delta \beta_j > \beta_j$ then it may be necessary to remove that phase. To do so it will be necessary to use equations 3.31-3.35 to avoid violating the material balance.
- 4. If for a component *i* there is a very large difference in the fugacity between phases (e.g. $|\ln \hat{f}_{i,j} \ln \hat{f}_{i,F}| > 1$) then for that component use equations 3.31-3.35 to update molar amount of that component in each phase.
- 5. After taking a step, if a phase is deleted, then use its composition estimate from 3.35 in the next iteration. If at the next step $\Delta \beta_j < 0$ for the deleted phase, then it should be removed from the system of equations, otherwise it can be re-introduced.
- 6. If following a step any of the phases are oscillating between vapour and liquid it indicates that a new phase must be introduced. If there is no vapour phase in the current mixture one can be introduced as an ideal gas (i.e. $\hat{\varphi}_{i,j}^{IG} = 1$). Otherwise if a liquid must be introduced, stability analysis can be attempted, if not successful then a switch to Q-function maximisation is necessary.

Often it is best to take only a small number of partial Newton steps before switching to a full Newton method. In the given implementation 5 steps of partial Newton were used before a switch to the full Newton method. One advantage of the partial Newton method is that it is likely to under-predict the step-size, reducing the likelihood of phase identification switching and oscillations. It also means that it is likely that if the method predicts a phase should be removed then it is safe to do so. The convergence of direct substitution and that of the partial Newton method are similar and either can be used.

3.3.3 Newton's method

One iteration with the full Newton method can be taken as:

1. For each phase evaluate the thermodynamic properties

$$\ln \hat{\varphi}_{i,j}, \quad \frac{\partial \ln \hat{\varphi}_{i,j}}{\partial n_{k,j}}, \quad \frac{\partial \ln \hat{\varphi}_{i,j}}{\partial T}, \quad H_j, \quad C_{p,j}$$

- 2. For each component define the phase present in the greatest amount as dependent through the material balance. The components in the remaining phases are the independent variables.
- 3. Evaluate the system of equations defined by equations 3.18 and 3.19 and the Jacobian defined in equations 3.20-3.22.
- 4. Factorise the Jacobian using a suitable method for a symmetric, indefinite matrix. If more than one eigenvalue is negative then it may indicate there will be convergence issues, the step can be attempted or can be damped by reducing the influence of the partial derivatives of the fugacity coefficients. In the presented implementation the derivatives were reduced by half once if more than one eigenvalue was negative, though there is little benefit compared to using more partial Newton steps.
- 5. Evaluate the step. For each phase evaluate $\Delta \beta_j = \sum_{i=1}^{C} \Delta n_{i,j}$. If for any phase $-\Delta \beta_j > \beta_j$ then it may be necessary to remove the phase. If the phase is present in only a small amount (e.g. $\beta_j < 0.01$) then a partial Newton step is used to ensure that the phase can be safely removed. Otherwise if the phase is present in a significant amount then it is possible the step is too large, using a step length modifier the step should be taken, ensuring that no component becomes negative.

- 6. Check for convergence. If converged output the result. If the deviation in enthalpy has increased significantly it is likely the step has been too large, apply a step length modifier ($\check{\alpha} = 1/3$ used in this implementation) and attempt the step again.
- 7. If it is clear that the solution is oscillating or there are excessive steps in temperature or phase fraction then a switch to Q-function maximisation may be necessary. In the presented implementation the maximum number of iterations taken before a switch to Q-function maximisation was $(F + 1) \times 10$, where F is the current number of phases.

3.3.4 Q-function maximisation

The use of a nested isothermal flash is often more costly than direct Newton's method for isenthalpic flash, however the cost can be minimised by using Q-function maximisation. Two implementations of Q-function maximisation are possible, one where stability analysis is only used at the local maximum of the Q-function, and a second where stability analysis is used at each iteration to ensure the global minimum of the Gibbs energy is found, this is more costly but necessary for some difficult cases. In general stability analysis is carried out at each step only when it is clear there are issues with convergence, in this implementation if a phase was introduced or removed multiple times, or after 10 iterations (where an iteration is the evaluation of the Newton step in temperature), stability analysis was used at each iteration. For example given a mixture of F phases one iteration is taken as

- 1. Carry out isothermal flash using the F phases to find the local minimum in Gibbs energy. Optionally carry out stability analysis with isothermal flash to find the global minimum.
- 2. Evaluate the Q-function from equation 3.25. Evaluate the Newton step from the Gradient and Hessian or from equations 3.18 3.22. Take the step in temperature and update the composition.
- 3. At the new temperature solve the isothermal flash using the F phases to find the local minimum in Gibbs energy. Optionally carry out stability analysis with isothermal flash to find the global minimum.

- Re-evaluate the Q-function, if it has increased then accept the step and check for convergence, otherwise use a line search in temperature until the Q-function has increased.
- 5. If converged then carry out stability analysis if it has not yet been checked.

Stability analysis is a computationally expensive element of isothermal flash calculations, in particular when multiple phases are involved. In general it is best to avoid it when possible. However in a number of cases it is necessary to carry out stability analysis multiple times when maximising the Q-function.

The enthalpy and heat capacity of example 1 at 1 bar is presented in figure 3.1. When close to a phase boundary the heat capacity of phase change in equation 3.28 increases rapidly, with a discontinuity at the boundary. This can lead to poor convergence when using a Q-function maximisation in the region close to the phase boundary, and is the problematic region when carrying out reservoir simulation with temperature as a variable. An overstep leading to the removal of a phase can lead to increase in the Q-function (and Gibbs energy), even if the phase should be present at equilibrium. Often close to a phase boundary it is necessary to carry out stability analysis at multiple iterations to avoid the trivial solution.

Another case where it may be necessary to carry out stability analysis before reaching a local solution is demonstrated in figure 3.2. This figure shows the enthalpy of the LLE, VLE and VLLE solutions to the isothermal flash for example 1 at 1 bar.

In the range between -6700K < H/R < -5175K it is not possible to find a solution using only two phases. It is necessary to introduce a third phase (aqueous). Given only two phases the solution will oscillate between the VLE and LLE solutions. In some cases when using the partial Newton or full Newton method an intermediate two-phase solution can be found, though one phase is intrinsically unstable.

3.4 Results

We deal with a number of examples in the results section. These are summarised in table 3.1. Each mixture is modelled as either an ideal solution (IS), using the Peng Robinson (PR) EoS [135] or the SRK EoS [175]. A detailed description of each mixture is given in appendix B.

For the ideal solution we have only a single methodology to solve the isenthalpic flash problem given in the implementation. This was limited to using only 25 iterations before



Fig. 3.1 The enthalpy and combined heat capacity (of both the pure phases and of phase change), for example 1 between 200K and 500K at 1 bar. Equation 3.27 is $-T^2 \times$ the combined heat capacity. Change from LLE to VLLE at 322.1K and from VLLE to VLE at 365.8K correspond to the discontinuities in the combined heat capacity.



Fig. 3.2 The enthalpy of the VLE, LLE and VLLE solutions to the isothermal flash at 1 bar between 200K-500K for example 1. It is not possible to meet an enthalpy constraint between H/R=-5175K and H/R=-6700K with only two phases.

	Components	Max phases	System description	Model
Example 1	20	3	heavy oil and water	PR
Example 2	7	3	synthetic oil and water	IS
Example 3	7	2	natural gas	SRK
Example 4	2	2	C_1 & n C_4 , narrow boiling	PR
Example 5	5	3	oil and water	PR
Example 6	5	4	$C_1, C_2, C_3, CO_2, H_2S$	SRK
Example 7	2	3	n-butane and water	PR

Table 3.1 Summary of mixtures considered in this work

a backup nested loop approach was used. To demonstrate the convergence of the ideal solution isenthalpic flash implementation example 1 is considered with the Wilson K-factor approximation (assuming only two phases), with the residual enthalpy found from equation 3.15. The ideal solution flash problem was solved using the implementation given at an enthalpy of H/R = -4000K and pressure of P = 20bar. An initial estimate of T = 300K and $\beta = 0.5$ was used. The temperature and vapour phase fraction are shown in figure 3.3 with the solution found to a tolerance in the l_2 norm of the system of equations less than 10^{-10} . On the fourth iteration the vapour phase was re-introduced and increased in fraction to $\beta = 0.345$ at the solution temperature of T = 511.2K. Even with a very poor initial estimate for the temperature, it is clear that the given implementation of isenthalpic flash can solve the phase split calculation rapidly.



Fig. 3.3 Convergence for ideal solution approximation of example 1. Initial estimate of $\beta = 0.5$ and T = 300K and a solution of $\beta = 0.345$ and T = 511.2K.

To demonstrate that the method can work over a larger range of conditions example 2 was flashed using a small step in enthalpy and pressure over a range of -6000K < H/R <

5000K (with a reference temperature of $T_{ref} = 300K$) and 1bar < P < 100bar. This approximately corresponds to temperatures of 120K-700K. The water in the oleic phase and the aqueous phase were modelled using equations 3.29 and 3.30. Two million isenthalpic flash conditions in total were specified and solved using the ideal solution implementation described above. To compare the computational cost of the method with isothermal flash, the solution temperature and specified pressure were used with the algorithm presented in Michelsen and Mollerup [117] chapter 11. The phase envelope and number of iterations to solve the ideal solution isothermal and isenthalpic flash are presented in figure 3.4. Each iteration is considered as solving for the Newton step.



Fig. 3.4 Comparison of the number of iterations necessary to solve the isenthalpic and isothermal flash for example 2. The colour indicates the number of iterations required to find the solution, with different scaling on the colours used.

Figure 3.4 shows that in most of the region scanned the number of iterations necessary is very small, this is despite a constant initialisation temperature of T = 300K which is very far from the solution at some specifications. Problems are encountered when close to the critical temperature of each component. This is noticeable on figure 3.4 where an increase in the number of iterations follows the isotherms close to the critical temperature of each component. The cause of this is the model used for the residual enthalpy which decreases to zero at the critical temperature (causing a small discontinuity in the heat capacity).

The ideal solution isenthalpic flash cost approximately 3.3 times as much as the ideal solution isothermal flash. Using only a nested isothermal flash for isenthalpic flash, the cost was 4.8 times more than the isothermal flash. The large increase in the cost of isenthalpic flash is due to the repeated evaluation of the fugacity coefficients and enthalpy
at each iteration and initial estimate of temperature being far from the solution. Isothermal flash only requires a single evaluation of the fugacity coefficients. When using the ideal solution model, the flash is only a small contribution to the overall simulation cost and the proposed method should be sufficient. Using an EoS is significantly more computationally demanding.

For the remaining examples (and example 1) an EoS is used to evaluate the fugacity coefficients and residual enthalpy. For compositional reservoir simulation the flash calculations may limit the size of the reservoir simulation. For isenthalpic flash to be viable it is necessary that the increase in computational cost is not prohibitive when compared to isothermal flash. For each of the examples a large region of the phase envelope was scanned and the time to carry out an isenthalpic flash recorded. At the solution temperature the problem was re-initialised and an isothermal flash was carried out for comparison.

To compare the results it is necessary to clarify the implementation details. The Wilson K-factor was used for initialisation, with an aqueous phase introduced if water was present in the example as described by equations 3.29 and 3.30. Following initialisation 5 partial Newton steps were used, with phases removed where necessary. If oscillations were detected then a new phase was introduced if possible or a switch to Q-function maximisation made. The solution was found using the full Newton method, with a limit of $(F - 1) \times 10$ steps before it was deemed a failed point and a switch made to Q-function maximisation, where each step is counted as the evaluation of the Newton step.

For isothermal flash the same Wilson K-factor approximation was used at the solution temperature to the isenthalpic flash. The initial estimate was improved using 3 steps of successive substitution followed by a switch to a second order minimiser. For two phases the ideally scaled restricted step was used [117]. For the multiphase case there is no ideal scaling factor, there are various possible implementations, often with Murray's method of lines preferred. Here we chose to use a trust region implementation with the Hessian described in Michelsen [110]. This often lead to more decompositions than using only a perturbed decomposition, however the number of iterations is similar (where each iteration is counted as the evaluation of the Newton step not once per decomposition).

The wall clock time of the isenthalpic flash, Q-function maximisation alone and isothermal flash was recorded. Each method was implemented in FORTRAN and the wall clock time of each method recorded along with the number of iterations. The results for each of the considered examples is given in table 3.2. Example 7 is not included as there is no 3-phase region in (P, T) space. The cost of each method is given relative to the cost of

the isothermal flash. A switch to Q-function maximisation was necessary in less than 1% of the cases.

Mixture	Cost relative to (P, T) flash			
	(P, H) Flash	Q-Function		
Example 1	1.12	3.77		
Example 3	1.65	5.39		
Example 4	1.75	10.84		
Example 5	1.63	5.64		
Example 6	1.71	6.34		

Table 3.2 Computational cost comparison of (P, H) and (P, T) flash

The phase envelope of example 3 is shown in figure 3.5 alongside the number of isothermal and isenthalpic flash iterations. This example is a relatively simple natural gas, it is relatively narrow boiling but would not present significant challenges when solved using a nested isothermal flash. In total isenthalpic flash required 1.07 times as many iterations as isothermal flash. All examples required between 1.05 - 1.3 times as many iterations for isenthalpic as isothermal flash over the full phase envelope.



Fig. 3.5 Comparison of the number of iterations necessary for isothermal flash and isenthalpic flash for example 3. The iteration counter is for only the second order method used.

The number of second order iterations required for (P, T) and (P, H) flash is small over most of the phase envelope. In the close to critical region both isothermal and isenthalpic flash require more iterations, though in total only a tiny fraction (0.01%) require a switch to Q-function maximisation. It is noticeable that outwith the two-phase region isothermal flash uses no iterations while isenthalpic flash often requires a small number. This is because with isothermal flash the Gibbs energy of the feed mixture composition can be compared with the initial estimate from the Wilson K-factor approximation and the estimate discarded if the two-phase Gibbs energy is greater than the single phase Gibbs energy. However this is not possible in isenthalpic flash, which must continue until the phase is removed by an iteration of the partial Newton method, which in some cases uses a small number of full Newton steps before it is clear that the phase can be safely removed.

Although table 3.2 indicates that the cost of Q-function maximisation is between 5-6 times greater than (P, T) flash, if the stability analysis used is tuned for the mixture then the cost can be significantly reduced. For example 3 it is necessary only to carry out stability analysis for one gas and one liquid estimate (e.g. from the Wilson K-factor approximation). Doing this reduces the cost for this example from 5.39 to 3.1 times greater than isothermal flash. Similar results are found for examples 1, 5, and 6.

Example 4 is a narrow boiling mixture, it is therefore difficult to solve using a nested isothermal flash. This can be viewed in table 3.2. Close to the bubble curve the phase fraction of vapour changes very rapidly from 0 to 0.99 in (P, T) space as the methane component evaporates. In this region the Hessian of the Q-function (equation 3.27) changes rapidly with the temperature (and is discontinuous at the phase boundary) in a manner similar to that shown in figure 3.1. This leads to oversteps, or understeps increasing the number of iterations necessary. The phase envelope and number of iterations required for (P, T) flash and (P, H) flash is given in figure 3.6.



Fig. 3.6 Comparison of the number of iterations necessary for isothermal flash and isenthalpic flash for example 4. The iteration counter is for only the second order method.

Solving the isenthalpic flash problem directly for this mixture is often successful. The mixture is narrow boiling in that for a very small change in temperature there is a very large change in enthalpy, however this is not a problem if we specify the enthalpy. A large change in enthalpy will only lead to a relatively small change in temperature and the problem can be solved quite easily. The additional cost of isenthalpic flash is not significantly different from the other mixtures for this narrow boiling example. For the Q-function maximisation oversteps were common and often it was necessary to use a fully robust implementation with stability analysis carried out at every iteration.

Example 5 is a mixture containing water. This mixture contains a heavy oil pseudocomponent and a light gas pseudo-component along with two intermediate components, and is typical of what may be used for the simulation of thermal recovery with a light solvent component. The phase envelope is given in figure 3.7. For this example the modified initialisation procedure including water was used.



Fig. 3.7 Comparison of the number of iterations necessary for isothermal flash and isenthalpic flash for example 5. The iteration counter is for only the second order method.

Using the modified initialisation procedure ensures that the heavy oil mixtures with water can be dealt with without any additional difficulty. The only region with a significant increase in the number of iterations when compared with the isothermal flash is the close to critical VLE region. In this region the initial estimate may indicate multiple phases, which must be removed before more accurate initial estimates are generated from stability analysis, and it is often necessary to switch to Q-function maximisation. Close to the VLLE to LLE and VLLE to VLE boundary there is not a significant change in the number of iterations.

Example 1 is similar to example 5 but with a larger number of components and less light components. Over the full phase envelope the conclusions are the same as example 5, with difficulty only in the close to critical region. However table 3.2 shows that the computational cost is much closer to that for isothermal flash. This is in part due to the increased number of components, the dominant term in the computational cost is the decomposition of the Jacobian (or Hessian) in this example. These are almost of the same size and therefore differ only slightly in cost. Though the additional cost compared to isothermal flash is moderate, the use of 20 components is often prohibitively expensive for reservoir simulation.

A more complex system is considered in example 6. This is not relevant to heavy oil reservoir simulation but does test the generality of the implementation for isenthalpic flash. Up to four phases can co-exist at low temperatures. The hydrogen sulphide, carbon dioxide and methane can each form a separate nearly pure phase along with a vapour phase. The region where up to four phases are in equilibrium is presented in figure 3.8 along with the number of iterations for convergence with the presented implementation of isenthalpic flash.



Fig. 3.8 Phase envelope and number of (P, H) flash iterations necessary. The enthalpy range corresponds to temperatures between 110K and 200K. The backup Q-function maximisation was necessary in 10% of cases.

The initialisation was based on the two-phase Wilson K-factor approximation. To introduce each of the remaining liquid phases it was necessary to carry out stability analysis. Without a good initial estimate for each of the new phases there is a significantly larger number of switches to Q-function maximisation (10% in this example). The region where this happened most often is visible in figure 3.8 as the region where more than 15 iterations were often necessary. Table 3.2 presents the computational time over the region of 1bar < P < 120bar and -2000K < H/R < 1000K where the cost, and number of switches to Q-function maximisation, was similar to other mixtures. Over the region presented in figure 3.8 the computational cost of isenthalpic flash was 2.3 times the cost of isothermal flash.

Example 7 is an equimolar mixture of water and n-butane. Often this mixture can have more phases present in equilibrium than components. The (P, H) phase envelope for the mixture is given in figure 3.9, this figure also shows the number of second order isenthalpic flash iterations necessary to solve the phase split calculation.



Fig. 3.9 Heat plot showing the number of second order iterations necessary to solve the phase split problem for an equimolar mixture of water and butane. The three phase region corresponds to a discontinuity in the enthalpy in the (P,T) space. The (P,H) region scanned corresponds to a temperature range of 300K to 580K.

Even in the region where there are more phases than components there are no significant problems encountered using the proposed methods. Q-function maximisation was used in less than 0.1% of cases. There are an increased number of iterations at the boundary between VLE and LLE and the boundary between two and three phases. This is often due to the introduction and removal of phases. When the initialisation, or stability analysis, indicated that more phases than components were necessary the type of root desired from the EoS was selected. This is a simple and effective way to deal with the case where there are more phases than components.

3.5 Conclusion

A new method and algorithm have been described to solve the ideal solution isenthalpic flash. With the combination of a nested isothermal flash the ideal solution isenthalpic flash is convergent in all tested cases. The ideal solution is commonly used in reservoir simulations. The cost of ideal solution isenthalpic flash is greater than that for isothermal flash, for the tested case the time for isenthalpic flash was around 3 times greater than isothermal flash. However the ideal solution flash often does not dominate reservoir simulation costs and with the given implementation can more easily deal with narrow boiling mixtures which may cause problems if temperature was used as a variable.

An extension of the two-phase Newton's method to the multiphase isenthalpic flash problem has been presented. This can be simplified using an ideal solution approximation to a partial Newton method. As a backup a robust Q-function maximisation is used. An implementation has been described which enables the addition and removal of phases during the course of iterations. The cost of isenthalpic flash using the described procedure is 1.1 to 2.3 times that of isothermal flash for the tested cases.

When using a partial Newton method early iterations can be slower than direct substitution. An update based on the equilibrium K-factors and the Rachford-Rice equations is presented which improves early iterations, and is well suited when there is a large deviation between component fugacities in different phases. Using this update a composition estimate is available for a phase that has been removed, this is useful for re-introduction of the phase or for checking its stability once the phase split calculation is concluded.

The Q-function maximisation was considered for multiphase isenthalpic flash. When using only a local minimum in the Gibbs energy the method is only marginally more computationally expensive than the presented isenthalpic flash. However a number of cases were used to demonstrate that it is often necessary to repeatedly carry out stability analysis to obtain the solution, leading to a restrictively slow implementation. The full cost of Q-function maximisation was 3-11 times more than isothermal flash. The Q-function maximisation should only be used as a backup, in particular for narrow boiling type mixtures.

For thermal simulation of an oil reservoir a third aqueous phase can be introduced during the initialisation. This makes the method convergent in a larger number of examples without resorting to Q-function maximisation. The cost of three-phase isenthalpic flash is very similar to three-phase isothermal flash using this initialisation method.

A narrow boiling example was considered and it was demonstrated that due to the narrow boiling nature in (P, T) space, Q-function maximisation struggles to find the solution. However when solving the equilibrium equations directly in (P, H) space, there is no problem with the presented method. This is the main benefit of using isenthalpic flash instead of isothermal flash.

A complex multiphase problem was investigated, and in the region where up to four phases were in equilibrium it was demonstrated that the isenthalpic flash could be solved rapidly and robustly. An increased number of switches to Q-function maximisation were necessary, however with a better initialisation (e.g. from a previous time-step) this would not be the case. The overall speed was around half the speed for isothermal flash for this complex example.

Finally a case where more phases than components are present in equilibrium was examined. It was shown that the presented implementations can easily deal with this case, though a comparison with isothermal flash is not possible. These cases are rarely encountered and the main difference between them and a narrow boiling mixture is that the root from the EoS must be selected.

Overall, the study in this chapter presents how to handle the general multiphase isenthalpic flash problem and how to adjust the method for heavy oil-water systems encountered in thermal recovery simulation. For the special case where ideal solution thermodynamics is used, a simple formulation is proposed to solve the problem. Although the focus of this paper is on multiphase isenthalpic flash, the methods discussed here can be easily extended to multiphase flash with other state function based specifications (e.g. (P, S), (V, T), (V, U) and (V, S)).

Chapter 4

Modified RAND Framework for Phase Split Calculations

4.1 Introduction

The classical example of the phase equilibrium problem is isothermal flash, with the temperature, pressure, and molar feed specified. This is at the heart of many process and reservoir simulation tools. The conventional approach to solve the isothermal flash problem involves alternating use of stability analysis [9] and phase split calculation, as described in section 1.3. Stability analysis based on the tangent plane distance criterion can in principle be used to determine if the current state is a global minimum in the Gibbs energy. The method proposed by Michelsen [109] and its variants are widely used for stability analysis in practical calculations. The problem is essentially a global search over all possible trial compositions and one can resort to global optimisation methods [75, 103]. Such methods are generally too expensive to use for multicomponent systems. The phase split calculation solves the equilibrium equations given a number of phases, the solution corresponds to the local minimum in the Gibbs energy [110]. If there is no advance knowledge about the maximum number of phases in a system, it is necessary to check the local minimum from the phase split calculation with stability analysis to ensure the Gibbs energy cannot be reduced further by the introduction of a new phase.

Chemical reaction equilibrium has the same equilibrium criterion as only physical (phase) equilibria, i.e. minimum in the Gibbs energy at a given temperature and pressure, although the calculation methods for the two types of equilibria have largely been developed separately. Smith and Missen [174] provide an excellent summary of the classical methods for chemical reaction equilibrium calculations. They distinguish between stoichiometric methods and non-stoichiometric methods. Among the non-stoichiometric ones, the RAND approach [197] was discussed under the category of Brinkley-NASA-RAND (BNR) algorithms [18, 77, 197]. They showed the RAND approach could be applied to a single phase reaction for ideal solution systems. The approach can also be extended to multiphase ideal solution systems with reactions. For ideal solution systems, the system of equations can be reduced to E + F linear equations, where E is the number of elements in the system and F the number of phases. Smith and Missen [174] gave a short discussion on the extension of RAND to non-ideal systems by providing the linearised equilibrium equation (first step of the RAND algorithm) for a single-phase system and the element balance equation. This results in C + E equations. No further discussion is given in their book on how to solve these equations. If there are F phases, the number of equations will become CF + E. Since chemical reaction systems often involve a large number of species such an approach can be impractical for a single phase [65]. Greiner [65] provided a practical approach to use RAND for non-ideal solutions, reducing the number of equations to E + F. A possible variant of Greiner's non-ideal RAND formulation and its extension to multiple phases was briefly outlined in the book of Michelsen and Mollerup [117].

There are numerous studies on chemical reaction equilibrium. In terms of flash algorithms with chemical reaction equilibirum, apart from those mentioned above or already summarised in Smith and Missen [174], several other important contributions include Gautam and Seider [62], Castier et al. [24], Michelsen [112], Perez Cisneros et al. [138], and Phoenix and Heidemann [145]. Although the method of Castier et al. [24] gives second order convergence, it is prone to problems caused by round-off errors. Another large category of calculation methods is global optimisation, such as McDonald and Floudas [103], McDonald and Floudas [104], Bonilla-Petriciolet and Segovia-Hernández [14] and Bonilla-Petriciolet et al. [13]. Similar to global optimisation for stability analysis, global optimisation for chemical reaction equilibrium is much less efficient and requires a huge number of iterations. Some recent algorithmic studies are reviewed by Bonilla-Petriciolet et al. [13].

A problem related to the isothermal flash equilibrium problem are the general state function based specification flash. The isenthalpic based flash is discussed in detail in chapter 3, however there are six state function based flash specifications as described in table 1.2 (where the (U, S, V, n) and (H, S, P, n) surfaces can be described using either the entropy, internal energy or enthalpy). Each of these specifications and a potential use is presented in table 4.1. How to solve each of these state function based flash specifications for two phases is discussed by Michelsen [115] who presented a Q-function maximisation with the isothermal flash nested in an inner loop. Another approach was also presented by Michelsen [115] who demonstrated that a similar Q-function approach could be used if the conventional (P, T) thermodynamics were abandoned in favour of the natural variables to solve an EoS (V, T). Numerous implementations to solve the (P, T) phase split problem using (V, T) based thermodynamics have been presented with early work given by Nagarajan et al. [124]. This area of research is of particular interest when using more complex EoS's [136], where the solution to the density root described in section 1.2 is more complex.

Flash specification	State function	Example use
(P,T)	G	Commonly used for transient simulation
(V,T)	A	Storage tank model
(P,H)	-S	Steady state flow
(P, S)	H	Reversible expansion and compression
(V, U)	-S	Unsteady state flow
(V,S)	U	None yet but fits the general scheme

Table 4.1 State function and associated flash specification

In this chapter we will first introduce a new modified RAND framework. An in detail discussion on the modified RAND method is given in section 4.2 where the isothermal flash will be considered in the presence of chemical reactions and the simplifications when there are no reactions is given. A detailed implementation is given in section 4.2.1 and a suggested procedure for correcting ascent steps given in section 4.2.2.

The extension to specifications other than (P, T) is also given. First we will consider how the state function based flash specifications can be solved using (P, T) based thermodynamics with the new modified RAND framework. This is done in section 4.3 in a manner similar to Michelsen [115] with the final matrix being general for all of the state function based flash specifications, even in the presence of chemical reactions.

The use of (P, T) based thermodynamics will be abandoned in section 4.4 where first vol-RAND will be presented. This method co-solves the pressure explicit EoS with the equilibrium equations. This is particularly useful for complex EoS's such as CPA or PC-SAFT. Vol-RAND can be used to solve both the (P, T) flash and the (V, T) flash using a suitable objective function. A generalisation based on vol-RAND is presented in section 4.4.2. This method has not been tested but presents a method to solve each of the state function based flash specifications by solving the EoS at the state function variables rather

than using them as a constraint. Some results for modified RAND and vol-RAND are presented in section 4.5.

4.2 Modified RAND formulation

Using the conventional (P, T) based thermodynamics the equilibrium equation 1.25 allow the isothermal phase split problem to be posed as a minimisation of the Gibbs energy given an arbitrary number of phases F:

$$\min G(T, P, \mathbf{n}) = \sum_{i=1}^{C} \sum_{j=1}^{F} \mu_{i,j} n_{i,j}$$
(4.1)

subject to the equality constraints, which in the presence of chemical reactions differs from equation 1.26. The components are not conserved but some reaction invariant elements are, leading to an elemental balance:

$$\sum_{i=1}^{C} \mathcal{A}_{l,i} \left(\sum_{j=1}^{F} n_{i,j} \right) - \hat{b}_l = 0, \quad l = 1, 2, ..., E$$
(4.2)

and inequality constraints (i.e. that no component can be present in a phase in a negative amount):

$$n_{i,j} \ge 0, \quad i = 1, 2, ..., C, \quad j = 1, 2, ..., F$$
(4.3)

The chemical potential described in equation 4.1 can be split into

$$\mu_{i,j} = \mu_i^0 + RT \ln \hat{f}_{i,j} = \mu_i^0 + RT (\ln x_{i,j} + \ln \hat{\varphi}_{i,j} + \ln P)$$
(4.4)

In the absence of chemical reactions it is possible to drop the reference state contribution to the chemical potential μ_i^0 . The Lagrangian for the constrained minimisation (equations 4.1 and 4.2) is:

$$\mathcal{L}(\boldsymbol{n}, \hat{\boldsymbol{\lambda}}) = \sum_{j=1}^{F} \sum_{i=1}^{C} n_{i,j} \mu_{i,j} - \sum_{l=1}^{E} \hat{\lambda}_l \left(\sum_{i=1}^{C} \mathcal{A}_{l,i} \left(\sum_{j=1}^{F} n_{i,j} \right) - \hat{b}_l \right)$$
(4.5)

where $\hat{\lambda}$ are the Lagrange multipliers and are equivalent to the equilibrium elemental potential [117]. The stationarity equations of 4.5 are:

$$\frac{\partial \mathcal{L}}{\partial n_{i,j}} = \mu_{i,j} - \sum_{l=1}^{E} \hat{\lambda}_l \mathcal{A}_{l,i} = 0, \quad \forall i, j$$
(4.6)

and

$$\frac{\partial \mathcal{L}}{\partial \hat{\lambda}_l} = -\sum_{i=1}^C \mathcal{A}_{l,i} \left(\sum_{j=1}^F n_{i,j} \right) + \hat{b}_l = 0, \quad \forall l$$
(4.7)

where equation 4.6 describes the equilibrium in the presence of chemical reactions and is similar to equation 1.25 and equation 4.7 describes the elemental balance.

We aim to use Newton's method to perform phase split calculations. To do so we first linearise equation 4.6 around the current composition, temperature, and pressure, then divide by RT to obtain for each phase

$$\frac{\mu_{i,j}}{RT} + \frac{1}{RT} \sum_{k=1}^{C} \frac{\partial \mu_{i,j}}{\partial n_{k,j}} \Delta n_{k,j} + \frac{1}{RT} \frac{\partial \mu_{i,j}}{\partial T} \Delta T + \frac{1}{RT} \frac{\partial \mu_{i,j}}{\partial P} \Delta P - \sum_{l=1}^{E} \lambda_l \mathcal{A}_{l,i} = 0 \quad (4.8)$$

with $\lambda_l = \hat{\lambda}_l / (RT)$. The Gibbs energy is a homogeneous function of degree one in the molar amounts of the components, an immediate consequence of which is:

$$\boldsymbol{n}_j^T \frac{\partial \boldsymbol{\mu}_j}{\partial n_{i,j}} = 0, \quad \forall i$$

commonly referred to as the Gibbs-Duhem equation. Equivalently this can be written as

$$\frac{\partial \boldsymbol{\mu}_j}{\partial \boldsymbol{n}_j} \boldsymbol{n}_j = \boldsymbol{0}, \quad \forall j$$
(4.9)

demonstrating that the matrix from the second term of equation 4.8 is singular with the vector of molar amounts of each component, n_j , lying in the null-space of the matrix. A consequence of this is that we cannot immediately isolate the composition correction from equation 4.8. Instead it is possible to use the description of the chemical potential, equation 4.4, and its derivative to split the matrix as:

$$\frac{1}{RT}\frac{\partial\mu_{i,j}}{\partial n_{k,j}} = \frac{\delta_{i,k}}{n_{i,j}} - \frac{1}{\beta_j} + \frac{\partial\ln\hat{\varphi}_{i,j}}{\partial n_{i,j}}$$
(4.10)

Here we introduce a matrix m_i for each phase with an element of this matrix defined by:

$$m_{i,k,j} = \beta_j \left(\frac{1}{RT} \frac{\partial \mu_{i,j}}{\partial n_{k,j}} + 1 \right) = \frac{\delta_{i,k}}{x_{i,j}} + \beta_j \frac{\partial \ln \hat{\varphi}_{i,j}}{\partial n_{k,j}}$$
(4.11)

Rewriting equation 4.8 in vector-matrix format:

$$(\boldsymbol{m}_j - \boldsymbol{1}\boldsymbol{1}^T) \Delta \boldsymbol{n}_j = \beta_j \left(\boldsymbol{\mathcal{A}}^T \boldsymbol{\lambda} - \frac{\boldsymbol{\mu}_j}{RT} - \boldsymbol{e}_j \Delta T - \boldsymbol{\gamma}_j \Delta P \right)$$
 (4.12)

with $\mathbf{11}^T$ the matrix of ones. For convenience we have defined:

$$\boldsymbol{e}_{j} = \frac{1}{RT} \frac{\partial \boldsymbol{\mu}_{j}}{\partial T}, \text{ and } \boldsymbol{\gamma}_{j} = \frac{1}{RT} \frac{\partial \boldsymbol{\mu}_{j}}{\partial P}$$
 (4.13)

Using the relation $\mathbf{1}^T \boldsymbol{n}_j = \beta_j$, we obtain:

$$\boldsymbol{m}_{j}\Delta\boldsymbol{n}_{j} = \mathbf{1}\Delta\beta_{j} + \beta_{j}\left(\boldsymbol{\mathcal{A}}^{T}\boldsymbol{\lambda} - \frac{\boldsymbol{\mu}_{j}}{RT} - \boldsymbol{e}_{j}\Delta T - \boldsymbol{\gamma}_{j}\Delta P\right)$$
(4.14)

From the Gibbs-Duhem equation (4.9) it is clear that $m_j x_j = 1$ and therefore $M_j 1 = x_j$, with $M_j = m_j^{-1}$. These relations are used to isolate the composition correction to each phase:

$$\Delta \boldsymbol{n}_{j} = \boldsymbol{x}_{j} \Delta \beta_{j} + \beta_{j} \boldsymbol{M}_{j} \left(\boldsymbol{\mathcal{A}}^{T} \boldsymbol{\lambda} - \frac{\boldsymbol{\mu}_{j}}{RT} - \boldsymbol{e}_{j} \Delta T - \boldsymbol{\gamma}_{j} \Delta P \right)$$
(4.15)

Multiplying equation 4.15 by $\mathbf{1}^T$ from the left we obtain:

$$\Delta\beta_j = \mathbf{1}^T \Delta \boldsymbol{n}_j = \mathbf{1}^T \left(\boldsymbol{x}_j \Delta\beta_j + \beta_j \boldsymbol{M}_j \left(\boldsymbol{\mathcal{A}}^T \boldsymbol{\lambda} - \frac{\boldsymbol{\mu}_j}{RT} - \boldsymbol{e}_j \Delta T - \boldsymbol{\gamma}_j \Delta P \right) \right)$$
(4.16)

Using the relations $\mathbf{1}^T \boldsymbol{x}_j = 1$ and $\mathbf{1}^T \boldsymbol{M}_j = \boldsymbol{x}_j^T$, the $\Delta \beta_j$ cancel to leave:

$$\boldsymbol{x}_{j} \left(\boldsymbol{\mathcal{A}}^{T} \boldsymbol{\lambda} - \boldsymbol{e}_{j} \Delta T - \boldsymbol{\gamma}_{j} \Delta P \right) = g_{j}, \quad \forall j$$
 (4.17)

with g_j is the molar reduced Gibbs energy

$$g_j = \frac{1}{RT} \sum_{i=1}^{C} x_{i,j} \mu_{i,j}$$
(4.18)

Linearisation around the elemental balance, equation 4.7 yields for each element:

$$\sum_{i=1}^{C} \mathcal{A}_{l,i} \left(\sum_{j=1}^{F} \left(n_{i,j} + \Delta n_{i,j} \right) \right) - \hat{b}_l = 0$$
(4.19)

Given a composition which meets the elemental balance, equation 4.19 can be rewritten for all elements as

$$\mathcal{A}\left(\sum_{j=1}^{F} \Delta \boldsymbol{n}_{j}\right) = \boldsymbol{0} \tag{4.20}$$

Substitution of equation 4.15 into equation 4.20 we obtain

$$\mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}M_{j}\right)\mathcal{A}^{T}\lambda + \mathcal{A}X\Delta\beta - \mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}M_{j}e_{j}\right)\Delta T - \mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}M_{j}\gamma_{j}\right)\Delta P = \mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}M_{j}\frac{\mu_{j}}{RT}\right) \quad (4.21)$$

with $X = (x_1, x_2, ..., x_F)$. For the isothermal flash equilibrium problem we specify the pressure and temperature. In this case the ΔP and ΔT terms can be set equal to zero. This simplifies equation 4.15 to:

$$\Delta \boldsymbol{n}_j = \boldsymbol{x}_j \Delta \beta_j + \beta_j \boldsymbol{M}_j \left(\boldsymbol{\mathcal{A}}^T \boldsymbol{\lambda} - \frac{\boldsymbol{\mu}_j}{RT} \right)$$
(4.22)

and equation 4.17 to:

$$\boldsymbol{X}^T \boldsymbol{\mathcal{A}}^T \boldsymbol{\lambda} = \boldsymbol{g} \tag{4.23}$$

with eequation 4.21 given by:

$$\mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}M_{j}\right)\mathcal{A}^{T}\lambda + \mathcal{A}X\Delta\beta = \mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}M_{j}\frac{\mu_{j}}{RT}\right)$$
(4.24)

These E + F equations, 4.23 and 4.24, relate the E + F variables $(\lambda, \Delta\beta)$ in isothermal multiphase flash required in equation 4.22. The system of equations to be solved for isothermal flash is:

$$\begin{pmatrix} \mathcal{A} \sum_{j=1}^{F} \beta_j M_j \mathcal{A}^T & \mathcal{A} X \\ (\mathcal{A} X)^T & \mathbf{0} \end{pmatrix} \begin{pmatrix} \boldsymbol{\lambda} \\ \Delta \boldsymbol{\beta} \end{pmatrix} = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$$
(4.25)

with

$$\boldsymbol{u}_{1} = \boldsymbol{\mathcal{A}}\left(\sum_{j=1}^{F} \beta_{j} \boldsymbol{M}_{j} \frac{\boldsymbol{\mu}_{j}}{RT}\right)$$

$$\boldsymbol{u}_{2,j} = \sum_{i=1}^{C} x_{i,j} \frac{\mu_{i,j}}{RT}, \quad \forall j$$
(4.26)

The update to the molar amounts of the components in each phase is then found from equation 4.22.

In the absence of chemical reactions it is possible to make a number of simplifications. The elemental feed becomes the component feed $b_i = z_i$, the formula matrix is the identity matrix $\mathcal{A} = \mathbf{I}$, and the reduced chemical potential can be replaced by the fugacity $\ln \hat{f}_j$ for each phase. The matrix in equation 4.25 reduces to

$$\begin{pmatrix} \sum_{j=1}^{F} \beta_j M_j & \mathbf{X} \\ \mathbf{X}^T & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{\lambda} \\ \Delta \mathbf{\beta} \end{pmatrix} = \begin{pmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \end{pmatrix}$$
(4.27)

with

$$\boldsymbol{u}_{1} = \sum_{j=1}^{F} \beta_{j} \boldsymbol{M}_{j} \ln \boldsymbol{\hat{f}}$$

$$\boldsymbol{u}_{2,j} = \sum_{i=1}^{C} x_{i,j} \ln \boldsymbol{\hat{f}}, \quad \forall j$$
(4.28)

An ideal solution approximation, as described in section 1.3, can be arrived at by assuming the composition derivatives of the fugacity coefficient are equal to zero. In this case the M_j matrix becomes diagonal with elements $x_{i,j}$. Therefore the top left $C \times C$ elements of matrix 4.27 are replaced by

$$\sum_{j=1}^{F} \beta_j \boldsymbol{M}_j = \boldsymbol{Z} \tag{4.29}$$

with Z a diagonal matrix with elements z_i . Instead of factorising the full RAND matrix, it is possible to reduce the size of the system of equations to be solved from C + F to F:

$$-\left(\boldsymbol{X}^{T}\boldsymbol{Z}^{-1}\boldsymbol{X}\right)\Delta\boldsymbol{\beta}=\boldsymbol{u}_{2}-\boldsymbol{X}^{T}\boldsymbol{Z}^{-1}\boldsymbol{u}_{1}$$
(4.30a)

$$\boldsymbol{\lambda} = \boldsymbol{Z}^{-1} \left(\boldsymbol{u}_1 - \boldsymbol{X} \Delta \boldsymbol{\beta} \right) \tag{4.30b}$$

Because Z is diagonal, no matrix inversion is needed. These equations 4.30 can be used as an alternative to the multiphase Rachford-Rice of Michelsen [114], either for successive substitution or as a partial Newton method with the fugacity coefficients updated at each iteration.

Although the method is derived using constrained minimisation, the convergence can be monitored using the Gibbs energy since the linear elemental balance constraints are satisfied at each iteration. Following an increase in the Gibbs energy line search can be used to find a suitable correction. Given a suitable initial estimate, the rate of convergence will be quadratic, in fact for the same initial estimate the update from modified RAND will be identical to the conventional method. The method is well suited to multiphase calculations as all components in all phases are treated in the same manner (unlike in the conventional method). This leads to a well structured and simple implementation.

4.2.1 Isothermal flash Implementation

The structure of the modified RAND procedure allows for chemical reactions to be easily incorporated, however for simplicity the following implementation is described in the absence of chemical reactions for F phases:

1. Calculate the total molar amount of each phase

$$\beta_j = \sum_{i=1}^C n_{i,j}$$

and the composition vectors

$$m{x}_j = m{n}_j / eta_j$$

Collect the composition vectors into a matrix

$$X = (x_1, x_2, ..., x_F)$$

2. Using a suitable equation of state evaluate the fugacity and the scaled composition derivatives of the fugacity coefficients.

$$\ln \hat{f}_{i,j}, \quad \beta_j \frac{\partial \ln \hat{\boldsymbol{\varphi}}_j}{\partial \boldsymbol{n}_j}$$

3. For each phase generate the matrix

$$oldsymbol{m}_j = \left(diag\left(rac{1}{oldsymbol{x}_j}
ight) + eta_j rac{\partial \ln \hat{oldsymbol{arphi}}_j}{\partial oldsymbol{n}_j}
ight)$$

and its inverse

$$oldsymbol{M}_j = oldsymbol{m}_j^{-1}$$

4. Form the system of equations

$$egin{pmatrix} \sum_{j=1}^F eta_j oldsymbol{M}_j & oldsymbol{X} \ oldsymbol{X}^T & oldsymbol{0} \end{pmatrix}$$

and the vectors

$$oldsymbol{u}_1 = \sum_{j=1}^F eta_j oldsymbol{M}_j \ln \hat{oldsymbol{f}}_j, \quad u_{2,j} = \sum_{i=1}^C x_{i,j} \ln \hat{oldsymbol{f}}_j \quad orall j$$

Then solve the symmetric system of equation to find the reduced equilibrium chemical potentials and the change in the phase molar amounts

$$egin{pmatrix} \sum_{j=1}^F eta_j M_j & oldsymbol{X} \ oldsymbol{X}^T & oldsymbol{0} \end{pmatrix} egin{pmatrix} oldsymbol{\lambda} \ \Deltaoldsymbol{eta} \end{pmatrix} = egin{pmatrix} oldsymbol{u}_1 \ oldsymbol{u}_2 \end{pmatrix}$$

5. Calculate the update to the mole amount of each component in each phase

$$\Delta \boldsymbol{n}_j = \boldsymbol{x}_j \Delta \beta_j + \beta_j \boldsymbol{M}_j \left(\boldsymbol{\mathcal{A}}^T \boldsymbol{\lambda} - \ln \hat{\boldsymbol{f}}_j \right)$$

6. Check that the step is in a descent direction in the Gibbs energy

$$\sum_{i=1}^{C} \sum_{j=1}^{F} \Delta n_{i,j} \ln \hat{f}_{i,j} < 0$$
(4.31)

If this inequality does not hold, then the Newton step is ascending in the Gibbs energy and a line-search will not lead to a reduction in the Gibbs energy, it is then necessary to modify the procedure and Newton step to a descent direction. This is dealt with in section 4.2.2. Otherwise given a suitable step length modifier the step will lead to a decrease in the Gibbs energy.

7. Take the step, ensuring there is a reduction in the Gibbs energy using a step length modifier if necessary. Check for convergence, if not converged then proceed to another iteration.

The logarithmic dependence of the chemical potential on the component mole fraction means that the inequality constraint can be easily met using a suitable step length modifier, or by using equations 3.31 to 3.35 for that component.

If a step shows that $-\Delta\beta_j > \beta_j$ then the phase may need to be removed from the current distribution to arrive at the local minimum in the Gibbs energy. This can be done using the method described in equations 3.31 to 3.35, or by fully solving the ideal solution approximation for example by using the algorithm described by Michelsen and Mollerup [117] in chapter 11.

4.2.2 Correction of the modified RAND step

For the (P, T) specification it is possible to monitor the convergence of the modified RAND method by using the system Gibbs energy. Each step should lead to a reduction in the Gibbs energy. In the majority of cases where the modified RAND correction corresponds to a descent direction, the proper stepping can be found through a line search. However in some rare cases the inequality given in equation 4.31 will not hold, in which case a line search between 0 and 1 will not lead to a reduction in the Gibbs energy.

During the iteration, if all phases are intrinsically stable (i.e. the Hessian of the Gibbs energy of a phase is not indefinite), the direction will be descending. If one or more phases are intrinsically unstable, the direction may become ascending in the Gibbs energy. An ascent direction can be revealed by checking equation 4.31. In general this inequality will only not hold in the near critical region or in some challenging multiphase mixtures.

An indefinite m matrix (corresponding to an unstable phase) will be revealed during the inversion of the m matrix (note the phase index is dropped in this discussion for convenience). It is possible to correct the direction to a descent direction by modifying the indefinite matrix to a positive definite one in a suitable manner. However an arbitrary correction to the m matrix will lead to the violation of the requirement that M1 = x which is used to obtain equation 4.15. An optimal correction is one which minimally impacts the positive curvature directions of the Hessian of the Gibbs energy, while correcting for the negative eigenvalue, and which does not violate the requirement of M1 = x. To find this update we first introduce a matrix \widetilde{Q} . The matrix m can be rewritten

$$\boldsymbol{m} = \boldsymbol{D}^{-1/2} \widetilde{\boldsymbol{Q}} \boldsymbol{D}^{-1/2} \tag{4.32}$$

where D is diagonal with elements x_i . The elements of \tilde{Q} are given by

$$\widetilde{Q}_{i,k} = \delta_{i,k} + \sqrt{x_i x_k} \frac{\partial \ln \hat{\varphi}_i}{\partial x_k}$$
(4.33)

For an ideal solution, all eigenvalues of this matrix equal 1. At the limit of intrinsic stability, exactly one eigenvalue is zero. The case of an indefinite M corresponds to one negative eigenvalue of \tilde{Q} (i.e. the phase is intrinsically unstable).

The numerically smallest eigenvalue of \widetilde{Q} can be evaluated using the inverse iteration

$$\widetilde{\boldsymbol{Q}}^{-1}\hat{\boldsymbol{u}} = \frac{1}{\lambda_{min}}\hat{\boldsymbol{u}}$$
(4.34)

with λ_{min} the minimum absolute eigenvalue and \hat{u} the corresponding normalised eigenvector. Equation 4.34 can be rewritten as:

$$\boldsymbol{D}^{1/2} \widetilde{\boldsymbol{Q}}^{-1} \boldsymbol{D}^{1/2} \boldsymbol{D}^{-1/2} \hat{\boldsymbol{u}} = \frac{1}{\lambda_{min}} \boldsymbol{D} \boldsymbol{D}^{-1/2} \hat{\boldsymbol{u}}$$
(4.35)

or equivalently,

$$\boldsymbol{D}^{-1}\boldsymbol{M}\hat{\boldsymbol{w}} = \frac{1}{\lambda_{min}}\hat{\boldsymbol{w}}, \quad \hat{\boldsymbol{u}} = \boldsymbol{D}^{1/2}\hat{\boldsymbol{w}}$$
 (4.36)

In general the numerically smallest eigenvalue of \widetilde{Q} is also negative. To correct for this negative eigenvalue we add to \widetilde{Q} the matrix $\epsilon \hat{u} \hat{u}^T$, where $\epsilon + \lambda_{min} = d > 0$. Here d is chosen to be a small positive number, e.g. 0.01. This corresponds to adding to \widetilde{Q}^{-1} the contribution $k\hat{u}\hat{u}^T$ with $k = 1/d - 1/\lambda_{min}$, and thus adding to M the contribution kvv^T , where $v_i = \hat{u}_i\sqrt{x_i}$. This update preserves the property $M\mathbf{1} = x$ due to the orthogonality of eigenvectors as both \hat{u} and \sqrt{x} are eigenvectors of \widetilde{Q} .

As we have already evaluated the matrix M, this eigenvalue and eigenvector are found with minimal additional effort. Substituting the corrected matrix into the system of equations for isothermal flash, equation 4.27, we obtain

$$\begin{pmatrix} \sum_{j=1}^{F} \beta_j \boldsymbol{M}_j & \boldsymbol{X} \\ \boldsymbol{X}^T & \boldsymbol{0} \end{pmatrix} \begin{pmatrix} \boldsymbol{\lambda} \\ \Delta \boldsymbol{\beta} \end{pmatrix} = \begin{pmatrix} \boldsymbol{u}_1 \\ \boldsymbol{u}_2 \end{pmatrix} + \hat{\alpha} \begin{pmatrix} \boldsymbol{v} \\ \boldsymbol{0} \end{pmatrix}$$
(4.37)

with

$$\hat{\alpha} = \beta_j k \boldsymbol{v}^T \left(\ln \hat{\boldsymbol{f}}_j - \boldsymbol{\lambda} \right)$$
(4.38)

The matrix on the left hand side is already available in a factorised form. The system of equations is solved to find

$$\begin{pmatrix} \boldsymbol{\lambda} \\ \Delta \boldsymbol{\beta} \end{pmatrix} = \begin{pmatrix} \boldsymbol{\lambda}_0 \\ \Delta \boldsymbol{\beta}_0 \end{pmatrix} + \hat{\alpha} \begin{pmatrix} \boldsymbol{\lambda}_1 \\ \Delta \boldsymbol{\beta}_1 \end{pmatrix}$$
(4.39)

The $\hat{\alpha}$ term is found from the closing equation

$$\hat{\alpha} = \beta_j k \boldsymbol{v}^T \left(\ln \hat{\boldsymbol{f}}_j - \boldsymbol{\lambda}_0 - \hat{\alpha} \boldsymbol{\lambda}_1 \right)$$
(4.40)

The update to the unstable phase is then calculated as:

$$\Delta \boldsymbol{x}_{j} = \boldsymbol{M}_{j} \left(\boldsymbol{\lambda} - \ln \hat{\boldsymbol{f}}_{j} \right) + k \boldsymbol{v}^{T} \left(\boldsymbol{\lambda} - \ln \hat{\boldsymbol{f}}_{j} \right) \boldsymbol{v}$$
(4.41)

$$\Delta \boldsymbol{n}_j = \boldsymbol{x}_j \Delta \beta_j + \beta_j \Delta \boldsymbol{x}_j \tag{4.42}$$

For the remaining phases the relation in equation 4.15 remains unchanged. We note that λ_0 and $\Delta\beta_0$ have already been evaluated to determine the direction in equation 4.31.

If the numerically smallest eigenvalue of \hat{Q} is positive additional steps will be necessary to identify the negative eigenvalue. If more than one matrix is indefinite then it may be necessary to correct all indefinite matrices. Such instances are rare in practical applications.

Though this correction is shown for only phase equilibria, the M matrix can in principle be updated in the same way and the procedure modified in a similar manner in the presence of chemical reactions. The update will preserve the property M1 = x and will not require the re-factorisation or inversion of any additional matrices.

The two-phase case, in the absence of chemical reactions, is a special case of multiphase flash. This can be posed in a simple manner using Newton's method on the Gibbs energy with one phase set as dependent. The molar amount of each component can be defined through the material balance:

$$n_{i,l} = z_i - n_{i,v} \tag{4.43}$$

the gradient of the reduced Gibbs energy is then:

$$f_i = \ln \hat{f}_{i,v} - \ln \hat{f}_{i,l} \tag{4.44}$$

an element of the Hessian is

$$H_{i,k} = \frac{1}{\beta_l} \left(\frac{\delta_{i,k}}{x_i} + \beta_l \frac{\partial \ln \hat{\varphi}_{i,l}}{\partial n_k} \right) + \frac{1}{\beta_v} \left(\frac{\delta_{i,k}}{y_i} + \beta_v \frac{\partial \ln \hat{\varphi}_{i,v}}{\partial n_k} \right) - \frac{1}{\beta_l \beta_v}$$
(4.45)

The correction is found from the Newton step

$$\Delta \boldsymbol{n}_v = -\boldsymbol{H}^{-1}\boldsymbol{f} \tag{4.46}$$

To avoid round-off errors the update should be applied to the component present in the smaller amount $(\Delta n_{i,l} = -\Delta n_{i,v})$.

If the Hessian is not positive definite the direction generated may not be towards a minimum in the Gibbs energy. For the two-phase case the Hessian is well scaled and an ideal solution correction vector for restricted step implementation is possible using the diagonal correction:

$$s_i = \frac{z_i}{x_{i,l} x_{i,v}} \tag{4.47}$$

The positive definite Hessian is found as

$$\hat{\boldsymbol{H}} = \boldsymbol{H} + \check{\alpha}\boldsymbol{s} \tag{4.48}$$

where $\check{\alpha}$ is evaluated in a way to ensure that the Hessian is positive definite (e.g. using the method of Hebden [71]), as recommended by Michelsen and Mollerup [117]. This method will lead to rapid convergence in the vast majority of cases, and the additional work of multiple factorisations to find the positive definite Hessian is often not prohibitive due to the small size of the two-phase Hessian.

An alternative is to use the procedure correction for the modified RAND method. The Hessian in equation 4.45 can be rewritten

$$\boldsymbol{H} = \frac{1}{\beta^l} \boldsymbol{m}^l + \frac{1}{\beta^v} \boldsymbol{m}^v - \frac{\mathbf{1} \mathbf{1}^T}{\beta^l \beta^v}$$
(4.49)

with the m matrix defined in equation 4.11. The Hessian will only be indefinite if at least one of the m matrices is indefinite.

We assume that m^l is indefinite with a single negative eigenvalue. The minimum eigenvalue λ_{min} and corresponding eigenvector \hat{u} of the \tilde{Q}_l matrix based on this m^l matrix can be evaluated from equation 4.36. To correct for the negative eigenvalue we add to m^l

the correction $k \boldsymbol{v} \boldsymbol{v}^T$ with $k + \lambda_{min} \geq 0$ with

$$v_i = \frac{u_i}{x_{i,l}}$$

An indefinite Hessian reveals itself in the factorisation step, however a new factorisation with the modified Hessian can be avoided. We may write

$$\boldsymbol{H}\Delta\boldsymbol{n}_v = -\boldsymbol{f} - \hat{\alpha}\boldsymbol{v} \tag{4.50}$$

with $\hat{\alpha} = \frac{k}{\beta_l} \boldsymbol{v}^T \Delta \boldsymbol{n}_v$. Using the factorised Hessian we find

$$\Delta \boldsymbol{n}_v = \Delta \boldsymbol{n}_v^0 - \hat{\alpha} \Delta \boldsymbol{n}_v^1 \tag{4.51}$$

with the closing relation

$$\hat{\alpha} = \frac{k}{\beta_l} \boldsymbol{v}^T \left(\Delta \boldsymbol{n}_v^0 - \hat{\alpha} \Delta \boldsymbol{n}_v^1 \right)$$
(4.52)

Usually $k = -\lambda_{min}$ is an adequate correction. Following the update to Δn_v the update will be in a descent direction however it may be necessary to use a line search to obtain a decrease in the objective function.

4.3 State function constraints

Though the isothermal flash is the conventional phase equilibrium problem there are a number of other flash problems which are commonly encountered. The example of isenthalpic flash was discussed in detail in chapter 3. This was based on the conventional flash framework where the equality constraints are eliminated by setting one phase as dependent on the others through the material balance. In a manner similar to Michelsen [115] it is possible to solve a number of other state function based flash specifications but starting from the modified RAND framework. From the derivation given in section 4.2 we have an equation for the update to the molar amount of each component in each phase (4.15)

$$\Delta \boldsymbol{n}_j = \boldsymbol{x}_j \Delta \beta_j + \beta_j \boldsymbol{M}_j \left(\boldsymbol{\mathcal{A}}^T \boldsymbol{\lambda} - \frac{\boldsymbol{\mu}_j}{RT} - \boldsymbol{e}_j \Delta T - \boldsymbol{\gamma}_j \Delta P \right)$$

with C + F + 2 variables. We also have C + F equations defined in equations 4.17 and 4.21.

$$oldsymbol{X}^T \left(oldsymbol{\mathcal{A}}^T oldsymbol{\lambda} - oldsymbol{e}_j \Delta T - oldsymbol{\gamma}_j \Delta P
ight) = oldsymbol{g}$$

$$\mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}\boldsymbol{M}_{j}\right)\mathcal{A}^{T}\boldsymbol{\lambda}+\mathcal{A}\boldsymbol{X}\Delta\boldsymbol{\beta}-\mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}\boldsymbol{M}_{j}\boldsymbol{e}_{j}\right)\Delta T$$
$$-\mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}\boldsymbol{M}_{j}\boldsymbol{\gamma}_{j}\right)\Delta P=\mathcal{A}\left(\sum_{j=1}^{F}\beta_{j}\boldsymbol{M}_{j}\frac{\boldsymbol{\mu}_{j}}{RT}\right)$$

The additional two equations can be defined from the constraints. From table 4.1 it is clear that there are four possible constraint equations. For the (P, S) and (V, S) specifications, the entropy is constrained:

$$S(T, P, \boldsymbol{n}) - S^{spec} = 0 \tag{4.53a}$$

For the (P, H) specification the enthalpy is constrained:

$$H(T, P, \boldsymbol{n}) - H^{spec} = 0 \tag{4.53b}$$

for the (V, T), (V, S) and (V, U) specifications the volume is constrained:

$$V^{spec} - V(T, P, \boldsymbol{n}) = 0 \tag{4.53c}$$

Finally for the (V, U) specification the internal energy is constrained:

$$U(T, P, \boldsymbol{n}) - U^{spec} \approx H(T, P, \boldsymbol{n}) - U^{spec} - PV^{spec}$$
(4.53d)

This approximation is exact at the solution and can be safely used.

Each of these four equality constraints are non-linear in the independent variables. Linearisation of each constraint yields:

$$\frac{S - S^{spec}}{RT} + \frac{C_p}{RT^2} \Delta T - \frac{1}{RT} \frac{\partial V}{\partial T} \Delta P - \sum_{j=1}^{F} \boldsymbol{e}_j^T \Delta \boldsymbol{n}_j = 0$$
(4.54a)

$$\frac{H - H^{spec}}{RT^2} + \frac{C_p}{RT^2}\Delta T - \frac{1}{RT}\left(\frac{\partial V}{\partial T} - \frac{V}{T}\right)\Delta P - \sum_{j=1}^F \boldsymbol{\xi}_j^T \Delta \boldsymbol{n}_j = 0$$
(4.54b)

$$\frac{V^{spec} - V}{RT} - \frac{1}{RT} \frac{\partial V}{\partial T} \Delta T - \frac{1}{RT} \frac{\partial V}{\partial P} \Delta P - \sum_{j=1}^{F} \boldsymbol{\gamma}_{j}^{T} \Delta \boldsymbol{n}_{j} = 0 \qquad (4.54c)$$

$$\frac{H - U^{spec} - PV^{spec}}{RT^2} + \frac{C_p}{RT^2} \Delta T - \frac{1}{RT} \left(\frac{\partial V}{\partial T} + \frac{V^{spec} - V}{T} \right) \Delta P - \sum_{j=1}^{F} \boldsymbol{\xi}_j^T \Delta \boldsymbol{n}_j = 0$$
(4.54d)

where we have defined

$$\boldsymbol{\xi}_{j} = \frac{1}{R} \frac{\partial \frac{\mu_{j}}{T}}{\partial T} \tag{4.55}$$

It is desirable to arrive at a single symmetric matrix for all six state-function based flash specifications. To do so it is necessary to make a number of simplifications. The temperature derivative of the reduced chemical potential can be split as

$$\frac{\partial \frac{\boldsymbol{\mu}_j}{T}}{\partial T} = \frac{1}{T} \frac{\partial \boldsymbol{\mu}_j}{\partial T} - \frac{\boldsymbol{\mu}_j}{T^2}$$
(4.56)

In the summation term in equation 4.54d, the second term from the RHS of equation 4.56 will be:

$$\sum_{j=1}^{F} \frac{\boldsymbol{\mu}_{j}^{T}}{RT^{2}} \Delta \boldsymbol{n}_{j}$$
(4.57)

At equilibrium, the reduced chemical potentials of each phase are related to the reduced equilibrium elemental potential through

$$\frac{\boldsymbol{\mu}_j}{RT} = \boldsymbol{\mathcal{A}}^T \boldsymbol{\lambda} \tag{4.58}$$

therefore

$$\sum_{j=1}^{F} \frac{\boldsymbol{\mu}_{j}^{T}}{RT^{2}} \Delta \boldsymbol{n}_{j} = \frac{1}{T} \sum_{j=1}^{F} \left(\boldsymbol{\mathcal{A}}^{T} \boldsymbol{\lambda} \right)^{T} \Delta \boldsymbol{n}_{j} = \frac{\boldsymbol{\lambda}^{T}}{T} \boldsymbol{\mathcal{A}} \left(\sum_{j=1}^{F} \Delta \boldsymbol{n}_{j} \right) = 0 \quad (4.59)$$

This is zero because, given a composition which satisfies the elemental balance, equation 4.20 is satisfied.

It is therefore possible to relace ξ_j in equations 4.54b and 4.54d with e_j for each phase. The pressure derivative in equation 4.54b is not used in any specification and can be dropped. At the solution, the volume will be identical to the volume specification, therefore the third term in equation 4.54d can be simplified to

$$\frac{1}{RT}\frac{\partial V}{\partial T}\Delta P$$

Using these simplifications the four equations in 4.54 can be rewritten as:

$$\frac{C_p}{RT^2}\Delta T - \frac{1}{RT}\frac{\partial V}{\partial T}\Delta P - \sum_{j=1}^F \boldsymbol{e}_j^T\Delta\boldsymbol{n}_j = r_T$$
(4.60a)

$$-\frac{1}{RT}\frac{\partial V}{\partial T}\Delta T - \frac{1}{RT}\frac{\partial V}{\partial P}\Delta P - \sum_{j=1}^{F}\boldsymbol{\gamma}_{j}^{T}\Delta\boldsymbol{n}_{j} = r_{P}$$
(4.60b)

where r_T and r_P are defined in table 4.2.

Table 4.2 The elements of r_T and r_P for a given specification

Flash specification	$ r_T $	r_P
(T, P)(P, H)(P, S)(V, T)(V, U)(V, S)	$ \begin{array}{c} - \\ \frac{1}{RT^2} \left(H^{spec} - H \right) \\ \frac{1}{RT} \left(S^{spec} - S \right) \\ - \\ \frac{1}{RT^2} \left(U^{spec} + PV^{spec} - H \right) \\ \frac{1}{RT} \left(S^{spec} - S \right) \end{array} $	$ \frac{1}{RT} \left(V - V^{spec} \right) $ $ \frac{1}{RT} \left(V - V^{spec} \right) $ $ \frac{1}{RT} \left(V - V^{spec} \right) $

The composition correction to each component in each phase defined in equation 4.15 is substituted into equations 4.60 to obtain:

$$-\sum_{j=1}^{F} \beta_{j} \boldsymbol{e}_{j}^{T} \boldsymbol{M}_{j} \boldsymbol{\mathcal{A}}^{T} \boldsymbol{\lambda} - \sum_{j=1}^{F} \boldsymbol{x}_{j}^{T} \boldsymbol{e}_{j} \Delta \beta_{j} + C_{x} \Delta T + \Omega \Delta P = r_{T} - \sum_{j=1}^{F} \beta_{j} \boldsymbol{e}_{j}^{T} \boldsymbol{M}_{j} \frac{\boldsymbol{\mu}_{j}}{RT} \quad (4.61)$$
$$-\sum_{j=1}^{F} \beta_{j} \boldsymbol{\gamma}_{j}^{T} \boldsymbol{M}_{j} \boldsymbol{\mathcal{A}}^{T} \boldsymbol{\lambda} - \sum_{j=1}^{F} \boldsymbol{x}_{j}^{T} \boldsymbol{\gamma}_{j} \Delta \beta_{j} + \Omega \Delta T + \Psi \Delta P = r_{P} - \sum_{j=1}^{F} \beta_{j} \boldsymbol{\gamma}_{j}^{T} \boldsymbol{M}_{j} \frac{\boldsymbol{\mu}_{j}}{RT} \quad (4.62)$$

Here we have used

$$C_{x} = \frac{C_{p}}{RT^{2}} + \sum_{j=1}^{F} \beta_{j} \boldsymbol{e}_{j}^{T} \boldsymbol{M}_{j} \boldsymbol{e}_{j}$$

$$\Omega = \sum_{j=1}^{F} \beta_{j} \boldsymbol{e}_{j}^{T} \boldsymbol{M}_{j} \boldsymbol{\gamma}_{j} - \frac{1}{RT} \frac{\partial V}{\partial T} = \sum_{j=1}^{F} \beta_{j} \boldsymbol{\gamma}_{j}^{T} \boldsymbol{M}_{j} \boldsymbol{e}_{j} - \frac{1}{RT} \frac{\partial V}{\partial T} \qquad (4.63)$$

$$\Psi = \sum_{j=1}^{F} \beta_{j} \boldsymbol{\gamma}_{j}^{T} \boldsymbol{M}_{j} \boldsymbol{\gamma}_{j} - \frac{1}{RT} \frac{\partial V}{\partial P}$$

A common symmetric matrix with the specifications given in table 4.2 from equations 4.17, 4.21, 4.61 and 4.62 is then:

$$\begin{pmatrix} \boldsymbol{\mathcal{A}} \sum_{j=1}^{F} \beta_{j} \boldsymbol{M}_{j} \boldsymbol{\mathcal{A}}^{T} & \boldsymbol{\mathcal{A}} \boldsymbol{X} & -\boldsymbol{t} & -\boldsymbol{q} \\ (\boldsymbol{\mathcal{A}} \boldsymbol{X})^{T} & \boldsymbol{0} & \boldsymbol{s}_{1} & \boldsymbol{s}_{2} \\ -\boldsymbol{t}^{T} & \boldsymbol{s}_{1}^{T} & \boldsymbol{C}_{x} & \boldsymbol{\Omega} \\ -\boldsymbol{q}^{T} & \boldsymbol{s}_{2}^{T} & \boldsymbol{\Omega} & \boldsymbol{\Psi} \end{pmatrix} \begin{pmatrix} \boldsymbol{\lambda} \\ \Delta \boldsymbol{\beta} \\ \Delta T \\ \Delta P \end{pmatrix} = \begin{pmatrix} \boldsymbol{u}_{1} \\ \boldsymbol{u}_{2} \\ \boldsymbol{u}_{3} \\ \boldsymbol{u}_{4} \end{pmatrix}$$
(4.64)

with

$$u_{3} = r_{T} - \sum_{j=1}^{F} \beta_{j} \boldsymbol{e}_{j}^{T} \boldsymbol{M}_{j} \frac{\boldsymbol{\mu}_{j}}{RT}$$

$$u_{4} = r_{P} - \sum_{j=1}^{F} \beta_{j} \boldsymbol{\gamma}_{j}^{T} \boldsymbol{M}_{j} \frac{\boldsymbol{\mu}_{j}}{RT}$$

$$\boldsymbol{t} = \boldsymbol{\mathcal{A}} \sum_{j=1}^{F} \beta_{j} \boldsymbol{M}_{j} \boldsymbol{e}_{j}$$

$$\boldsymbol{q} = \boldsymbol{\mathcal{A}} \sum_{j=1}^{F} \beta_{j} \boldsymbol{M}_{j} \boldsymbol{\gamma}_{j}$$

$$s_{1,j} = -\boldsymbol{x}_{j}^{T} \boldsymbol{e}_{j} \quad \forall j$$

$$s_{2,j} = -\boldsymbol{x}_{j}^{T} \boldsymbol{\gamma}_{j} \quad \forall j$$
(4.65)

Once the system of equations is solved using the symmetric matrix, the update to the molar amount of each component in each phase is found from equation 4.15. To select each flash specification, the only change necessary is given in table 4.2. Only the (P, T) specification has a suitable objective function to minimise (the Gibbs energy). For the other state function based flash specifications, the Newton iteration with accurate initial estimates is expected to converge in the majority of cases and a fall back method is needed for non-convergent situations. An implementation similar to that described in chapter 3 would be suitable.

In the absence of chemical reactions it is possible to make a number of simplifications. The elemental feed becomes the component feed $b_i = z_i$, the formula matrix is the identity matrix $\mathcal{A} = \mathbf{I}$, and the reduced chemical potential can be replaced by the fugacity $\ln \hat{f}_j$ for each phase. The matrix in equation 4.64 becomes

$$\begin{pmatrix} \sum_{j=1}^{F} \beta_j \boldsymbol{M}_j & \boldsymbol{X} & -\boldsymbol{t} & -\boldsymbol{q} \\ \boldsymbol{X}^T & \boldsymbol{0} & \boldsymbol{s}_1 & \boldsymbol{s}_2 \\ -\boldsymbol{t}^T & \boldsymbol{s}_1^T & \boldsymbol{C}_x & \boldsymbol{\Omega} \\ -\boldsymbol{q}^T & \boldsymbol{s}_2^T & \boldsymbol{\Omega} & \boldsymbol{\Psi} \end{pmatrix} \begin{pmatrix} \boldsymbol{\lambda} \\ \Delta \boldsymbol{\beta} \\ \Delta T \\ \Delta P \end{pmatrix} = \begin{pmatrix} \boldsymbol{u}_1 \\ \boldsymbol{u}_2 \\ \boldsymbol{u}_3 \\ \boldsymbol{u}_4 \end{pmatrix}$$
(4.66)

with

$$u_{1} = \sum_{j=1}^{F} \beta_{j} M_{j} \ln \hat{f}$$

$$u_{2,j} = \sum_{i=1}^{C} x_{i,j} \ln \hat{f} \quad \forall j$$

$$u_{3} = r_{T} - \sum_{j=1}^{F} \beta_{j} e_{j}^{T} M_{j} \ln \hat{f}$$

$$u_{4} = r_{P} - \sum_{j=1}^{F} \beta_{j} \gamma_{j}^{T} M_{j} \ln \hat{f}$$

$$t = \sum_{j=1}^{F} \beta_{j} M_{j} e_{j}$$

$$q = \sum_{j=1}^{F} \beta_{j} M_{j} \gamma_{j}$$

$$(4.67)$$

The other terms remain unchanged. This is again a symmetric matrix for any specification given in table 4.2

Again an ideal solution approximation, as described in section 1.3, can be arrived at by assuming the composition derivatives of the fugacity coefficient are equal to zero. It is then possible to reduce the size of the system of equations to be solved from C + F + 2 to F + 2 for (V, U) and (V, S) based flash specifications and to F + 1 for (V, T), (P, H) and (P, S) based specifications.

4.4 Non-PT based thermodynamics formulations

It is common to solve the EoS at a specified pressure. However the EoS is often a function for the Helmholtz energy with the natural variables of temperature and volume. A

formulation which takes advantage of the natural variables instead of solving the EoS for volume at a given pressure may prove advantageous.

The resulting vol-RAND method using the (n, T, V) based thermodynamics can be used to solve both the (V, T) and (P, T) based phase split calculations. It can in principle be applied to the other four types of flash specifications discussed in this work: (P, H), (P, S), (U, V), and (V, S), as is described in appendix C. Furthermore, we present a generalisation in section 4.4.2, showing that other formulations using (n, P, H), (n, P, S), (n, U, V), and (n, V, S) based thermodynamics are also possible. the generalised formulation is particularly useful for flash specifications using the same set of variables. We present here only its derivation and no test has been made so far.

4.4.1 Vol-RAND formulation

Instead of expressing the Gibbs energy using the pressure, temperature and molar amounts of all components in all phases, we express the Helmholtz energy using the volume, temperature and molar amounts and minimise it:

$$\min A(\boldsymbol{n}, T, V) = \sum_{i=1}^{C} \sum_{j=1}^{F} n_{i,j} \mu_{i,j} - PV$$
(4.68)

subject to the elemental balance constraints

$$\sum_{i=1}^{C} \mathcal{A}_{l,i} \left(\sum_{j=1}^{F} n_{i,j} \right) - \hat{b}_l = 0, \quad l = 1, 2, ..., E$$
(4.69)

the volume balance

$$\sum_{j=1}^{F} V_j - V^{spec} = 0, \quad j = 1, 2, ..., F$$
(4.70)

and the inequality constraints

$$n_{i,j} \ge 0$$
 $i = 1, 2, ..., C, j = 1, 2, ..., F$ (4.71)

The Lagrangian for the constrained minimisation is

$$\mathcal{L}(\boldsymbol{n}, \boldsymbol{V}, \hat{\boldsymbol{\lambda}}, P^{eq}) = \sum_{i=1}^{C} \sum_{j=1}^{F} n_{i,j} \mu_{i,j} - \sum_{j=1}^{F} V_j P_j - \sum_{l=1}^{E} \hat{\lambda} \left(\sum_{i=1}^{C} \mathcal{A}_{l,i} \left(\sum_{j=1}^{F} n_{i,j} \right) - b_l \right) - P^{eq} \left(V^{spec} - \sum_{j=1}^{F} V_j \right)$$
(4.72)

Where $\hat{\lambda}$ and P^{eq} are the Lagrange multipliers, these are equivalent to the equilibrium elemental potentials and the equilibrium pressure. The stationarity equations are:

$$\frac{\partial \mathcal{L}}{\partial n_{i,j}} = \mu_{i,j} - \sum_{l=1}^{E} \hat{\lambda}_l \mathcal{A}_{l,i} = 0, \quad \forall i, j$$
(4.73)

$$\frac{\partial \mathcal{L}}{\partial \lambda_l} = -\sum_{i=1}^C \mathcal{A}_{l,i} \left(\sum_{j=1}^F n_{i,j} \right) + \hat{b}_l = 0, \quad \forall l$$
(4.74)

$$\frac{\partial \mathcal{L}}{\partial V_j} = -P_j + P^{eq} = 0, \quad \forall j$$
(4.75)

$$\frac{\partial \mathcal{L}}{\partial P^{eq}} = V^{spec} - \sum_{j=1}^{F} V_j = 0$$
(4.76)

Where the equilibrium equations are 4.73 and 4.75. The composition derivative of the Helmholtz energy is the chemical potential

$$\left(\frac{\partial A_j}{\partial n_{i,j}}\right)_{V,T,n_{k,j}} = \mu_{i,j}$$

and the volume derivative is the negative phase pressure

$$\left(\frac{\partial A_j}{\partial V_j}\right)_{T,\boldsymbol{n}_j} = -P_j$$

For convenience we will refer to the derivatives of the Helmholtz energy using the following terminology: (24)

$$A_{n_i,j} = \left(\frac{\partial A_j}{\partial n_i}\right)_{T,\boldsymbol{n}_j} = \mu_i$$

and the same for all other used derivatives of the Helmholtz energy. Carrying out linearisation around the equilibrium equations (4.73, and 4.75) we arrive at

$$\boldsymbol{A}_{\boldsymbol{n},j} + \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j} \Delta \boldsymbol{n}_j + \boldsymbol{A}_{\boldsymbol{n},V,j} \Delta V + \boldsymbol{A}_{\boldsymbol{n},T,j} \Delta T - \boldsymbol{\mathcal{A}}^T \hat{\boldsymbol{\lambda}} = 0$$
(4.77)

$$A_{V,j} + \boldsymbol{A}_j^T \Delta \boldsymbol{n}_j + A_{V,V,j} + A_{V,T,j} \Delta T - P^{eq} = 0, \quad \forall j$$
(4.78)

where

$$oldsymbol{A}_{oldsymbol{n},oldsymbol{n},j}=rac{\partialoldsymbol{\mu}_j}{\partialoldsymbol{n}_j}$$

is a matrix of size $C \times C$. The composition derivative of the chemical potential at constant volume and temperature $A_{n,n,j}$ is non-singular everywhere except at the spinodal. Therefore the update to the molar amount of each component in each phase can be immediately isolated as

$$\Delta \boldsymbol{n}_{j} = \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \left(\boldsymbol{\mathcal{A}}^{T} \hat{\boldsymbol{\lambda}} - \boldsymbol{A}_{\boldsymbol{n},j} - \boldsymbol{A}_{\boldsymbol{n},V,j} \Delta V_{j} - \boldsymbol{A}_{\boldsymbol{n},T,j} \Delta T \right)$$
(4.79)

Since the Helmholtz energy is a homogeneous function of degree one in the molar amount of each component and the volume (and its temperature derivative is also a homogeneous function of degree one) it derivatives satisfy:

$$\boldsymbol{A}_{\boldsymbol{n},j}^{T}\boldsymbol{n}_{j} + A_{V,j}V_{j} = A_{j}$$

$$(4.80)$$

$$\boldsymbol{A}_{\boldsymbol{n},T,j}^{T}\boldsymbol{n}_{j} + A_{V,T,j}V = A_{T,j} = -S_{j}$$
(4.81)

$$\boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}\boldsymbol{n}_j + \boldsymbol{A}_{\boldsymbol{n},V,j}V_j = \boldsymbol{0}$$
(4.82)

and

$$\boldsymbol{A}_{\boldsymbol{n},V,j}^{T}\boldsymbol{n}_{j} + A_{V,V,j}V_{j} = 0$$
(4.83)

From equation 4.81 we can show that

$$m{A}_{m{n},m{n},j}^{-1}m{A}_{m{n},V,j}=-rac{m{n}_{j}}{V_{j}}=-m{
ho}_{j}$$

Substituting this into equation 4.79 we obtain:

$$\Delta \boldsymbol{n}_{j} = \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \left(\boldsymbol{\mathcal{A}}^{T} \hat{\boldsymbol{\lambda}} - \boldsymbol{A}_{\boldsymbol{n},j} - \boldsymbol{A}_{\boldsymbol{n},T,j} \Delta T \right) + \boldsymbol{\rho}_{j} \Delta V_{j}$$
(4.84)

This composition correction can then be substituted into equation 4.78 to find:

$$A_{V,j} - \boldsymbol{\rho}_{j}^{T} \left(\boldsymbol{\mathcal{A}}^{T} \hat{\boldsymbol{\lambda}} - \boldsymbol{A}_{\boldsymbol{n},j} \right) + \left(\boldsymbol{A}_{\boldsymbol{n},V,j}^{T} \boldsymbol{\rho}_{j} + A_{V,V,j} \right) \Delta V_{j} - \left(\boldsymbol{\rho}_{j}^{T} \boldsymbol{A}_{\boldsymbol{n},T,j} + A_{V,T,j} \right) \Delta T + P^{eq} = 0, \quad \forall j \quad (4.85)$$

From equation 4.82 it is clear that the third term of equation 4.85 is equal to zero. From equation 4.81 we can replace the fourth term with the entropy over the volume:

$$\boldsymbol{\rho}_{j}^{T}\boldsymbol{\mathcal{A}}^{T}\hat{\boldsymbol{\lambda}} + \frac{S_{j}}{V_{j}}\Delta T = \boldsymbol{\rho}_{j}^{T}\boldsymbol{\mu}_{j} + A_{V,j} + P^{eq}$$
(4.86)

Linearising around equation 4.74 we obtain

$$\mathcal{A}\left(\sum_{j=1}^{F} \left(\Delta \boldsymbol{n}_{j}\right)\right) = \boldsymbol{0}$$
(4.87)

given an initial estimate that meets the material balance. Substituting in equation 4.84 leads to:

$$\mathcal{A}\left(\sum_{j=1}^{F} \mathbf{A}_{n,n,j}^{-1}\right) \mathcal{A}^{T} \hat{\boldsymbol{\lambda}} + \mathcal{A} \mathbf{R} \Delta \boldsymbol{V} - \mathcal{A}\left(\sum_{j=1}^{F} \mathbf{A}_{n,n,j}^{-1} \mathbf{A}_{n,T,j}\right) \Delta T = \mathcal{A}\left(\sum_{j=1}^{F} \mathbf{A}_{n,n,j}^{-1} \boldsymbol{\mu}_{j}\right)$$
(4.88)

Here we have used $\mathbf{R} = (\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, ..., \boldsymbol{\rho}_F)$. The *E* equations 4.88 together with the *F* equations 4.86 relate the E + F + 2 variables $(\hat{\boldsymbol{\lambda}}, \boldsymbol{V}, T, P^{eq})$. This leaves the usual 2 degrees of freedom.

Using this formulation it is possible to construct either isothermal isobaric (P, T) or isothermal isochoric (V, T) flash as a minimisation with the objective functions $Q = A + VP^{eq}$ and Q = A respectively. To carry out (V, T) flash one of the phase volumes can be set as dependent using equation 4.76. It is also possible to arrive at a symmetric system of equations if the energy (enthalpy, entropy or internal energy) of the mixture is known instead of the temperature and used as a constraint in a similar manner to that carried out in section 4.3 (using similar simplifications). The system of equations is given in appendix C.

For non-reactive systems equation 4.86 can be simplified to

$$\boldsymbol{\rho}_{j}^{T}\hat{\boldsymbol{\lambda}} + \frac{S_{j}}{V_{j}}\Delta T = \boldsymbol{\rho}_{j}^{T}\boldsymbol{\mu}_{j} + A_{V,j} + P^{eq}$$
(4.89)

and equation 4.88 to

$$\left(\sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1}\right)\hat{\boldsymbol{\lambda}} + \boldsymbol{R}\Delta\boldsymbol{V} - \sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \boldsymbol{A}_{\boldsymbol{n},T,j} \Delta T = \sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \boldsymbol{\mu}_{j}$$
(4.90)

In some cases it may be convenient to use:

$$\boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j} = \frac{\partial \boldsymbol{\mu}_j}{\partial \boldsymbol{n}_j} = \frac{1}{V} \frac{\partial \boldsymbol{\mu}_j}{\partial \boldsymbol{n}_j}$$
(4.91)

This may be advantageous if one specification is that one phase is incipient (i.e. that its phase fraction is zero).

A similar implementation can be used for vol-RAND at a given (P, T) specification as was used for modified RAND. Given the volume and molar amount of each component in each phase, one iteration would proceed as

1. Calculate the molar density of each component in each phase

$$\rho_{i,j} = \frac{n_{i,j}}{V_j}$$

and collect the density vectors into a matrix

$$R = (\rho_1, \rho_2, ..., \rho_F)$$

2. Use a suitable EoS to evaluate the chemical potential and the necessary derivatives

$$\boldsymbol{\mu}_j = \frac{\partial A_j}{\partial \boldsymbol{n}_j}, \quad \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j} = \frac{\partial \boldsymbol{\mu}_j}{\partial \boldsymbol{n}_j}, \quad P_j = \frac{\partial A_j}{\partial V_j}$$

3. Form the system of equations

$$\begin{pmatrix} \sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} & \boldsymbol{R} \\ \boldsymbol{R}^{T} & \boldsymbol{0} \end{pmatrix} \begin{pmatrix} \hat{\boldsymbol{\lambda}} \\ \Delta \boldsymbol{V} \end{pmatrix} = \begin{pmatrix} \sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \boldsymbol{\mu}_{j} \\ \boldsymbol{\rho}_{j}^{T} \boldsymbol{\mu}_{j} + A_{V,j} + P^{eq} & \forall j \end{pmatrix}$$

- 4. Solve for the equilibrium chemical potentials and the change in the phase volumes
- 5. Calculate the update to the molar amount of each component in each phase

$$\Delta \boldsymbol{n}_{j} = \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \left(\hat{\boldsymbol{\lambda}} - \boldsymbol{\mu}_{j} \right) + \boldsymbol{\rho}_{j} \Delta V_{j}$$

- 6. Take the step with a suitable step length modifier to avoid violation of the inequality constraint (i.e. no component can become negative in any phase). It is also necessary to ensure that the volume specification for a phase does not decrease below the minimum possible volume for the phase.
- 7. Re-evaluate the Helmholtz energy from the EoS and check for a reduction in a suitable objective function

$$Q = \sum_{j=1}^{F} A_j + \sum_{j=1}^{F} V_j P^{eq}$$

If there is an increase in the objective function then the step length can be reduced, and the step repeated.

This procedure will be quadratically convergent provided with a suitable initial estimate. Unfortunately there is no simplifying ideal solution approximation with the volume and temperature specified. Successive substitution cannot be easily formulated. This is only possible for the ideal gas which is of little interest to the multiphase case.

For the case where (V, T) is specified instead of (P, T) a very similar implementation can be used. The general matrix required for the (V, T), (V, S) and (V, U) specifications is given in appendix C. This can be used for the (V, T) specification where the temperature is known (and the row and column corresponding to the temperature change can be removed).

4.4.2 Generalisation to other state functions

There are a number of differences between modified RAND and vol-RAND, the most obvious of which is that vol-RAND uses a thermodynamic model solved at a given (V,T)while modified RAND uses a thermodynamic model solved at a given (P,T). With vol-RAND it is possible to pose both the (V,T) and (P,T) phase split calculations as minimisations while for modified RAND it is possible only for (P,T). In the case of other specifications (including (V,T)) it is necessary to introduce non-linear constraints. An alternative method to solve the remaining flash specifications ((P,H), (P,S), (V,S) and (V,U)) would be to solve the EoS at the flash specification (i.e. for (P,H) flash solve the EoS at a given pressure and enthalpy (n, H, P)). This would then allow for each of the flash specifications described in table 4.1 to be posed as unconstrained minimisations. Starting from a general state function:

$$\hat{M}\left(\boldsymbol{n}, \tilde{\boldsymbol{b}}, \hat{\boldsymbol{c}}\right)$$
 (4.92)

where \hat{M} is a homogeneous function of degree one in its extensive properties, n are the mole numbers of each component, \tilde{b} a vector of independent extensive variables, with intensive conjugates \hat{a} , and the remaining intensive variables \hat{c} . The possible variables for \hat{a} , \tilde{b} and \hat{c} are given in table 4.3

Table 4.3 Flash specifications and their extensive variables, the intensive conjugate and any remaining intensive variables

Flash specification	$\tilde{\boldsymbol{b}}$	\hat{a}	\hat{c}
(P,T)	-	-	P, T
(V,T)	V	P	T
(P,H)	H	T	P
(P,S)	S	1/T	P
(V, S)	V, S	P, 1/T	-
(V, U)	V, U	P, T	-

If we assume there are C variables of n, F phases, and N additional extensive variables \tilde{b} , the equilibrium conditions for this state function are

$$\hat{M}_{n,j} - \lambda = 0, \quad j = 1, 2, ..., F$$
 (4.93a)

$$\hat{M}_{\tilde{b}_l,j} - \hat{a}_l = \mathbf{0} \quad j = 1, 2, ..., F, \quad l = 1, 2, ..., N$$
 (4.93b)

Note that λ represents Lagrange multipliers at this point rather than specifically either reduced chemical potentials or chemical potentials. We use:

 $\hat{M}_{n,j}$

to represent the partial derivative

$$\left(\frac{\partial \hat{M}_j}{\partial n_{i,j}}\right)_{\tilde{\boldsymbol{b}},\hat{\boldsymbol{c}},n_k},\quad\forall i$$

with \tilde{b} , \hat{c} , and $n_{k\neq i}$ kept constant for phase j. Following the modified RAND methodology we linearise around the equilibrium equations:

$$\hat{\boldsymbol{M}}_{\boldsymbol{n},j} + \hat{\boldsymbol{M}}_{\boldsymbol{n},\boldsymbol{n},j} \Delta \boldsymbol{n}_j + \sum_{l=1}^{N} \hat{\boldsymbol{M}}_{\boldsymbol{n},\tilde{b}_l,j} \Delta \tilde{b}_{l,j} - \boldsymbol{\lambda} = \boldsymbol{0} \quad \forall j$$
(4.94)

$$\hat{M}_{\tilde{b}_l,j} + \hat{M}_{\tilde{b}_l,n,j}^T \Delta n_j + \sum_{k=1}^N \hat{M}_{\tilde{b}_l,\tilde{b}_k,j} \Delta \tilde{b}_{k,j} - \hat{a}_l = 0 \quad \forall j,l$$
(4.95)

for convenience we omit the linearisation of the additional intensive properties (\hat{c}). Assuming that the matrix of second derivatives of n is non-singular (generally true if N > 0), the composition correction is immediately isolated as:

$$\Delta \boldsymbol{n}_{j} = \left(\hat{\boldsymbol{M}}_{\boldsymbol{n},\boldsymbol{n},j}\right)^{-1} \left(\boldsymbol{\lambda} - \hat{\boldsymbol{M}}_{\boldsymbol{n},j} - \sum_{l=1}^{N} \hat{\boldsymbol{M}}_{\boldsymbol{n},\tilde{b}_{l},j} \Delta \tilde{b}_{l,j}\right)$$
(4.96)

It is possible to include reactions in this formulation, however for convenience and clarity these will be omitted. The material balance is therefore given as:

$$\sum_{j=1}^{F} \boldsymbol{n}_j - \boldsymbol{z} = \boldsymbol{0}$$
(4.97)

then following linearisation we find:

$$\sum_{j=1}^{F} \Delta \boldsymbol{n}_j = \boldsymbol{0} \tag{4.98}$$

given an initial estimate which is equal to the feed amount. Substituting in equation 4.96 to equation 4.98 we obtain:

$$\sum_{j=1}^{F} \left(\hat{M}_{n,n,j} \right)^{-1} \lambda - \sum_{l=1}^{N} \sum_{j=1}^{F} \hat{M}_{n,n,j}^{-1} \hat{M}_{n,\tilde{b}_{l},j} \Delta \tilde{b}_{l,j} = \sum_{j=1}^{F} \left(\hat{M}_{n,n,j} \right)^{-1} \hat{M}_{n,j} \quad (4.99)$$
Substituting equation 4.96 into equation 4.95 we find for each extensive variable and phase:

$$\hat{M}_{\tilde{b}_{l},j} + \hat{M}_{\boldsymbol{n},\tilde{b}_{l},j}^{T} \hat{M}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \left(\boldsymbol{\lambda} - \hat{M}_{\boldsymbol{n},j} \right) + \sum_{k=1}^{N} \left(\hat{M}_{\tilde{b}_{l},\tilde{b}_{k},j} - \sum_{m=1}^{F} \hat{M}_{\boldsymbol{n},\tilde{b}_{l},m}^{T} \hat{M}_{\boldsymbol{n},\boldsymbol{n},m}^{-1} \hat{M}_{\boldsymbol{n},\tilde{b}_{k},m} \right) \Delta \tilde{b}_{k,j} - \hat{a}_{l} = 0 \quad (4.100)$$

The $C + F \times N$ equations 4.100 and 4.99 relate the $C + F \times N$ variables λ , \tilde{b} . The update to the molar amount of each component in each phase can be found from equation 4.96.

If we consider the case where there is only a single extensive variable \tilde{b}_j then, since \hat{M} is a homogeneous function of degree one we can define

$$\hat{M}_{\boldsymbol{n},\boldsymbol{n},j}\boldsymbol{n}_j + \hat{M}_{\boldsymbol{n},\tilde{b}}\tilde{b}_j = \boldsymbol{0}, \quad \forall j$$
(4.101)

From this we can find

$$\hat{M}_{\boldsymbol{n},\boldsymbol{n},j}^{-1}\hat{M}_{\boldsymbol{n},j} = -\frac{\boldsymbol{n}_j}{\tilde{b}_j}, \quad \forall j$$
(4.102)

and

$$\hat{\boldsymbol{M}}_{\boldsymbol{n},\tilde{b},j}^{T}\boldsymbol{n}_{j}+\hat{M}_{\tilde{b},\tilde{b},j}\tilde{b}_{j}=0,\quad\forall l,j$$
(4.103)

The two equations 4.102 and 4.103 can be used to simplify equations 4.100 and 4.99 to:

$$\hat{M}_{\tilde{b},j} + \hat{M}_{n,\tilde{b},j}^T \hat{M}_{n,n,j}^{-1} \left(\boldsymbol{\lambda} - \hat{M}_{n,j} \right) - \hat{a} = 0 \quad \forall j$$
(4.104)

and

$$\sum_{j=1}^{F} \left(\hat{M}_{\boldsymbol{n},\boldsymbol{n},j} \right)^{-1} \boldsymbol{\lambda} + \sum_{j=1}^{F} \frac{\boldsymbol{n}_{j}}{\tilde{b}_{j}} \Delta \tilde{b}_{j} = \sum_{j=1}^{F} \left(\hat{M}_{\boldsymbol{n},\boldsymbol{n},j} \right)^{-1} \hat{M}_{\boldsymbol{n},j}$$
(4.105)

With the composition correction (equation 4.96) reduced to:

$$\Delta \boldsymbol{n}_{j} = \hat{\boldsymbol{M}}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \left(\boldsymbol{\lambda} - \hat{\boldsymbol{M}}_{\boldsymbol{n},j} \right) + \frac{\boldsymbol{n}_{j}}{\tilde{b}_{j}} \Delta \tilde{b}_{j}, \quad \forall j$$
(4.106)

We can then arrive at a simpler system of equations using equations 4.105 and 4.104:

$$\begin{pmatrix} \sum_{j=1}^{F} \hat{M}_{n,n,j}^{-1} & \hat{R} \\ \hat{R}^{T} & 0 \end{pmatrix} \begin{pmatrix} \lambda \\ \Delta \tilde{b} \end{pmatrix} = \begin{pmatrix} \sum_{j=1}^{F} \hat{M}_{n,n,j}^{-1} \hat{M}_{n,j} \\ u_2 \end{pmatrix}$$
(4.107)

where

$$\hat{\boldsymbol{R}} = \left(\frac{\boldsymbol{n}_1}{\tilde{b}_1}, \frac{\boldsymbol{n}_2}{\tilde{b}_2}, \dots, \frac{\boldsymbol{n}_F}{\tilde{b}_F}\right)$$
(4.108)

and

$$u_{2,j} = \left(rac{oldsymbol{n}_j}{ ilde{b}_j}
ight)^T \hat{oldsymbol{M}}_{oldsymbol{n},j} + \hat{a} \quad orall j$$

The correction to the linearly dependent variables is found from equation 4.106. If we do not know the value of the conjugated intensive property \hat{a} but instead the sum of the extensive property $\tilde{b}^{spec} = \sum_{j=1}^{F} \tilde{b}_j$ then it is possible to set one phase as dependent for the given variable:

$$\Delta \tilde{b}_F = -\sum_{j=1}^{F-1} \Delta \tilde{b}_j + \tilde{b}^{spec} - \sum_{j=1}^F \tilde{b}_j$$
(4.109)

where given an initial estimate which is at \tilde{b}^{spec} the equation is reduced to

$$\Delta \tilde{b}_F = -\sum_{j=1}^{F-1} \Delta \tilde{b}_j \tag{4.110}$$

Substituting the relevant row and column in equation 4.107 reduces the matrix size by 1 to C + F - 1.

The reason that this generalisation is not suitable for the modified RAND formulation is that the $\hat{M}_{n,n,j}$ matrix is singular (Gibbs-Duhem equation) at a specified (P,T). One alternative to the given formulation for modified RAND is to define one or more component as an independent extensive variable $n_{i,j} = \tilde{b}_{i,j}$ and using relation 4.110. In fact if all of the components are defined in this way then the conventional isothermal flash framework is obtained.

We here describe the molar amounts of each component as separate from the independent extensive variables. This is for convenience only and it is possible to treat any of the extensive variables (i.e. volume, energy or molar amounts of a component) as an independent extensive variable or vice versa with the volume or energy defined in the same manner as a component. All that is necessary for this derivation is that one extensive variable is defined using equation 4.110 to avoid a singular matrix $\hat{M}_{n,n}$.

Other than the vol-RAND implementation which fits this framework one possible implementation of the general RAND formulation is to solve the thermodynamics at a given (P, H), as was done by Brantferger et al. [17] and Sun et al. [178]. This would then simplify the (P, H) flash implementation to an unconstrained maximisation of the entropy. This implementation has not been tested as part of this work. The state function for (P, H)

flash is the negative entropy, as given in equation 3.1. We know from table 1.2 that

$$\left(\frac{\partial S}{\partial \boldsymbol{n}}\right)_{H,P} = -\frac{\boldsymbol{\mu}}{T}, \text{ and } \left(\frac{\partial S}{\partial H}\right)_{\boldsymbol{n},P} = \frac{1}{T}$$

The entropy is a homogeneous function of degree 1 in the enthalpy and molar amount of each component (similar to the Helmholtz energy but replacing volume with enthalpy, and temperature with pressure). Therefore we can replace equation 4.101 and 4.103 with

$$\boldsymbol{S}_{\boldsymbol{n},\boldsymbol{n},j}\boldsymbol{n}_j + \boldsymbol{S}_{\boldsymbol{n},H,j}H_j = \boldsymbol{0}$$
(4.111)

and

$$\boldsymbol{S}_{\boldsymbol{n},H,j}^{T}\boldsymbol{n}_{j} + S_{H,H,j}H_{j} = 0, \quad \forall j$$
(4.112)

Allowing us to find the molar inverse enthalpy

$$S_{n,n,j}^{-1}S_{n,H,j} = -\frac{n_j}{H_j}$$
 (4.113)

Applying equation 4.96 to the (P, H) flash we find

$$\Delta \boldsymbol{n}_{j} = -\boldsymbol{S}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \left(\boldsymbol{\lambda} - \frac{\boldsymbol{\mu}_{j}}{T} \right) + \frac{\boldsymbol{n}_{j}}{H_{j}} \Delta H_{j}$$
(4.114)

and to equation 4.105 to find the C equations:

$$-\sum_{j=1}^{F} S_{n,n,j}^{-1} \lambda + \sum_{j=1}^{F} \frac{n_j}{H_j} \Delta H_j = -\sum_{j=1}^{F} S_{n,n,j}^{-1} S_{n,j}$$
(4.115)

and the remaining F equations from 4.104:

$$\left(\frac{\boldsymbol{n}_j}{H_j}\right)^T \boldsymbol{\lambda} = \left(\frac{\boldsymbol{n}_j}{H_j}\right)^T \frac{\boldsymbol{\mu}_j}{T_j} - S_{H,j} + \frac{1}{T^*}$$
(4.116)

Giving the system of equation:

$$\begin{pmatrix} -\sum_{j=1}^{F} \boldsymbol{S}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} & \hat{\boldsymbol{R}} \\ \hat{\boldsymbol{R}} & \boldsymbol{0} \end{pmatrix} \begin{pmatrix} \boldsymbol{\lambda} \\ \Delta \boldsymbol{H} \end{pmatrix} = \begin{pmatrix} -\sum_{j=1}^{F} \boldsymbol{S}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} & \boldsymbol{\mu} \\ \begin{pmatrix} n_{j} \\ H_{j} \end{pmatrix}^{T} & \boldsymbol{\mu} \\ T - S_{H,j} + \frac{1}{T} & \forall j \end{pmatrix}$$
(4.117)

with $\hat{\mathbf{R}} = \left(\frac{\mathbf{n}_1}{H_1}, \frac{\mathbf{n}_2}{H_2}, ..., \frac{\mathbf{n}_F}{H_F}\right)$. Solving for $\boldsymbol{\lambda}$ and the change in phase enthalpy ΔH_j would then allow for the change in molar amounts of all components in all phases to be found

from equation 4.114. Alternatively if the enthalpy of the mixture is known but not the temperature then one phase can be set as dependent through equation 4.110, the new system of equations is then solved to find the new phase enthalpies and pressure at a given (P, H) specification. In such a scenario the entropy can be monitored to ensure it is increasing at each step to guarantee convergence.

4.5 **Results**

There are a number of different phase split calculations considered in this chapter. The results will be split to reflect this. First the isothermal flash methods using modified RAND and vol-RAND will be compared to the conventional isothermal flash method (section 4.5.1). The procedure correction for modified RAND will be presented in section 4.5.2 with a comparison made to the conventional isothermal flash method. Finally two examples will be presented for state function based flash specifications using the modified RAND framework in section 4.5.3. The examples used are described in appendix B.

4.5.1 Comparison of methods for phase split calculation

The first check is on the rate of convergence of the proposed method. The maximum deviation in the fugacity between a component in two phases is plotted against the iteration number in figure 4.1 for example three. The rate of convergence is approximately the same for all of the second order methods. The rate of convergence for successive substitution is linear, as expected. The solution has a vapour phase fraction of $\beta = 0.9169$ using the SRK EoS.

Not only is the rate of convergence for the conventional method and the modified RAND method the same but the update to the molar amounts of the components in each phase is the same, other than due to round-off errors. The same second order information is available to both methods. The vol-RAND method has slightly different non-linearities as it is carried out at a specified volume and temperature, and therefore co-solves the EoS, though often the rate of convergence is almost identical. A similar plot is given in figure 4.2 where the convergence for each of the methods is plotted for a mixture of two, and then three phases. The initial estimate is from stability analysis followed by a two-phase VLE phase split calculation after which a near pure water phase is introduced and then a three-phase split calculation.



Fig. 4.1 Plot showing the convergence of isothermal flash using various implementations for a 7-component mixture (example three) at 10 bar and 160K. All implementations used two steps of successive substitution followed by the chosen method. The initial estimate was generated from the Wilson K-factor approximation.



Fig. 4.2 Plot showing the convergence of example one at 510K and 50 bar. Note that each method has two segments, corresponding to the two-phase solution and the three-phase solution, respectively. The initial stability analysis introduces a vapour phase to the feed. The two-phase solution converges at $\beta_v = 0.549$ and $\beta_l = 0.451$, after which a water phase is introduced by stability analysis and the solution finally converges at $\beta_v = 0.150$, $\beta_l = 0.516$ and $\beta_w = 0.334$. The first two steps following stability analysis are successive substitution for all methods and for both two-phase and three-phase solutions. For the three second order methods the water phase was introduced after 6 iterations, while for successive substitution it was introduced after 13 iterations.

At two-phase equilibrium the molar phase fractions are $\beta_v = 0.549$, $\beta_l = 0.451$ and at three-phase equilibrium the molar phase fractions are $\beta_v = 0.150$, $\beta_l = 0.516$, and $\beta_w = 0.334$. Again for all of the second order methods tested the rate of convergence is almost identical, and successive substitution is once again linearly convergent. After introducing each new phase the first two steps taken use successive substitution and so are the same for each method. Since the update to the modified RAND is identical to the conventional method it is expected that the convergence of both methods will be the same, though minor differences due to round-off are encountered.

The computational cost of each method is compared in table 4.4. For this a 17component mixture containing water, carbon dioxide, and hydrogen sulphide was used (example 8). Each of the methods were implemented with FORTRAN using the LAPACK library for factorisation, solving systems of equations, and inversion, otherwise compiler optimisation options were not used. A flash calculation was carried out at 370K and 2 bar using three different thermodynamic models. This involved: starting with the feed phase; introducing a vapour phase following stability analysis; solving the phase split calculation; introducing a water rich phase from stability analysis; and finally solving the phase split calculation again. The CPU time required for the second order phase split calculations was recorded for each of the models (not including stability analysis). The computational cost of one iteration is presented in table 4.4 where each method is compared to using the conventional method with SRK for two phases.

Equation of state	Two-phase flash								
	Conventional method	Modified RAND	Vol-RAND						
SRK	1	2.03	2.00						
CPA1	2.47	4.05	2.11						
CPA2	4.63	6.62	2.38						
	Three-phase flash								
SRK	2.98	2.89	2.88						
CPA1	5.41	5.40	3.08						
CPA2	8.65	8.45	3.50						

Table 4.4 Computational cost of isothermal flash using the conventional method, modified RAND and vol-RAND for a 17 component mixture (example 3). The cost is given for one iteration relative to one iteration of the two-phase split calculation with SRK.

The solution molar phase fractions for SRK are $\beta_v = 0.6633$, $\beta_l = 0.1101$, and $\beta_w = 0.2265$, for CPA1 $\beta_v = 0.7188$, $\beta_l = 0.1080$, and $\beta_w = 0.1732$, and for CPA2 $\beta_v =$

0.7187, $\beta_l = 0.1081$, and $\beta_w = 0.1732$. CPA1 considered only the water as associating (two association sites) while CPA2 considered both water and hydrogen sulphide as associating and carbon dioxide as solvating (five association sites). As the number of association sites increases the complexity of the model increases. For reservoir fluid-water systems, it is generally sufficient to consider just the self-association of water molecules by use of CPA1 [199], cross association (CPA2) can be needed for an accurate description of the carbon dioxide or hydrogen sulphide rich phases [186].

When using pressure based thermodynamics there is a significant additional cost when using a more complex EoS. However if the vol-RAND method is used, where the EoS is co-solved with the equilibrium equations the additional cost of CPA is relatively small. This is clear from table 4.4 where the vol-RAND method is only slightly slower when using CPA compared to SRK, for two phases vol-RAND with CPA1 takes almost the same time as modified RAND with SRK this is also true for three phases. This is because the association equations must only be solved once at each iteration when the volume is specified, whereas they must be repeatedly solved if the pressure is specified. The difference in computational cost is particularly clear if there are multiple associating components (CPA2), with vol-RAND taking less than half the computational time of modified RAND. For the cubics (SRK) the benefit of using a volume based formulation is minor. As both vol-RAND and modified RAND share a similar structure (F inversions of size C and one factorisation of size F + C) their computational cost is almost the same for SRK where the evaluation of the density root is relatively simple.

As the number of phases increases, the cost of the modified RAND method will decrease relative to the cost for the conventional method. This is because the $O(n^3)$ terms scale better with the modified RAND method where there are F inversions of size C and one factorisation of size F + C. This is compared to the conventional approach where there is a single factorisation of size $C \times (F - 1)$. For two phases the conventional approach is to be preferred, for three phases both methods will be about the same and for four or more phases the modified RAND approach is preferred. Example six at 120K and 1 bar can have up to four phases in equilibrium. This was flashed and the CPU time for the second order phase split calculation recorded for the two-phase, three-phase and four-phase calculations. Example six as described in the appendix was then modified with the molar amount of the ethane component split between multiple identical components, this allows for the same flash to be carried out (with identical results) but with a larger system of equations. The results for up to 100 components are presented in figure 4.3.



Fig. 4.3 Ratio of CPU time for the RAND method against the conventional method. The RAND method scales better as the number of phases increases.

The results in figure 4.3 are not smooth. This is likely due to some optimisation carried out by the compiler which is better for some methods than others. However the trends found follow the expectation that as the number of phases increases, the relative cost of the modified RAND method decreases. For two phases the modified RAND method is always more computationally demanding.

4.5.2 **Procedure correction**

None of the examples considered insofar have utilised the correction to ensure a descent direction, however such a correction is vital if the method is to be used for large scale simulation where a robust implementation is necessary. Moreover it is necessary that the correction does not significantly hinder the rate of convergence. For two-phase flash the current state of the art is to use a restricted step method with an ideal solution based correction factor, equation 4.47. For multiphase flash there is no obvious ideal correction factor. Michelsen [110] recommended the use of a perturbed decomposition routine followed by a suitable line search algorithm. This avoids repeated factorisations of the large multiphase Hessian when compared to the restricted step approach, however can have adverse affects on the rate of convergence [55]. In this work a trust region type update was used for the conventional approach with more than two phases without ideal scaling using the Hessian described by Michelsen [110]. This method requires more decompositions of the large C(F-1) matrix than using a perturbed decomposition routine, however can result in fewer outer loop iterations (which are compared here). A similar method using the K factors to improve the scaling of the Hessian is presented by Petitfrere and Nichita [144]. These methods are compared to the correction to the modified RAND method presented in section 4.2.2. This correction only modifies the derivative properties of the phase which is not positive.

Although it is rare for one phase to be unstable (i.e. for the Hessian of the Gibbs energy of that phase to be indefinite) during flash calculations, it is possible with poor initialisation, or if the mixture is close to the critical point. Example three with a temperature of 202.997K and pressure of 58.7bar is very close to the critical point. The procedure correction for the modified RAND framework is compared to the restricted step using the ideal solution update step at these conditions. Following stability analysis of the feed mixture a trial phase at a minimum in the tangent plane distance is identified. Two steps of successive substitution are taken before switching to the second order method with the phase fraction and maximum difference between component fugacities shown in figure 4.4.



Fig. 4.4 Comparison of the convergence of a near critical 7-component natural gas mixture, example three, using the correction to the modified RAND method presented here (dashed) and an restricted step implementation using an ideal solution diagonal correction (solid). The error is the maximum absolute difference between the fugacity of a components in the two phases.

After two steps of successive substitution, the incipient phase has a phase fraction of $\beta = 0.008$. The direction of the step is evaluated using equation 4.31. This is found as

$$\sum_{j=1}^{F} \sum_{i=1}^{C} \Delta n_{i,j} \ln \hat{f}_{i,j} = 4 \times 10^{-6}$$

Since this is greater than 0, a line search alone will not yield a decrease in the Gibbs energy. Correction to the modified RAND step is necessary. The minimum absolute eigenvalue for the Hessian of the two-phase mixture, equation 4.45, is -1×10^{-7} .

In this case the phase present in the greater amount is indefinite. The smallest eigenvalue of the Q matrix is $\lambda_{min} = -0.0121$. Using this with a value of d = 0.01 we find $\hat{\alpha} = 0.021$ from equation 4.40. The change to the equilibrium chemical potential and the change in the flow of each component in the incipient phase, before and after correction, is shown in table 4.5.

Before the modified RAND step is corrected, the change in the molar amounts of each component indicates that the phase present in a smaller amount should be removed (returning to the trivial solution). Following correction of the modified RAND step the phase fraction increases from $\beta = 0.008$ to $\beta = 0.271$, the final solution phase fraction is $\beta = 0.573$.

Component		λ	$\Delta \boldsymbol{n}$			
methane	3.6095	3.6095	-0.5553	0.2502		
ethane	-1.6647	-1.6564	-0.0138	0.0062		
propane	-4.3428	-4.3376	-0.0034	0.0015		
n-butane	-6.1390	-6.1444	-0.0020	0.0009		
n-pentane	-8.1262	-8.1488	-0.0010	0.0005		
n-hexane	-10.5054	-10.5507	-0.0003	0.0002		
nitrogen	0.2717	0.2608	-0.0089	0.0040		

Table 4.5 Equilibrium chemical potential and change in the incipient phase flow before and after correction of the modified RAND step.

In the presented example, figure 4.4, which has been described in detail the use of the correction to the modified RAND method requires less iterations than the use of an ideal solution correction to the two-phase Hessian. Figure 4.5 shows the convergence for both the conventional method (as described in this section using trust region for multiphase split calculation) and for the modified RAND method.



Fig. 4.5 Heat map of second order iterations to converge phase split calculation for example 6 in four phase region.

The plots in figure 4.5 have different maximum and minimum values. The modified RAND method does not exceed 20 iterations, whereas the conventional method required a maximum of 28 iterations. Over the presented area the modified RAND method used an average of 9.2 iterations while the conventional method used 10.3 iterations (these number are relatively large due to them being the sum of two-, three- and four-phase phase split calculations in some regions). It is often necessary to use a correction step in the presented example due to difficulties with multiphase mixtures. After each phase was introduced

from stability analysis, two steps of successive substitution were used to improve the initial estimate. In the presented region the RAND correction is better than the trust region implementation.

As well as complex multiphase mixtures, the presented correction is suitable for mixtures close to in the critical region. The mixture given in figure 4.6 is close to the tri-critical point of example eight.



Fig. 4.6 Number of RAND iterations to obtain convergence close to the tri-critical point for mixture of methane, ethane and n-octane, example 3. Three phase contained region inside of the black line and single phase region present to the left hand side.

Example eight is modelled with 0 k_{ij} using SRK where the predicted tri-critical point is at molar compositions of $C_8 = 0.64\%$, $C_2 = 21.8\%$ at a temperature of 225.5K, and a pressure of 69.5bar [116]. The given composition is $C_8 = 1\%$, and $C_2 = 21.8\%$ leading to a small, nearly critical, three-phase region. The number of iterations for the modified RAND approach (where the modified RAND step is often corrected) is given in figure 4.6. Even in this complex region the number of iterations does not exceed 39. In the same region the number of iterations using the conventional approach (ideal solution restricted step for two-phases and the trust region implementation described above) can be as high as 100 with the same convergence criteria.

4.5.3 State function based flash specification

Flash calculation with state function based specifications are more complex to solve than the conventional isothermal flash. We adopt the solution strategy recommended by [115] where a Newton approach is used to handle the majority of cases and a Q-function maximisation is used as a fall back method. Michelsen [115] demonstrated the strategy only for two-phase cases using the conventional flash formulation. Here, we apply the modified RAND framework, with additional constraints to multiphase flash given a V, Uspecification. The solution strategy adapted to the modified RAND formulation is as follows:

1. The initial estimate is generated using the Wilson K-factor approximation

$$\hat{\varphi}_{i,v} = 1, \quad \hat{\varphi}_{i,l} = \frac{P_{c,i}}{P} \ln\left(5.373(1+\omega_i)\left(1-\frac{T_{c,i}}{T}\right)\right)$$
(4.118)

The temperature and pressure are found by solving the Wilson equation with its temperature and pressure derivatives to meet the specified constraints.

- 2. The ideal solution approximation is used with the modified RAND method for two steps to improve the initial estimate. The system of equations to be solved, equation 4.66 is reduced in size from C + F + 2 to F + 2.
- 3. The full modified RAND, equation 4.66, is used to converge the system of equations until the deviation from specified constraints and fugacity of each component differed by less than 10^{-10} .
- 4. Once converged stability analysis is used to check if an additional phase can be introduced. If a new phase can be introduced then the composition from stability analysis is used in zero amount and returned to step 2.
- 5. If the total number of iterations (where each decomposition of the full modified RAND matrix (equation 4.66) is counted as one iteration) exceeds $10 \times F$ then Q-function maximisation [115] is used to find the solution. This is also used when the pressure or temperature are oscillating to extremely large or negative values. The Q-function maximisation uses isothermal modified RAND to solve the phase split

calculation and carries out stability analysis to identify the global minimum in the Gibbs energy.

For example three a window of specifications between 100K < T < 300K and 1bar < P < 100bar was scanned. At each (P, T) specification the solution to the flash problem was found using isothermal modified RAND. At the solution the internal energy and volume of the mixture was recorded. The problem was then re-initialised with the (U, V) specification and the solution strategy given above carried out. The number of iterations was recorded, with each decomposition of the full modified RAND matrix (equation 4.66) counted as an iteration (not the ideal solution simplification). These iterations are plotted on a heat map with the phase envelope in figure 4.7.



Fig. 4.7 Modified RAND iterations to solve the (U, V) flash problem for example three, a 7component natural gas mixture. One iteration is counted as the factorisation of the full modified RAND matrix.

The given range of temperatures and pressures corresponds to an approximate region of 0.0366L/mol< V < 25L/mol and -1950K< U/R < -290K. The computational cost of the (U, V) flash was 1.7 times the cost for the isothermal flash (including cases where Q-function maximisation was necessary). A switch to Q-function maximisation was

necessary in 1% of cases. It is clear from the figure that over the majority of the phase envelope the number of iterations necessary to solve the (U, V) flash using the modified RAND matrix is quite small, with problems encountered close to the critical point. In some cases close to the critical point three phases were introduced in error before one being removed, often this required a switch to Q-function maximisation.

To demonstrate the multiphase capabilities of the modified RAND approach the (U, V) flash was used for a more complex five-component mixture (example six). The phase envelope and number of iterations to solve the (U, V) flash problem are presented in figure 4.8.



Fig. 4.8 Number of iterations to solve the UV flash phase split calculation for a complex 5-component mixture, (example six) with up to 4 phases where the three liquids are either methane rich, hydrogen sulphide rich or carbon dioxide rich.

For example six there are difficulties in the LLE region at low temperatures and high pressures. This is in part due to the difficulty to match the volume with (U, V) flash often leading to temperatures outwith the bounds of the ideal gas heat capacity equation, or leading to poor initial estimates which need more iterations to converge. Only 3% of cases

required a switch to Q-function maximisation. The total computational time taken for (U, V) flash was 2 times the time taken for (P, T) flash.

Even in the most complex 4 phase region the method is reasonably robust. Figure 4.9 shows the number of iterations necessary in this region and the dotted region shows the approximate region where Q-function maximisation was necessary. The limit of iterations was set at 30 before switching to Q-function maximisation for this figure. In much of the dotted region a switch was made because the pressure or temperature were oscillating to very large or small values.



Fig. 4.9 Phase envelope for a complex 5-component mixture with 4 phases (example six), showing the number of iterations to obtain convergence in the 4 phase region. Dotted region shows approximate region where Q-function maximisation was necessary.

Even in the four phase region convergence is generally obtained in a reasonable number of iterations as shown in figure 4.9, with only 8% of cases using the backup Q-function maximisation. The total cost of (U, V) flash was only 2.3 times that of (P, T) flash in this region. The intermediate solutions for three-phase and four-phase examples are presented in table 4.6.

Conditio	ns	K-Wilson		2-phase		3-phase		4-phase		Iterations	
$\frac{U}{R}(K)$	$V(\frac{L}{mol})$	Т	Р	Т	Р	Т	Р	Т	Р	(U,V)	(P,T)
-1492.7	6.939	132.5	0.91	122.0	0.93	127.2	0.97	130	1	11	11
-1408.9	7.802	144.5	0.97	137.3	0.98	139.2	0.99	140	1	13	13
-1471.7	2.322	151.1	2.95	133.3	2.85	139.1	2.96	140	3	14	11
-1691.9	0.360	162.9	9.90	144.4	7.06	150	8.5	3-pha	ase	7	6

Table 4.6 (U, V) flash specifications and intermediate solutions in T (K) and P (bar) for five component mixture, example six. Also compares the number of iterations to the (P, T) specification at the solution conditions.

The initial estimate generated by the Wilson K-factor approximation is often in close agreement with the final temperature of the mixture. The largest deviation from the final temperature for the conditions presented in table 4.6 was 13K and 1.5bar. The intermediate solutions may move further from the final mixture temperature as the non-idealities are taken into account. Improved initial estimates would be available if implemented in a reservoir simulator (e.g. from previous time steps).

Examples using the general framework using thermodynamic models solved at various specifications, as described in section 4.4.2 are not included. The vol-RAND method has been implemented and tested, however other methods have not yet been tested and only the derivation is shown.

4.6 Conclusion

In this chapter we have fully derived two new RAND-based formulations named modified RAND and vol-RAND. Modified RAND solves for the equilibrium elemental potentials and molar phase amounts, while vol-RAND co-solves a pressure explicit EoS with the equilibrium equations for the elemental potentials and phase volumes. Modified RAND uses thermodynamics at a specified (P, T) while vol-RAND uses thermodynamics at a specified (V, T). A generalisation to the other flash specifications has been given with a possible implementation for (P, H) based thermodynamics discussed, though not implemented as part of this work.

One important advantage of the RAND based formulations is their simple structured implementation, with all components in all phases treated in the same manner. No terms tend towards infinity as the phase boundary is approached and it is possible to introduce phases directly from stability analysis with a zero amount though a few steps of successive substitution are preferred. Both modified RAND and vol-RAND show the same quadratic

convergence rates as the conventional second order minimisation method. In terms of the $\mathcal{O}(n^3)$ operations, modified RAND scales better with the number of phases than the conventional method. Modified RAND is slower than the conventional method for two phases, similar in speed for three-phase flash, and faster for four-phase flash. For complex EoS's like the non-cubic CPA with an association term, vol-RAND is advantageous, especially in multiphase calculations.

The modified RAND formulation has been extended from only (P, T) flash to five other state function based flash specifications. Only the (P, T) specifications is a minimisation where an objective function (the Gibbs energy) can be checked at each step. The other specifications can be solved by Newton's method using a common Jacobian matrix. In the majority of cases, using a suitable initialisation, it is possible to find the solution rapidly. A switch to Q-function maximisation may be necessary in a small number of cases.

Using the modified RAND method for isothermal flash in the close to critical region may generate an ascent direction in the Gibbs energy. A method to correct the direction has been presented. This correction applies only to the unstable phases while not changing the properties of the matrices for the other phases. The method can be used without an additional factorisation while maintaining the excellent convergence properties of the second order modified RAND method. This has been presented for a close to critical two-phase mixture, a complex multiphase mixture, and a three component mixture close to the tri-critical point.

Chapter 5

EoS Based Thermal Reservoir Simulation

The final aim of this work is to develop an EoS based, fully implicit, thermal reservoir simulator by upgrading an existing isothermal compositional simulator. Thermal reservoir simulation has been an area of interest for a long time, with early attempts at simulators from Shutler [172] in one dimension and extended to two dimensions by Shutler [173]. Coats [37, 38] proposed a model coupling thermal and compositional simulation for fully implicit three-dimensional reservoir simulation for the purpose of steam injection. Often the aqueous phase is treated in a simplified manner, with gas components excluded, or included using simple K-factor correlations [34].

It is common during reservoir simulation to treat the aqueous phase as a pure component. This is done in both the thermal simulator CMG STARS and in the modern INTERSECT simulator. CMG STARS only allows for a simple ideal solution approximation of the fluid properties without a more accurate EoS. These assumptions can lead to a number of inaccuracies during simulation.

Even when EoS's are incorporated into a thermal reservoir simulator it is common to only use the vdW1f mixing rules, though some recent work has attempted to include more complex models such as CPA [122] or PC-SAFT [119] (generally neglecting the association term). An alternative to the non-cubic EoS's is the excess Gibbs energy mixing rules used with PR or SRK in the Huron-Vidal framework [79]. This model has a similar computational cost as the vdW1f mixing rules once the temperature dependent terms are set up, whereas CPA and PC-SAFT can be an order of magnitude more expensive than the vdW1f mixing rules depending on the number of associating components. Some recent work has been carried out to include the solubility of components in the aqueous phase (e.g. [171] using the CMG STARS simulator for DME co-solvent SAGD).

Brantferger et al. [17] developed a thermal simulator using an EoS to describe all of the phases in equilibrium. They also use the internal energy as a primary variable instead of temperature, this leads to the isenthalpic flash specification which is solved in their work by directly maximising the entropy. This avoids problems with variable switching which is otherwise necessary when the number of phases is greater than the number of components. Petitfrere [143] developed a reservoir simulator for simulation of steam injection with extra-heavy oil using the PR EoS [135] with the vdW1f mixing rules.

In this work a compositional thermal simulator has been developed with the option to use more complex EoS's. The more complex thermodynamic models given in chapter 2 are incorporated into the reservoir simulator. A comparison between the vdW1f mixing rules and the HV model using NRTL_{HV} is made in section 5.2. The modified RAND implementation was used to solve the phase split calculation. The conventional method for phase split calculation was also used to verify that the results obtained were correct.

5.1 Compositional Reservoir Simulator (COSI)

COSI is a compositional, isothermal, fully implicit reservoir simulator. It was originally developed by the Danish National Laboratory, the Technical University of Denmark and COWIconsult. It can be used as a black oil or compositional simulator, though the black oil model is not described here. The mass conservation and saturation constraint are used as the primary set of equations. The primary variables are the oil phase pressure and the mass flows of each component. The phases are modelled using the SRK or PR EoS. The numerical formulation relies on an integral finite difference method. The volume discretised equations are solved using a fully implicit method. A brief description of the original simulator is given below, summarised from the manual (COSI-Formulations and Basic Algorithsm v1.0).

5.1.1 COSI description

Though the COSI simulator can handle two porous media which communicate through exchange functions (for fractured reservoirs) the description given here is for only a single media. Given F flowing phases of C components the mass conservation for each

component inside the porous media is given by:

$$\frac{\partial}{\partial t} \left(\phi \sum_{j=1}^{F} \chi_{i,j} \hat{\rho}_j S_j \right) + \boldsymbol{\nabla} \cdot \left(\sum_{j=1}^{F} \chi_{i,j} \hat{\rho}_j \boldsymbol{u}_j \right) + q_i = 0, \quad \forall i$$
(5.1)

where χ is the component mass fraction defined as

$$\chi_{i,j} = \frac{MM_i n_{i,j}}{\sum_{k=1}^{C} MM_k n_{k,j}}$$
(5.2)

 MM_i is the molecular weight of component *i* in g/mol. The phase mass density is defined as

$$\hat{\rho}_j = \frac{\sum_{i=1}^C n_{i,j} M M_i}{V_j}$$
(5.3)

and S is the saturation defined as

$$S_j = \frac{V_j}{\sum_{m=1}^F V_m} \tag{5.4}$$

Diffusion can be included however was neglected in this work. The first term on the LHS of equation 5.1 is the accumulation term, the second is due to the advective flux across the boundaries and the third the source/sink terms. In all tested examples it was assumed that there was no flow of components at the reservoir boundary, therefore the source/sink terms were only due to the wells. The flow in the porous media is modelled using Darcy's law

$$\boldsymbol{u}_j = -\frac{kr_j}{\mu_j}k(\boldsymbol{\nabla}\Phi), \quad \forall j$$
 (5.5)

where $\nabla \Phi$ is the potential due to gravity and pressure. As well as the component conservation, the saturation constraint is used to define the system of equations

$$\sum_{j=1}^{F} S_j - 1 = 0 \tag{5.6}$$

To solve the PDEs for the mass conservation a numerical model must be used. COSI uses the integral finite difference method. The total domain is discretised into a number of smaller sub domains NV. The mass balance (equation 5.1) and saturation constraint (equation 5.6) must then be satisfied in each control volume. Integrating the mass conservation equation over the cell volume for each cell and making use of divergence theorem

we arrive at

$$\frac{d}{dt} \int_{V_k} \phi \sum_{j=1}^F (\chi_{i,j} \hat{\rho} S) dV + \int_{A_k} \sum_{j=1}^F (\chi_{i,j} \hat{\rho} \boldsymbol{u}_j) dA - \int_{V_k} q_i dV = 0$$
(5.7)

It is necessary to use volume average and surface average quantities. The accumulation is described for each cell and the average flux is taken at the cell boundary between cell k and cell l. The average interface velocity is defined as

$$u_{j,kl} = \frac{1}{L_{kl}} \left(kk_{r,j}\hat{\mu}_j \right) \left((P_k - P_l)_j + g_n \nabla \left(\hat{\rho}_j \hat{H} \right)_{kl} \right)$$
(5.8)

with \hat{H} representing the height of the cell

$$\boldsymbol{\nabla}\left(\hat{\rho}_{j}\hat{H}\right)_{kl} = \frac{(V_{k}\hat{\rho}_{j} + V_{l}\hat{\rho}_{j})(\hat{H}_{k} - \hat{H}_{l})}{V_{k} + V_{l}}$$
(5.9)

For the evaluation of the component flux, the interface mobility $kr_j/\hat{\mu}_j$, density $\hat{\rho}_j$, and mass concentration $\chi_{i,j}$ were defined using the upstream cell average using the current time step values. The mass conservation equations can be written in a compact form with

$$\frac{d}{dt}(\zeta_{i,k}) = \psi_{i,k} \tag{5.10}$$

where $\zeta_{i,k}$ is the accumulation and $\psi_{i,k}$ is the flux of component *i* in cell *k*. Then using a discrete time step:

$$\zeta_{i,k}^{n+1} - \zeta_{i,k}^{n} + \Delta t \psi_{i,k}^{n+1} = 0$$
(5.11)

where the flux is evaluated at time step (n + 1). The system of equations to be solved at each time step is then

$$\hat{\boldsymbol{\Psi}}(\boldsymbol{y}) = \boldsymbol{0} \tag{5.12}$$

where \boldsymbol{y} is the vector of primary variables $(\boldsymbol{y} = (\boldsymbol{m}, P)^T)$ of the mass flow \boldsymbol{m} and the oil pressure P. The set of equations $\hat{\boldsymbol{\Psi}}$ is defined by equation 5.11 and equation 5.6.

$$\hat{\Psi}_{k} = \begin{cases} (\zeta^{n+1} - \zeta^{n})_{i,k} - \Delta t \psi^{n+1}_{i,k} \forall i \\ \sum_{j=1}^{F} S^{n+1}_{j,k} - 1 \end{cases} = \mathbf{0}$$
(5.13)

This system of equations is then solved using Newton's method

$$J\Delta y + \hat{\Psi} = 0 \tag{5.14}$$

An initial time step is set then subsequent time steps are evaluated based on the truncation error (and a specified tolerance) and the number of Newton iterations necessary to solve the system of equations.

The oleic and vapour phase densities and compositions are found using an EoS. COSI can use either SRK or PR. The isothermal phase split calculation is solved by use of the Rachford-Rice equations and successive substitution. The Wilson K-factor initial estimate is used for the phase split calculation. Two-sided stability analysis (starting from the liquid like and vapour like Wilson K-factor estimates) is used if only a single phase is found from the phase split calculation. Stability analysis skipping of Rasmussen et al. [149] is used for the two-phase flash. The dominant eigenvalue method is used for acceleration of both the phase split and stability analysis calculation. The aqueous phase is a pure water component with a set density. The viscosity of the oleic liquid and vapour phase was found using the Lorenz-Bray-Clark (LBC) correlation [100]. The water phase viscosity is set to a constant value. The porosity of each cell is calculated from the pressure and rock compressibility

$$\phi_k = \phi_k^0 + P \frac{d\phi}{dP}$$

The phase permeabilities are determined using interpolation from tables. If there are three phases in equilibrium the oil phase relative permeability is determined as

$$kr_o = \frac{kr_{o,w}kr_{o,g}}{kr_{o,cw}} \tag{5.15}$$

where kr is the relative permeability and $kr_{o,cw}$ is the relative permeability of the oil at connate water saturation. The relative permeability of the aqueous and vapour phase are set as the values from the oil-water relative permeability table and the oil-gas relative permeability table respectively.

5.1.2 Integration of multiphase flash and thermal effects to COSI

To incorporate thermal effects into COSI it was considered necessary to first replace the original treatment of water as a pure phase and to then introduce an additional partial

differential equation (for the energy balance) and variable. Temperature was chosen as the additional primary variable.

The energy balance is described by:

$$\frac{\partial}{\partial t} \left(\sum_{j=1}^{F} U_j + U_r \right) + \boldsymbol{\nabla} \cdot \left(\sum_{j=1}^{F} \hat{\xi}_j \rho_j \boldsymbol{u}_j \right) + \boldsymbol{\nabla} \cdot (\kappa \boldsymbol{\nabla} T) + q_H = 0$$
(5.16)

with κ the combined thermal conductivity of the fluid and rock. $\hat{\xi}$ is defined as the specific mass enthalpy

$$\hat{\xi}_{j} = \frac{H_{j}}{\sum_{k=1}^{C} M M_{k} n_{k,j}}$$
(5.17)

Integrating the energy conservation equation over the cell volume, making use of divergence theorem once again, we arrive at

$$\frac{d}{dt} \int_{V_k} \sum_{j=1}^F U_j + U_r dV + \int_{A_k} \sum_{j=1}^F (\hat{\xi}_{i,j} \hat{\rho} \boldsymbol{u}_j) dA + \int_{A_k} \kappa(\boldsymbol{\nabla} T) dA - \int_{V_k} q_H dV = 0 \quad (5.18)$$

The specific mass enthalpy at the interface was defined using the upstream value. The interface heat capacity κ_{kl} was defined using a harmonic mean value

$$\kappa_{kl} = \frac{2}{\frac{1}{\kappa_k} + \frac{1}{\kappa_l}} \tag{5.19}$$

The energy conservation equations can be written in a compact form with

$$\frac{d}{dt}(\hat{\zeta}_k) = \hat{\psi}_k \tag{5.20}$$

where $\hat{\zeta}_k$ is the accumulation of energy in cell k and $\hat{\psi}_k$ the flux into and out of the cell (including source/sink terms). The system of equations is then

$$\widehat{\boldsymbol{\Psi}}(\boldsymbol{y}) = \boldsymbol{0} \tag{5.21}$$

with \boldsymbol{y} the primary variables $(\boldsymbol{y} = (\boldsymbol{m}, P, T)^T)$ of the mass flow (\boldsymbol{m}) , the oil pressure (P) and the temperature (T). The set of equations is defined as:

$$\hat{\Psi}_{k} = \begin{cases} (\zeta^{n+1} - \zeta^{n})_{i,k} - \Delta t \psi_{i,k}^{n+1} \forall i \\ (\hat{\zeta}^{n+1} - \hat{\zeta}^{n})_{k} - \Delta t \hat{\psi}_{k}^{n+1} &= \mathbf{0} \\ \sum_{j=1}^{F} S_{j,k}^{n+1} - 1 \end{cases}$$
(5.22)

This is once again solved using Newton's method. The original solver used a block based ILU_0 with the TFQMR [58] Krylov space method. This was found to struggle in some cases and was replaced with an ILU_2 preconditioner with the orthomin [190] method. The orthomin method with an ILU_2 preconditioner was also found to reduce the computational time required for the tested examples.

As well as adding the energy balance it was necessary to add multiphase flash to the original COSI simulator. The isothermal flash is often a large portion of the cost of the full reservoir simulation and it is necessary to use an efficient flash algorithm to reduce its cost as much as possible. The original flash in COSI was replaced with:

1. If no previous information is available then go to step 5. If previous information is available then find an initial estimate of the molar amounts of each component in each phase as

$$n_{i,j} = z_i \theta_{i,j} \quad \forall i,j \tag{5.23}$$

where $\hat{\theta}_{i,j}$ was stored from the previous timestep as

$$\hat{\theta}_{i,j} = \frac{n_{i,j}}{z_i} \quad \forall i,j \tag{5.24}$$

- 2. If there is more than one phase then solve the phase split calculation using successive substitution for two iterations followed by the modified RAND method described in chapter 4 until the solution is found, remove phases as necessary. If a phase is removed then carry out stability analysis at step 5.
- 3. Check the change in temperature, pressure and composition since a full stability analysis was last carried out. If there has been a large change then stability analysis will be carried out this time. The parameters used were based on those of Rasmussen et al. [149]:

$$|z_i - z_{i,old}| \ge \frac{\lambda_{old}}{10}$$

$$|P - P_{old}| \ge \frac{\lambda_{old}P}{10}$$
$$|T - T_{old}| \ge 10\lambda_{old}$$

If any of these inequalities holds then stability analysis will be carried out. The λ_{old} used here is the minimum eigenvalue of the scaled Hessian of all of the equilibrium phases:

$$H_{i,j} = \delta_{i,j} + \sqrt{x_i x_j} \left(\frac{\partial \ln \hat{\varphi}_i}{\partial x_j} \right)$$

If the smallest eigenvalue was greater than 0.4 then 0.4 was used for λ_{old} , this is an extra precaution used because the shadow region method has not been extensively tested for multiphase flash. This is found at no additional cost as it is evaluated during stability analysis (when checking along the direction of the eigenvector corresponding to the minimum eigenvalue for a new, close to critical trial phase as described by Michelsen [109]).

- 4. If the previous step found one or more trial shadow phases (i.e. a phase with a positive minimum in the tangent plane distance) then use the previous estimate and carry out stability analysis to find a new minimum. If the new minimum is negative then solve the phase split calculation as described before. The shadow phase approach described above is general for more than two phases and any number of potential trial phases are possible.
- 5. If necessary from previous steps, due to a change in conditions or the removal of a phase, then carry out full stability analysis. If the current estimate has more than one phase then continue to stability analysis in step 6. If the initial estimate is only single phase then use the Wilson K-factor with the modifications for the aqueous phase as described in chapter 3 section 3.2.5 to find initial estimates for the three phase fugacity coefficients. Solve the ideal solution problem using multiphase Rachford-Rice, and then fully solve the phase split calculation.
- 6. For stability analysis the trial phases used are initialised as a trial phase based on selected pure components (lightest hydrocarbon, heaviest hydrocarbon, water and a selection of other components), an ideal gas trial phase, and a Wilson K-factor liquid trial phase. If any negative tangent plane distances are found then carry out a phase split calculation. If any positive minima are found then record the composition as a shadow phase. Finally carry out a search along the eigenvector corresponding to the minimum eigenvalue of the scaled Hessian of the phase Gibbs energy (record the

minimum eigenvalue as it is used with the stability analysis skipping parameters). If stability analysis is carried out then update the values of $z_{i,old}$, P_{old} , T_{old} , and λ_{old} for the stability analysis skipping.

7. Output the results of the flash.

The multiphase stability analysis skipping is not investigated in detail in this work. One drawback is that shadow region where a positive minimum in the TPD can be identified can be very small for the appearance of additional liquid phases. For this reason an upper limit was set on λ_{old} of 0.4, additionally it is possible to check the stability of some components prone to forming additional phases (e.g. CO_2) even when all others are skipped. For water there is often a relatively large shadow phase region.

The density of each phase is evaluated using the EoS (including the aqueous phase). The enthalpy of each phase is found from the residual contribution from the EoS and the ideal gas contribution, using the ideal gas heat capacity correlation:

$$\frac{C_p^{IG}}{R} = C_1 + C_2 T + C_3 T^2 + C_4 T^3$$
(5.25)

A reference temperature of 300K is used for the ideal gas enthalpy.

The viscosity of the oleic liquid and vapour phase is again found using the LBC correlation. For simplicity, the aqueous phase is assumed to be pure water in the viscosity modelling with the pressure effect neglected. The correlation used for the water/aqueous phase is from DIPPR:

$$\hat{\mu} = \exp(C_1 + C_2/T + C_3 \ln(T) + C_4 T^{C_5})$$
(5.26)

The parameters used are:

$$C_1 = -52.843, \quad C_2 = 3703.6 \quad C_3 = 5.866, \quad C_4 = -5.879 \times 10^{-29}, \quad C_5 = 10$$

The relative permeability models remain unchanged from the original formulation. Temperature dependent models have not been included. If there are more than three phases in equilibrium it is assumed that the oil saturation is found as the summation of all the oleic phases for the purpose of finding the relative permeability, with the same relative permeability used for all oleic phases (though each had a different viscosity).

The thermal conductivity of the oil is set as a constant at 0.14 W/(m K). The thermal conductivity of the vapour is 0.05 W/(m K). The thermal conductivity of the rock is 3.17

W/(m K). The thermal conductivity of the aqueous phase is based on the correlation from DIPPR:

$$\kappa_i = C_1 + C_2 T + C_3 T^2 + C_4 T^3 \tag{5.27}$$

with

$$C_1 = -0.432, \quad C_2 = 0.0057255, \quad C_3 = -8.078 \times 10^{-6}, \quad C_4 = 1.861 \times 10^{-9}$$

The mixed thermal conductivity is found from the correlation of Anand et al. [5] as used by CMG STARS:

$$\kappa = (1 - \sqrt{S_w + S_o})\kappa_{g-r} + \sqrt{S_w + S_o}\kappa_{L-r}$$
(5.28)

where the mixed liquid rock thermal conductivity is described as

$$\kappa_{L-r} = \kappa_L a^b \tag{5.29}$$

with

$$a = \kappa_r / \kappa_L, \quad b = 0.28 - 0.757 \log_{10} \phi - 0.057 \log_{10} a, \quad \kappa_L = \frac{S_o \kappa_o + S_w \kappa_w}{S_o + S_w}$$

and the mixed gas rock thermal conductivity found as

$$\kappa_{g-r} = \kappa_g c^d \tag{5.30}$$

with

$$c = \kappa_r / \kappa_g, \quad b = 0.28 - 0.757 \log_{10} \phi - 0.057 \log_{10} c$$

The loss of energy to the overburden and under-burden is found using the correlation of Vinsome and Westerveld [191]:

$$Q = \kappa_r A \left(\frac{T^n - T^0}{0.5\sqrt{\eta t}} - p \right)$$
(5.31)

where T^n represents the temperature at the current time step, and T^0 the initial temperature, with

$$p = \frac{\frac{\eta \Delta t (T^n - T^0)}{0.5\sqrt{\eta t}} + \tau^{n-1} - \frac{(0.5\sqrt{\eta t})^3 (T^n - T^{n-1})}{\eta \Delta t}}{3(0.5\sqrt{\eta t})^2 + \eta \delta t}$$

$$q = \frac{p\sqrt{\eta t} - (T^n - T^0) + \frac{0.25\eta t(T^n - T^{n-1})}{\eta \delta t}}{0.5\eta t}$$
$$\tau^n = 0.5(T^n - T^0)\sqrt{\eta t} + 0.25p\eta t + 2q(0.5\sqrt{\eta t})^3$$

and

$$\eta = \kappa_r / C_{p,r}$$

The heat capacity of the rock is set at a constant of $2347310 \text{ J/(m}^3 \text{ K)}$.

The internal energy of each control volume is found as

$$U = \sum_{j=1}^{F} H_j + U_r - \sum_{j=1}^{F} V_j P$$
(5.32)

Other contributions to the internal energy are ignored.

The source and sink terms used are based on a specified bottom hole pressure. At the given pressure the flux of fluid across the sandface and into (or out of) the well was evaluated along with its derivatives and added to the source and sink terms in the applicable reservoir cells. If the well rate is specified rather than the bottom hole pressure then the well is fully solved at each Newton iteration.

All of the derivative properties, except for those from the LBC correlation, are determined analytically to minimise the required computational time. (C + 2) forward difference evaluations are used to find the numerical derivatives to the LBC correlation for each oleic and vapour phase (C component mass flow, one pressure and one temperature derivative).

The original convergence criteria for COSI is that the truncation error is below a certain threshold and

$$1 - \sum_{j=1}^{F} S_j < 0.005 \quad \forall NV$$
 (5.33)

To this an additional requirement of

$$\sqrt{\frac{\sum_{i=1}^{N_{RHS}} RHS_i^2}{NV}} < 1 \tag{5.34}$$

was found necessary to ensure that the internal energy equations are solved to a suitable tolerance. Following 30 Newton iterations without convergence the step is repeated with a reduced time step. The maximum allowable time step is set to 30 days for the given example.

For the Jacobian the mass and energy balance derivatives were scaled by the control volume of each cell, with units of kg/m³ for equation 5.1 and MJ/m³ for equation 5.16. The pressure derivatives were found in bar and the temperature derivatives in Kelvin.

5.2 Results

The results from this work are preliminary and have not been investigated in detail. They are presented here to demonstrate that the original COSI code has been developed from having a two-phase flash with a pure water phase using only SRK and PR for the vapour and oil phase to a fully compositional (including aqueous phase) simulator which can include an energy balance and be used with more complex mixing rules for the thermodynamic model. This is demonstrated here for a simple reservoir model with a relatively complex fluid description utilising two thermodynamic models. Some more complex features have been tested though the reliability of the results is not clear (e.g. a four-phase mixture has been tested to verify that the derivative properties are correct and the simulation can run but a full run with reliable results has not been obtained). Some elements of the reservoir simulation must be improved before more complex models are considered, this is discussed more in the conclusions.

The reservoir model is based on the one described by Petitfrere [143]. The reservoir description is given in table 5.1

Property	Value
Cell dimension	$15 \times 15 \times 15$
Number of cells	$30 \times 30 \times 1$
Porosity	0.3
Cell x-Permeability	300×150 mD, $300 \times 15,000$ mD, and 300×150 mD
Cell y-Permeability	300×150 mD, $300 \times 15,000$ mD, and 300×150 mD
Initial pressure	30 bar
Initial temperature	298.15K
Connate water saturation	0.2

Table 5.1 Reservoir description

For this simulation an eight component mixture (including water) was used. This ranged from ethane and carbon dioxide to C_{36} . No oil pseudo-components were used, well defined components were chosen so that binary parameter regressed in chapter 2 could be used. The fluid properties are described in table 5.2.

Component	Initial amount (%)	$\mid T_c(\mathbf{K})$	P_c (bar)	ω	MM
CO_2	0.025	304.21	73.83	0.2236	44.01
C_2	0.025	305.32	48.72	0.0995	30.07
C_3	2.51	369.83	42.48	0.1523	44.096
\mathbf{C}_6	2.56	507.6	30.25	0.3013	86.177
C_{10}	28.85	617.7	21.1	0.4923	142.285
C_{20}	28.85	768	11.6	0.90688	282
C_{36}	37.18	874	6.8	1.526	506
H_2O	N/A	647.13	220.55	0.345	18.015

Table 5.2 Reservoir fluid properties



Fig. 5.1 Relative permeability curves for water with oil and oil with gas.

The molar amount of the water is not specified, instead it is evaluated based on the connate water saturation at the initial reservoir condition. To find the molar amount an estimate was taken for the split between water and oil, the amount of water in the mixture was then iteratively updated until the saturation based on the amount of water was the same as the connate water saturation. Newton iteration was used with bisection to find the required amount of water to reach the connate water saturation at the initial time. The amount of water differed depending on the thermodynamic model used and as such is not a single value. Furthermore when tested on a 3D model (not described here) the ratio of water to oil differs depending on the depth and thermodynamic model used. The connate water saturation was set at 0.2 with the relative permeability given in figure 5.1.

Since a thermal simulation was considered it was necessary to use a correlation for the ideal gas heat capacity. The correlation from DIPPR was used to generate pseudo data which was then fitted to a more simple polynomial, this removes the requirement to evaluate the hyperbolic sine and cosine functions. The parameters for the ideal gas heat capacity equation are given in table 5.3.

Component	C ₁	$ \mathbf{C}_2 \times 10^2 (K^{-1}) $	$ \mathbf{C}_3 \times 10^5 (K^{-2}) $	$C_4 \times 10^9 (K^{-3})$
CO_2	1.952	1.193	-1.319	6.075
C_2	0.639	3.119	-1.100	0.144
C_3	-1.353	4.172	-2.853	9.444
\mathbf{C}_6	-3.807	8.626	-6.251	20.195
C_{10}	-6.949	14.494	-10.672	33.125
\mathbf{C}_{20}	-12.762	28.903	-23.009	82.235
C_{36}	-13.892	46.175	-30.876	87.082
H_2O	4.031	-0.083	0.327	-1.572

Table 5.3 Ideal gas heat capacity parameters

Two models were used for this reservoir fluid. The first was PR78 with the vdW1f mixing rules using only a k_{ij} . The second was PR78 with the HV NRTL_{HV} mixing rules, reduced to the vdW1f mixing rules for a number of binary pairs. The binary parameters for the vdW1f mixing rules are given in table 5.4. The binary parameters for the NRTL_{HV} mixing rule are given in tables 5.5 and 5.6, all cells labelled as k_{ij} in table 5.5 use the vdW1f mixing rule parameters from table 5.4.

Components	CO_2	C_2	C ₃	C ₆	C ₁₀	C ₂₀	C ₃₆	H_2O
CO_2	0	0.12	0.12	0.12	0.104	0.077	0.059	0.175
C_2	0.12	0	0	0	0.01	-0.008	0.029	0.455
C_3	0.12	0	0	0	0.003	-0.007	0.012	0.509
C_6	0.12	0	0	0	0	0	0	0.5
C_{10}	0.104	0.01	0.003	0	0	0	0	0.45
C_{20}	0.077	-0.008	-0.007	0	0	0	0	0.45
C_{36}	0.059	0.029	0.012	0	0	0	0	0.45
H_2O	0.175	0.455	0.509	0.5	0.45	0.45	0.45	0

Table 5.4 k_{ij} parameters for 8-component mixture

The injection fluid is 3.3% of each ethane, propane and carbon dioxide and 90 % water. The injection temperature was 525K (superheated vapour). The injection pressure is 10 bars greater than the reservoir pressure (40 bar) and the production pressure 2 bars lower than the reservoir pressure (28 bar). The simulation was allowed to run for 10 years. The computational cost of the two methods is very similar. The additional cost of NRTL

Components	CO ₂	C_2	C_3	C_6	C ₁₀	C ₂₀	C ₃₆	H ₂ O
CO_2	0	k_{ij}	k_{ij}	k_{ij}	$ k_{ij}$	k_{ij}	-2040	-730
C_2	k_{ij}	0	k_{ij}	k_{ij}	k_{ij}	k_{ij}	k_{ij}	-600
C_3	k_{ij}	k_{ij}	0	k_{ij}	k_{ij}	k_{ij}	k_{ij}	2500
\mathbf{C}_6	k_{ij}	k_{ij}	k_{ij}	0	k_{ij}	k_{ij}	k_{ij}	450
C_{10}	k_{ij}	k_{ij}	k_{ij}	k_{ij}	0	k_{ij}	k_{ij}	900
C_{20}	k_{ij}	k_{ij}	k_{ij}	k_{ij}	k_{ij}	0	k_{ij}	k_{ij}
C_{36}	390	k_{ij}	k_{ij}	k_{ij}	k_{ij}	k_{ij}	0	k_{ij}
H_2O	2500	3040	2730	1630	2090	k_{ij}	k_{ij}	0

Table 5.5 Energy parameters for $\mathrm{NRTL}_{\mathrm{HV}}$ mixing rule A_{ji}/R (K)

Table 5.6 Non-randomndess parameters for NRTL_{HV} mixing rule α

Components	CO ₂	C_2	C3	C ₆	C ₁₀	C ₂₀	C ₃₆	H ₂ O
CO_2	0	0	0	0	0	0	0.32	0.08
C_2	0	0	0	0	0	0	0	0.08
C_3	0	0	0	0	0	0	0	0.28
C_6	0	0	0	0	0	0	0	0.12
C_{10}	0	0	0	0	0	0	0	0.12
C_{20}	0	0	0	0	0	0	0	0
C_{36}	0.32	0	0	0	0	0	0	0
H ₂ O	0.08	0.08	0.28	0.12	0.12	0	0	0

over the vdW1f mixing rules is small once the temperature dependent terms have been calculated which is necessary only once per grid block and time step (since the temperature is specified). The temperature profile for the two simulations is shown in figure 5.2 at 1 year, figure 5.3 at 4 years, figure 5.4 at 7 years and figure 5.5 at 10 years.



Fig. 5.2 Temperature profile for thermal reservoir simulation after 1 year and the temperature difference between the two thermodynamic models used in units of Kelvin.

The colours represent the same temperature on each plot, however for the temperature difference plot the range of the colour is changed depending on the maximum and minimum deviations. The largest difference in the temperature occurs after 7 years where the use of PR with HV has some cells close to the front which are 50K less than PR with vdW1f. This indicates that the temperature front of the vdW1f model is ahead of the model using PR with HV. Differences in the temperature can also be found at the the fronts travelling along the y-direction and the front moving in the x-direction. The shape of the temperature front is driven primarily by the fluid flow. The conductive contribution to the energy flux is relatively small in comparison to the advective term. Similar plots for the saturation of the oil in the reservoir are given in figures 5.6 to 5.9.

A relatively sharp displacement front is visible in figure 5.6 however becomes more disperse in figures 5.7 and 5.8. The front is moving ahead of the thermal front in this case. This is in part due to the use of the LBC correlation which is not accurate for heavier


Fig. 5.3 Temperature profile for thermal reservoir simulation after 4 years and the temperature difference between the two thermodynamic models used in units of Kelvin.



(c) T Difference (HV-vdW1f)

Fig. 5.4 Temperature profile for thermal reservoir simulation after 7 years and the temperature difference between the two thermodynamic models used in units of Kelvin.



Fig. 5.5 Temperature profile for thermal reservoir simulation after 10 years and the temperature difference between the two thermodynamic models used in units of Kelvin.



(c) So Difference (HV-vdW1f)

Fig. 5.6 Oil saturation profile for thermal reservoir simulation after 1 year and the difference between the two thermodynamic models used.



Fig. 5.7 Oil saturation profile for thermal reservoir simulation after 4 years and the difference between the two thermodynamic models used.



(c) So Difference (HV-vdW1f)

Fig. 5.8 Oil saturation profile for thermal reservoir simulation after 7 years and the difference between the two thermodynamic models used.



Fig. 5.9 Oil saturation profile for thermal reservoir simulation after 10 years and the difference between the two thermodynamic models used.

mixtures. There are relatively large differences between the results obtained using the two thermodynamic models at the fronts. However the size of the swept region is similar with both models. How the different models affect the production and injection of each component is presented in figure 5.10.

The injection and production profiles when using the two models are very similar. The production of the components which are not injected (figure 5.10b) are almost identical for the two models up until water breakthrough. This is likely due to both models using the PR EoS, therefore the density of the mixtures will be very similar. It is not until breakthrough that slight differences are encountered. The PR HV mixing rules predicts 1.3% more cumulative production of C_{36} after 10 years while requiring only 98.4% as much injection fluid. Between approximately 2000-2700 days there is an increased rate of water production which then drops off after 2700 days to a steady state. This is the time between the initial water breakthrough into the well and the time when there is steam breakthrough as shown on figures 5.4 and 5.5.

A second simulation was run using the same reservoir grid and fluid but with an initial pressure of 100 bar. The injection fluid is at 110bar with a temperature of 590K (fully



Fig. 5.10 Production and injection of each component and totals. Solid line represents the use of the PR with HV thermodynamic model while the dashed line represent PR with the vdW1f mixing rules.



vapour) and the production pressure is 98 bar. The same plots as described before are presented for this simulation.

(c) T Difference (HV-vdW1f)

Fig. 5.11 Temperature profile for thermal reservoir simulation after 1 year and the temperature difference between the two thermodynamic models used in units of Kelvin.

One notable difference between the simulation at 30 bar and the simulation at 100 bar is that at 100 bar the differences between the two EoS models are less pronounced in the production and injection curves (figure 5.19) than at 30 bar (figure 5.10). However the differences between the saturation plots and the temperature profiles is actually larger (note that the maximum and minimum are further apart at 100 bar than at 30 bar). The breakthrough of water is earlier at 100 bar than at 30 bar. This can be observed both in the saturation plots where the displacement front moves faster and in the water production plot where water breakthrough occurs at around 1400 days at 30 bar and at 1200 days at 100 bar. This is in part due to the increased mass flow rate into the reservoir from the injection well due to the increased density of the injected vapour. The overall production of hydrocarbon components is not much different between the two simulations in spite of the increased injection rate in the second example.



Fig. 5.12 Temperature profile for thermal reservoir simulation after 4 years and the temperature difference between the two thermodynamic models used in units of Kelvin.





Fig. 5.13 Temperature profile for thermal reservoir simulation after 7 years and the temperature difference between the two thermodynamic models used in units of Kelvin.



Fig. 5.14 Temperature profile for thermal reservoir simulation after 10 years and the temperature difference between the two thermodynamic models used in units of Kelvin.



(c) So Difference (HV-vdW1f)

Fig. 5.15 Oil saturation profile for thermal reservoir simulation after 1 year and the difference between the two thermodynamic models used.



Fig. 5.16 Oil saturation profile for thermal reservoir simulation after 4 years and the difference between the two thermodynamic models used.



(c) So Difference (HV-vdW1f)

Fig. 5.17 Oil saturation profile for thermal reservoir simulation after 7 years and the difference between the two thermodynamic models used.



Fig. 5.18 Oil saturation profile for thermal reservoir simulation after 10 years and the difference between the two thermodynamic models used.

5.3 Conclusions

The simulator developed is based on COSI. COSI is a compositional isothermal simulator with only SRK or PR available and could only carry out two-phase flash with the water treated as a pure phase. The simulator has been extended to a fully compositional simulator with a compositional treatment of an aqueous, vapour and any number of oleic phases. An energy balance has been added to account for thermal effects. Conductive and advective heat flux have been included. The thermal conductivity can be found using correlations from DIPPR or given set values with non-linear mixing of the thermal conductivity of the fluid with the rock included. The ideal gas heat capacity can be found using a number of simple correlations including that given in DIPPR, though often a simple polynomial is preferred to the DIPPR correlation since the DIPPR correlation can be computationally demanding. The original thermodynamic routines have been replaced with a general interface which can utilise any suitable thermodynamic model and is currently able to use PR and SRK with the vdW1f mixing rules, and HV with NRTL_{HV} mixing rules. CPA has also been tested though reliable results have not yet been obtained. The original flash routine utilising only successive substitution has been replaced with the modified RAND implementation and multiphase Rachford-Rice, the conventional multiphase flash has also



Fig. 5.19 Production and injection of each component and totals. Solid line represents the use of the PR with HV thermodynamic model while the dashed line represent PR with the vdW1f mixing rules.

been added (though was only used to check the results from modified RAND). A robust stability analysis has been included along with multiphase stability analysis skipping. The numerical solver has been replaced with an ILU_2 pre-conditioner using either orthomin or GMRES (with orthomin found to be better for the tested examples).

Though it is possible to run 3D cases using the simulator, only a simple 2D case has been presented here as volume translation has not yet been incorporated. Using just the PR or SRK EoS without correcting the density of the aqueous phase can lead to incorrect predictions that the aqueous phase is less dense than the oleic phase. The simple case was demonstrated using both the PR with vdW1f mixing rules and PR with HV and NRTL_{HV} mixing rules. Differences in the overall injection and production of 2% were found using the simple test case. Though these differences may not appear significant the additional cost of the NRTL_{HV} model is very minor compared to using the vdW1f mixing rules alone. For the tested examples the use of the NRTL_{HV} model required 7.5% more CPU time than the use of vdW1f mixing rules (when the simulation was carried out on a single thread).

Further work is necessary to make the simulator more stable and to make the code run in parallel. More viscosity correlations are necessary to attempt to model a heavy oil simulation where the LBC correlation may not be suitable. It is suspected that the poor reliability of results when using CPA is due to implementation issues with the denisty root solver. This needs to be improved or volume-based thermodynamic methods such as vol-RAND used to mitigate the problems. For thermal simulation it is often desired to use (PH) flash instead of (PT) flash. This should be added as an option to ensure that problems are not encountered with narrow boiling fluids and when there are more phases than components. The well models should be updated to include additional options, such as steam trap control. Before reliable results can be obtained for 3D simulation a volume translation must be included when using the PR or SRK EoS.

Chapter 6

Conclusions and Future Work

This chapter aims to summarise some of the results from this work and to present possible future directions for development. To summarise the work that has been carried out we have: carried out a model comparison to select the suitable thermodynamic models for the simulation of production of heavy oil; developed a robust and rapid isobaric isenthalpic flash algorithm, with modifications for calculations involving water; developed new methods for phase split calculation, with the framework extended to include both chemical reactions and non-isothermal phase split calculations; developed a method to co-solve the EoS with the equilibrium equations; and added a thermal calculation capability to an existing isothermal compositional reservoir simulator.

In the chapter 2 of this thesis it was necessary to develop a robust regression tool which could be used with any of the tested thermodynamic models. Using the developed tool, 17 models were compared for 45 binary mixtures consisting of 31 pure components. Of the tested models it was found that the commonly used cubic EoS with the vdW1f mixing rules were excellent for all binary pairs when using two binary interaction parameters except for binary pairs including water. If the equilibrium of the aqueous phases is considered important to the work the the more flexible Huron-Vidal model using the NRTL_{HV} activity coefficient model was found to be best along with the cubic plus association EoS when including the solvation components into the aqueous phases. The PC-SAFT EoS was also reviewed, however with the pure component correlations used for C_{20} plus it was found to give poor saturation point results. The zero pressure mixing rule MHV1 and MHV2 were found to be suitable for nearly symmetric pairs and pairs including water, however struggled for pairs of hydrocarbons with CO₂ and highly asymmetric hydrocarbon pairs. The recommended models for use are NRTL_{HV} which can be reduced to the vdW1f mixing

rules for select pairs. CPA is also suitable though the additional complexity of the model and associated computational cost to solve may be a concern for reservoir simulation.

For future work with the regression tool developed it is possible to include more binary pairs or thermodynamic models in the comparison. It may be desired in future work to develop some temperature dependent binary interaction parameters over the range of temeratures of interest to heavy oil reservoir simulation. Some new parameter sets could also be tested for the PC-SAFT EoS for which there is still ongoing work to find suitable pure component parameter correlations.

There are two major issues with the flash calculations used for thermal recovery. The first is how to treat the energy balance and the second is how to solve phase split calculation involving multiple phases (up to four fluid phases are possible during heavy oil recovery).

One possibility to avoid a number of issues with the energy balance is to solve the isenthalpic flash equilibrium problem. This is analysed in detail in chapter 3. The conventional second order approach to solving state function based flash specifications is extended from two-phase to multiphase problems. The resulting framework is used in an algorithm with both first order and second order implementations. The algorithm is further tailored to mixtures containing water, and some improved steps proposed to avoid violation of the inequality constraint in flash calculations using the equilibrium K-value equations. The presented algorithm, both in its general form and for mixtures containing water, is then compared to isothermal flash and Q-function maximisation for a number of mixtures. It is found to have only a moderate computational cost penalty compared to isothermal flash (<15%). A case where there are more phases than components is also tested and the presented algorithm shown to be suitable.

A new multiphase flash framework is proposed in chapter 4. This is based on similar work carried out for chemical reaction equilibria, and the resulting methods are derived assuming that chemical reactions are involved though the results presented are only for phase equilibria calculations. The modified RAND framework is well structured with all components in all phases treated in the same way, this leads to a well structured implementation where errors can be easily avoided. The modified RAND framework is then developed to consider corrections to the Newton step when it is ascending in the Gibbs energy, and to extend the method from isothermal isobaric phase split calculations to a range of other state function based phase split calculations. A method similar to modified RAND is developed to co-solve the pressure explicit EoS with the equilibrium equations. Both modified RAND and vol-RAND are compared to the conventional isothermal flash. It is shown that vol-RAND is well suited to complex EoS's, such as CPA or PC-SAFT. The

modified RAND formulation is shown to have excellent second order convergence. The structure of the modified RAND formulation means that its computational cost scales better than the conventional method as the number of phases is increased. For two phases the conventional approach is preferred, while for three phases both methods perform similarly, for four or more phases modified RAND is less computationally demanding.

A significant amount of work has been carried out to develop phase split calculations. Further work is necessary to further develop the vol-RAND methodology to make it robust enough for implementation in simulation tools. This area is of particular interest for the use of new, more complex EoS's which are often prohibitively computationally demanding. However when co-solved with the phase equilibrium equations, the additional computational overhead is shown to be very small. While the modified RAND and vol-RAND method have been developed for state function based flash calculations it may be desireable to carry out each of these state function based calculations by solving the EoS at the given state function variables. This leads to a simple minimisation without nonlinear constraints. A derivation for this has been given in chapter 4 though testing of the method has not yet been carried out and significantly more work is necessary to arrive at a final solution.

The results from chapters 2 and 4 were then incorporated into a newly developed thermal, multiphase, EoS based reservoir simulator as described in chapter 5. The energy balance equation is added along with the advective and conductive flux of energy between the grid-blocks. The loss of energy to the overburden and under-burden is taken into account. A nonlinear mixing model for the thermal conductivity of the fluid and rock is added. The initial two-phase flash is replaced with a multiphase flash implementation utilising a general thermodynamic input which has been demonstrated for the vdW1f mixing rules and the Huron-Vidal model in a simple test case.

Though the reservoir simulator has been demonstrated for a simple test case, further work is still necessary to obtain reliable results. It would be desirable to include an isenthalpic flash instead of isothermal flash, which can struggle for narrow-boiling fluids. The EoS's currently used in the simulator also require some minor improvements. Future work may aim to include a volume translation in the cubic EoS's and to improve the reliability of the density solver in CPA. Alternatively implementation of a volume based phase split calculation would avoid the difficulties encountered with CPA. The simulation results given so far are preliminary, and to conclude which models are best suited to thermal simulation would require more complex reservoir models, and fluid descriptions.

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Appendix A

Tabulated model comparison results and binary interaction parameters for chapter 2

This appendix will present the optimum binary interaction parameters for the binary pairs investigated in this work. The parameters have not been tested for multicomponent mixtures. The meaning of BIP1 2 and 3 changes depending on the model used. For the vdW mixing rules with SRK and PR BIP1 is the k_{ij} from equation 2.2a and BIP2 is the l_{ij} from equation 2.1b. For CPA BIP1 is the k_{ij} and if present BIP2 is the cross association volume for solvating pairs (note this was not regressed but set to a given value when solvation is possible). For PC-SAFT BIP1 is the k_{ij} from equation 2.19. For the g^E models using NRTL or NRTL_{HV} the BIP1, BIP2, and BIP3 are $\frac{C_{ji}}{R}$, $\frac{C_{ij}}{R}$ (units of K) and $\tilde{\alpha}_{ji}$ respectively.

The asterisk in each table for each binary pair represents the model with the minimum objective function for each binary pair. The reported deviations are the mean absolute deviation for the model, the model with the asterisk may not correspond to the model with the smallest deviation. This is because data points which cannot be represented by a model are discarded.

Table A.1 Binary parameters and deviations for ethane binary pairs

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₁₀	PR vdW	0.01	0.0	N/A	2.72	0.91
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ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)				
C ₁₀	PR vdW	0.0	0.01	N/A	4.18	0.90				
C ₁₀	PR vdW	0.01	0.0	N/A	2.72	0.91				
C ₁₀	PR MHV1	40	-350	0.52	7.45	0.77				
C ₁₀	PR MHV2	120	-320	0.52	11.60	0.81				
C ₁₀	PR HV NRTL	-360	400	0.16	5.42	0.93				
C ₁₀	PR HV NRTL _{HV}	-900	250	0.08	3.00	0.87				
C ₁₀	SRK vdW	0.001	0.0	N/A	2.98	0.75				
C ₁₀	SRK vdW	0.0	-0.002	N/A	2.85	0.75				
C ₁₀ *	SRK vdW	0.007	0.002	N/A	2.57	0.74				
C ₁₀	SRK MHV1	40	-360	0.52	7.31	0.68				
C ₁₀	SRK MHV2	140	-340	0.52	11.56	0.71				
C ₁₀	SRK HV NRTL	200	-170	0.2	3.34	0.75				
C ₁₀	SRK HV NRTL _{HV}	-500	120	0.0	2.78	0.74				
C ₁₀	PC-SAFT	0.007	N/A	N/A	3.45	0.63				
C ₁₂	PR vdW	0.008	0.0	N/A	2.39	N/A				
C ₁₂	PR vdW	0.0	-0.004	N/A	3.17	N/A				
C ₁₂	PR vdW	0.014	0.005	N/A	1.91	N/A				
C ₁₂	PR MHV1	130	-410	0.52	7.51	N/A				
C ₁₂	PR MHV2	190	-290	0.44	17.67	N/A				
C ₁₂	PR HV NRTL	370	-180	0.48	3.47	N/A				
C ₁₂	PR HV NRTL _{HV}	280	0	0.28	2.28	N/A				
C ₁₂	SRK vdW	0.008	0.0	N/A	2.37	N/A				
C ₁₂	SRK vdW	0.0	-0.004	N/A	3.16	N/A				
C ₁₂ *	SRK vdW	0.011	0.003	N/A	2.06	N/A				
C ₁₂	SRK MHV1	40	-340	0.8	6.97	N/A				
C ₁₂	SRK MHV2	230	-320	0.52	17.49	N/A				
C ₁₂	SRK HV NRTL	360	-180	0.56	2.88	N/A				
C ₁₂	SRK HV NRTL _{HV}	200	0	0.32	2.32	N/A				
C ₁₂	PC-SAFT	0.009	N/A	N/A	1.88	N/A				
C ₁₆	PR vdW	0.01	0.0	N/A	4.65	N/A				
C ₁₆	PR vdW	0.0	0.004	N/A	5.06	N/A				
C ₁₆ *	PR vdW	0.022	0.015	N/A	3.77	N/A				
C ₁₆	PR MHV1	260	-600	0.52	16.23	N/A				
C ₁₆	PR MHV2	400	-640	0.52	29.87	N/A				
C ₁₆	PR HV NRTL	750	-280	0.48	5.81	N/A				
C ₁₆	PR HV NRTL _{HV}	-1780	290	0.04	5.40	N/A				
C ₁₆	SRK vdW	0.003	0.0	N/A	5.02	N/A				
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 Table A.1 – continued from previous page
ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)			
C ₁₆	SRK vdW	0.0	0.002	N/A	5.15	N/A			
C ₁₆	SRK vdW	0.016	0.009	N/A	3.66	N/A			
C ₁₆	SRK MHV1	20	-500	0.52	23.68	N/A			
C ₁₆	SRK MHV2	60	-500	0.52	36.46	N/A			
C ₁₆	SRK HV NRTL	370	-310	0.12	7.69	N/A			
C ₁₆	SRK HV NRTL _{HV}	-500	130	0.44	4.72	N/A			
C ₁₂	PC-SAFT	0.004	N/A	N/A	6.67	N/A			
C ₂₀	PR vdW	-0.008	0.0	N/A	6.91	N/A			
C ₂₀	PR vdW	0.0	0.012	N/A	4.47	N/A			
C ₂₀ *	PR vdW	0.016	0.025	N/A	3.81	N/A			
C ₂₀	PR MHV1	280	-770	0.52	16.11	N/A			
C ₂₀	PR MHV2	570	-830	0.52	36.00	N/A			
C ₂₀	PR HV NRTL	820	-320	0.52	6.43	N/A			
C ₂₀	$PR \; HV \; NRTL_{HV}$	-1420	210	0.12	6.69	N/A			
C ₂₀	SRK vdW	-0.009	0.0	N/A	7.02	N/A			
C ₂₀	SRK vdW	0.0	0.013	N/A	4.84	N/A			
C ₂₀	SRK vdW	0.009	0.016	N/A	3.98	N/A			
C ₂₀	SRK MHV1	320	-790	0.52	16.91	N/A			
C ₂₀	SRK MHV2	700	-870	0.52	36.10	N/A			
C ₂₀	SRK HV NRTL	800	-360	0.48	6.18	N/A			
C ₂₀	SRK HV NRTL _{HV}	-700	130	0.4	5.54	N/A			
C ₂₀	PC-SAFT	-0.002	N/A	N/A	6.9	N/A			
C ₂₂	PR vdW	-0.013	0.0	N/A	10.31	N/A			
C ₂₂	PR vdW	0.0	0.013	N/A	4.99	N/A			
C ₂₂	PR vdW	0.022	0.022	N/A	2.72	N/A			
C ₂₂	PR MHV1	220	-710	0.52	10.54	N/A			
C ₂₂	PR MHV2	540	-720	0.52	48.56	N/A			
C ₂₂	PR HV	1020	-290	0.52	5.02	N/A			
C ₂₂	PR HV _{mod}	-800	200	0.52	2.8	N/A			
C ₂₂	SRK vdW	-0.016	0.0	N/A	10.69	N/A			
C ₂₂	SRK vdW	0.0	0.012	N/A	5.77	N/A			
C ₂₂ *	SRK vdW	0.021	0.02	N/A	2.35	N/A			
C ₂₂	SRK MHV1	300	-740	0.52	10.76	N/A			
C ₂₂	SRK MHV2	530	-740	0.52	49.66	N/A			
C ₂₂	SRK HV NRTL	960	-310	0.52	4.78	N/A			
C ₂₂	SRK HV NRTL _{HV}	-960	180	0.52	3.03	N/A			
C ₂₂	PC-SAFT	0.006	N/A	N/A	2.57	N/A			
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Table A.1 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
				<u> </u> 		<u>`</u>
C ₂₄	PR vdW	-0.004	0.0	N/A	16.44	N/A
C ₂₄	PR vdW	0.0	0.017	N/A	10.34	N/A
C ₂₄	PR vdW	0.022	0.024	N/A	5.32	N/A
C ₂₄	PR MHV1	510	-830	0.52	12.17	N/A
C ₂₄	PR MHV2	700	-950	0.52	43.04	N/A
C ₂₄	PR HV NRTL	1450	-250	0.52	9.24	N/A
C ₂₄ *	PR HV NRTL _{HV}	-1620	200	0.12	4.83	N/A
C ₂₄	SRK vdW	0.009	0.0	N/A	15.93	N/A
C ₂₄	SRK vdW	0.0	0.014	N/A	10.90	N/A
C ₂₄	SRK vdW	0.022	0.021	N/A	4.07	N/A
C ₂₄	SRK MHV1	550	-850	0.52	12.55	N/A
C ₂₄	SRK MHV2	690	-960	0.52	43.67	N/A
C ₂₄	SRK HV NRTL	1170	-330	0.52	11.58	N/A
C ₂₄	SRK HV NRTL _{HV}	-1190	-20	0.32	8.41	N/A
C ₂₄	PC-SAFT	0.001	N/A	N/A	5.16	N/A
C ₂₈	PR vdW	-0.023	0.0	N/A	21.5	0.05
C ₂₈	PR vdW	0.0	0.027	N/A	8.46	0.05
C ₂₈	PR vdW	0.023	0.034	N/A	4.66	0.04
C ₂₈	PR MHV1	60	-950	0.52	21.05	0.06
C ₂₈	PR MHV2	680	-1060	0.52	58.33	0.05
C ₂₈	PR HV NRTL	1680	-370	0.52	9.2	0.04
C ₂₈	PR HV NRTL _{HV}	-1850	200	0.16	8.1	0.04
C ₂₈	SRK vdW	-0.022	0.0	N/A	19.56	0.04
C ₂₈	SRK vdW	0.0	0.024	N/A	8.53	0.05
C ₂₈ *	SRK vdW	0.028	0.031	N/A	4.14	0.04
C ₂₈	SRK MHV1	70	-960	0.52	26.63	0.07
C ₂₈	SRK MHV2	700	-1070	0.52	58.83	0.06
C ₂₈	SRK HV NRTL	1290	-410	0.52	13.04	0.04
C ₂₈	SRK HV NRTL _{HV}	-1480	170	0.24	7.60	0.03
C ₂₈	PC-SAFT	0.001	N/A	N/A	4.84	0.12
C ₃₆	PR vdW	0.029	0.0	N/A	27.23	N/A
C ₃₆	PR vdW	0.0	0.049	N/A	15.57	N/A
C ₃₆	PR vdW	0.023	0.039	N/A	6.69	N/A
C ₃₆	PR MHV1	60	-1170	0.52	22.65	N/A
C ₃₆	PR MHV2	940	-1320	0.52	44.98	N/A
C ₃₆	PR HV NRTL	2100	-650	0.52	15.97	N/A
C ₃₆	PR HV NRTL _{HV}	-2400	190	0.16	9.05	N/A
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 Table A.1 – continued from previous page

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ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₃₆	SRK vdW	0.039	0.0	N/A	24.6	N/A
C ₃₆	SRK vdW	0.0	0.048	N/A	18.65	N/A
C36*	SRK vdW	0.03	0.035	N/A	5.69	N/A
C ₃₆	SRK MHV1	100	-1190	0.52	23.01	N/A
C ₃₆	SRK MHV2	980	-1330	0.52	44.66	N/A
C ₃₆	SRK HV NRTL	1990	-430	0.52	9.88	N/A
C ₃₆	SRK HV NRTL _{HV}	-2000	170	0.2	7.81	N/A
C ₃₆	PC-SAFT	-0.001	N/A	N/A	3.72	N/A
C ₄₄	PR & vdW	-0.158	0.0	N/A	10.78	N/A
C ₄₄	PR & vdW	0.0	0.032	N/A	6.54	N/A
C ₄₄	PR & vdW	-0.05	0.022	N/A	4.33	N/A
C ₄₄	PR & MHV1	-90	-1030	0.52	18.90	N/A
C ₄₄	PR & MHV2	-50	1490	0.28	49.37	N/A
C ₄₄	PR & HV NRTL	-340	130	0.04	2.68	N/A
C ₄₄	$PR \ \& \ HV \ NRTL_{HV}$	-1360	160	0.52	9.07	N/A
C ₄₄	SRK vdW	-0.15	0.0	N/A	10.45	N/A
C ₄₄	SRK vdW	0.0	0.029	N/A	4.93	N/A
C44	SRK vdW	-0.044	0.021	N/A	3.67	N/A
C ₄₄	SRK MHV1	-90	-1030	0.52	18.47	N/A
C ₄₄	SRK MHV2	20	1390	0.36	48.76	N/A
C44*	SRK HV NRTL	-700	480	0	2.53	N/A
C ₄₄	SRK HV NRTL _{HV}	-1370	160	0.52	8.91	N/A
C ₄₄	PC-SAFT	-0.001	N/A	N/A	2.69	N/A

Table A.1 – continued from previous page

Table A.2 Binary parameters and deviations for propane binary pairs

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)	
C ₁₀	PR vdW	0.003	0	N/A	2.33	0.24	
C ₁₀	PR vdW	0	-0.001	N/A	2.44	0.23	
C ₁₀	PR vdW	0.015	0.014	N/A	1.95	0.17	
C ₁₀	PR MHV1	-60	-180	0.24	3.28	0.16	
C ₁₀	PR MHV2	-1000	840	0	5.01	0.33	
C ₁₀	PR HV NRTL	180	-120	0.4	2.83	0.28	
C ₁₀	PR HV NRTL _{HV}	320	-60	0.16	2.25	0.24	
C ₁₀	SRK vdW	0.001	0	N/A	2.22	0.28	
Continued on next page							

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)		
0			0.001	2110		0.07		
C_{10}	SRK vdW	0	0.001	N/A	2.26	0.27		
C_{10}	SKK VOW	0.005	0.005	N/A	2.07	0.27		
C_{10}	SRK MHVI	-20	-220	0.4	3.16	0.25		
C_{10}	SRK MHV2	0	-160	0.24	5.05	0.39		
C ₁₀	SRK HV NRTL	100	-80	0.44	2.54	0.27		
C ₁₀	SRK HV NRTL _{HV}	-1100	370	0	3.23	0.34		
C_{10}^{*}	PC-SAFT	0.003	N/A	N/A	1.93	0.38		
C ₁₂	PR vdW	0.042	0	N/A	2.42	1.30		
C ₁₂	PR vdW	0	-0.032	N/A	4.55	1.39		
C ₁₂	PR vdW	0.037	-0.004	N/A	2.41	1.32		
C ₁₂	PR MHV1	190	-350	0.52	2.82	1.33		
C ₁₂	PR MHV2	190	-270	0.48	6.61	1.36		
C ₁₂	PR HV NRTL	530	-170	0.52	2.90	1.39		
C ₁₂ *	PR HV NRTL _{HV}	-1900	570	0	2.37	1.37		
C ₁₂	SRK vdW	0.045	0	N/A	2.52	1.57		
C ₁₂	SRK vdW	0	-0.034	N/A	4.73	1.67		
C ₁₂	SRK vdW	0.036	-0.007	N/A	2.59	1.61		
C ₁₂	SRK MHV1	290	-430	0.4	3.06	1.53		
C ₁₂	SRK MHV2	170	-260	0.52	6.75	1.37		
C ₁₂	SRK HV NRTL	530	-180	0.52	2.86	1.59		
C ₁₂	SRK HV NRTL _{HV}	-470	270	0.36	2.36	1.57		
C ₁₂	PC-SAFT	0.025	N/A	N/A	4.4	1.63		
C ₁₄	PR vdW	0.007	0	N/A	1.97	N/A		
C ₁₄	PR vdW	0	0.021	N/A	2.03	N/A		
C ₁₄	PR vdW	0.008	0.016	N/A	1.91	N/A		
C ₁₄	PR MHV1	210	-690	0.28	3.06	N/A		
C ₁₄	PR MHV2	400	-580	0.44	3.30	N/A		
C ₁₄	PR HV NRTL	-680	450	0.52	3.49	N/A		
C ₁₄ *	PR HV NRTL _{HV}	-2130	500	0.08	2.74	N/A		
C ₁₄	SRK vdW	0.005	0	N/A	1.78	N/A		
C ₁₄	SRK vdW	0	0.039	N/A	2.74	N/A		
C ₁₄	SRK vdW	0.004	0.046	N/A	2.82	N/A		
C ₁₄	SRK MHV1	-110	-480	0.52	3.42	N/A		
C ₁₄	SRK MHV2	380	-590	0.44	3.54	N/A		
C ₁₄	SRK HV NRTL	-620	460	0.52	3.26	N/A		
C ₁₄	SRK HV NRTL _{HV}	-860	200	0.36	2.96	N/A		
C ₁₄	PC-SAFT	-0.008	N/A	N/A	3.83	N/A		
	Continued on next page							

 Table A.2 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₂₀	PR vdW	-0.007	0	N/A	3.70	N/A
C ₂₀	PR vdW	0	0.008	N/A	2.78	N/A
C ₂₀	PR vdW	0.013	0.017	N/A	1.76	N/A
C ₂₀	PR MHV1	50	-460	0.52	4.87	N/A
C ₂₀	PR MHV2	-310	880	0.28	11.08	N/A
C ₂₀	PR HV NRTL	750	-260	0.52	2.96	N/A
C ₂₀	PR HV NRTL _{HV}	-2490	460	0.04	2.56	N/A
C ₂₀	SRK vdW	-0.007	0	N/A	3.57	N/A
C ₂₀	SRK vdW	0	0.005	N/A	2.57	N/A
C ₂₀	SRK vdW	0.01	0.014	N/A	1.62	N/A
C ₂₀	SRK MHV1	-70	-370	0.8	4.93	N/A
C ₂₀	SRK MHV2	-320	940	0.28	11.9	N/A
C ₂₀	SRK HV NRTL	600	-200	0.68	2.65	N/A
C ₂₀	SRK HV NRTL _{HV}	-590	200	0.56	2.30	N/A
C ₂₀ *	PC-SAFT	0.003	N/A	N/A	1.53	N/A
C ₃₂	PR vdW	0.014	0	N/A	4.08	N/A
C ₃₂	PR vdW	0	0.059	N/A	3.16	N/A
C ₃₂	PR vdW	0.013	0.035	N/A	1.55	N/A
C ₃₂	PR MHV1	680	-1010	0.51	4.55	N/A
C ₃₂	PR MHV2	840	-1170	0.51	23.81	N/A
C ₃₂	PR HV NRTL	1860	-550	0.48	1.85	N/A
C ₃₂	$PR \; HV \; NRTL_{HV}$	-2280	310	0.04	1.31	N/A
C ₃₂	SRK vdW	0.032	0	N/A	2.40	N/A
C ₃₂	SRK vdW	0	0.069	N/A	4.19	N/A
C ₃₂	SRK vdW	0.023	0.031	N/A	1.39	N/A
C ₃₂	SRK MHV1	4400	-700	0.68	12.23	N/A
C ₃₂	SRK MHV2	3830	-690	0.92	10.89	N/A
C ₃₂	SRK HV NRTL	1580	-270	0.64	1.59	N/A
C ₃₂ *	SRK HV NRTL _{HV}	1900	-20	0.04	1.30	N/A
C ₃₂	PC-SAFT	-0.016	N/A	N/A	8.7	N/A
C ₃₆	PR vdW	0.028	0	N/A	4.8	N/A
C ₃₆	PR vdW	0	0.056	N/A	2.25	N/A
C ₃₆	PR vdW	0.0	0.056	N/A	2.25	N/A
C ₃₆	PR MHV1	810	-1100	0.51	4.84	N/A
C ₃₆	PR MHV2	1000	-1340	0.51	2.63	N/A
C36*	PR HV NRTL	2140	-840	0.39	2.37	N/A
C ₃₆	PR HV NRTL _{HV}	-2810	310	0.04	1.92	N/A
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Table A.2 – continued from previous page

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ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₃₆	SRK vdW	0.028	0	N/A	3.84	N/A
C ₃₆	SRK vdW	0	0.066	N/A	2.84	N/A
C ₃₆	SRK vdW	0.012	0.048	N/A	1.97	N/A
C ₃₆	SRK MHV1	160	-1200	0.48	9.62	N/A
C ₃₆	SRK MHV2	1090	-1410	0.52	19.70	N/A
C ₃₆	SRK HV NRTL	-2620	1000	0.2	7.48	N/A
C ₃₆	SRK HV NRTL _{HV}	-3260	2300	0.52	7.13	N/A
C ₃₆	PC-SAFT	-0.023	N/A	N/A	9.21	N/A
C ₃₈	PR vdW	0.019	0	N/A	4.54	N/A
C ₃₈	PR vdW	0	0.076	N/A	3.13	N/A
C ₃₈	PR vdW	0.014	0.027	N/A	2.53	N/A
C ₃₈	PR MHV1	770	-1120	0.51	10.14	N/A
C ₃₈	PR MHV2	990	-1370	0.51	28.59	N/A
C ₃₈	PR HV NRTL	2280	-680	0.42	1.93	N/A
C ₃₈	$PR \; HV \; NRTL_{HV}$	-2620	310	0.04	1.61	N/A
C ₃₈	SRK vdW	0.033	0	N/A	3.83	N/A
C ₃₈	SRK vdW	0	0.088	N/A	4.25	N/A
C ₃₈	SRK vdW	0.021	0.048	N/A	1.48	N/A
C ₃₈	SRK MHV1	140	-800	0.76	4.62	N/A
C ₃₈	SRK MHV2	4180	-770	0.92	11.43	N/A
C ₃₈	SRK HV NRTL	2210	-630	0.44	2.21	N/A
C ₃₈ *	SRK HV NRTL _{HV}	-1330	210	0.48	1.17	N/A
C ₃₈	PC-SAFT	-0.016	N/A	N/A	10.89	N/A
C ₄₀	PR vdW	0.031	0	N/A	6.74	N/A
C ₄₀	PR vdW	0	0.088	N/A	5.41	N/A
C ₄₀	PR vdW	0.014	0.06	N/A	3.91	N/A
C ₄₀	PR MHV1	760	-1130	0.51	5.94	N/A
C ₄₀	PR MHV2	1050	-1490	0.51	28.97	N/A
C ₄₀	PR HV NRTL	2460	-640	0.42	4.55	N/A
C ₄₀	$PR \; HV \; NRTL_{HV}$	-2550	310	0.05	3.81	N/A
C ₄₀	SRK vdW	0.038	0	N/A	5.65	N/A
C ₄₀	SRK vdW	0	0.103	N/A	5.89	N/A
C ₄₀	SRK vdW	0.027	0.052	N/A	3.71	N/A
C ₄₀	SRK MHV1	-150	-830	0.76	5.91	N/A
C ₄₀	SRK MHV2	4550	-890	0.88	10.5	N/A
C ₄₀	SRK HV NRTL	2420	-510	0.44	4.59	N/A
C40*	SRK HV NRTL _{HV}	-1580	220	0.4	3.48	N/A
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 Table A.2 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₄₀	PC-SAFT	-0.019	N/A	N/A	13.44	N/A
C ₄₄	PR vdW	0.021	0	N/A	6.58	N/A
C ₄₄	PR vdW	0	0.078	N/A	5.08	N/A
C44*	PR vdW	0.012	0.064	N/A	1.89	N/A
C ₄₄	PR MHV1	910	-1280	0.47	6.57	N/A
C ₄₄	PR MHV2	1150	-1460	0.51	34.1	N/A
C44	PR HV	270	-730	0.4	17.22	N/A
C44	PR HV _{mod}	-2680	300	0.06	2.12	N/A
C ₄₄	SRK vdW	0.036	0	N/A	6.46	N/A
C ₄₄	SRK vdW	0	0.122	N/A	5.42	N/A
C ₄₄	SRK vdW	0.029	0.043	N/A	3.90	N/A
C ₄₄	SRK MHV1	600	-1160	0.52	6.78	N/A
C ₄₄	SRK MHV2	4750	-1200	0.56	35.77	N/A
C ₄₄	SRK HV	2720	-380	0.44	2.98	N/A
C ₄₄	SRK HV _{mod}	2730	10	0.04	2.19	N/A
C ₄₄	PC-SAFT	-0.012	N/A	N/A	12.0	N/A
C ₄₆	PR vdW	0.005	0	N/A	15.82	N/A
C ₄₆	PR vdW	0	0.089	N/A	5.49	N/A
C46	PR vdW	-0.005	0.099	N/A	6.04	N/A
C46	PR MHV1	900	-1270	0.5	7.31	N/A
C46	PR MHV2	1170	-1550	0.51	36.62	N/A
C46	PR HV NRTL	27000	-1000	0.39	6.32	N/A
C ₄₆ *	$PR \; HV \; NRTL_{HV}$	-3300	120	0.28	5.75	N/A
C ₄₆	SRK vdW	0.031	0	N/A	11.98	N/A
C ₄₆	SRK vdW	0	0.117	N/A	6.75	N/A
C ₄₆	SRK vdW	-0.007	0.128	N/A	7.22	N/A
C ₄₆	SRK MHV1	880	-1410	0.44	8.95	N/A
C ₄₆	SRK MHV2	4560	-850	0.92	11.94	N/A
C ₄₆	SRK HV NRTL	4020	-2010	0.2	6.92	N/A
C ₄₆	SRK HV NRTL _{HV}	-2370	230	0.2	5.92	N/A
C ₄₆	PC-SAFT	-0.017	N/A	N/A	15.55	N/A
C ₅₄	PR vdW	0.022	0	N/A	8.65	N/A
C ₅₄	PR vdW	0	0.118	N/A	4.48	N/A
C ₅₄	PR vdW	0.012	0.086	N/A	2.6	N/A
C ₅₄	PR MHV1	740	-1410	0.47	8.53	N/A
C ₅₄	PR MHV2	1360	-1790	0.51	38.91	N/A
Ca	PR HV NRTL	3040	-760	0.44	6.73	N/A

Table A.2 – continued from previous page

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Table A.2 – continued from previous page								
ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)		
C ₅₄	PR HV NRTL _{HV}	-3370	310	0.05	3.25	N/A		
C ₅₄	SRK vdW	0.038	0	N/A	10.38	N/A		
C ₅₄	SRK vdW	0	0.155	N/A	5.44	N/A		
C ₅₄	SRK vdW	0.024	0.101	N/A	2.36	N/A		
C ₅₄	SRK MHV1	1160	-1800	0.36	10.57	N/A		
C ₅₄	SRK MHV2	4120	-940	0.92	13.93	N/A		
C ₅₄	SRK HV NRTL	-5440	200	0.4	4.57	N/A		
$C_{54}*$	SRK HV NRTL _{HV}	3620	20	0.04	3.26	N/A		
C ₅₄	PC-SAFT	-0.01	N/A	N/A	7.2	N/A		
C ₆₀	PR vdW	0.019	0	N/A	22.42	N/A		
C ₆₀	PR vdW	0	0.09	N/A	11.18	N/A		
C ₆₀ *	PR vdW	0.011	0.072	N/A	6.41	N/A		
C ₆₀	PR MHV1	1200	-1410	0.5	20.81	N/A		
C ₆₀	PR MHV2	1260	-1720	0.51	57.31	N/A		
C ₆₀	PR HV	3150	-580	0.45	16.14	N/A		
C ₆₀	PR HV _{mod}	-3710	290	0.07	8.74	N/A		
C ₆₀	SRK vdW	0.039	0	N/A	28.15	N/A		
C ₆₀	SRK vdW	0	0.116	N/A	18.93	N/A		
C ₆₀	SRK vdW	0.028	0.072	N/A	7.9	N/A		
C ₆₀	SRK MHV1	7320	-1370	0.52	27.91	N/A		
C ₆₀	SRK MHV2	4730	-940	0.92	36.95	N/A		
C ₆₀	SRK HV	-5880	-660	0.2	8.84	N/A		
C ₆₀	SRK HV _{mod}	-7990	6740	0.28	6	N/A		
C ₆₀	PC-SAFT	-0.005	N/A	N/A	11.86	N/A		

 Table A.2 – continued from previous page

Table A.3 Binary parameters and deviations for carbon dioxide binary pairs

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)	
C ₈	PR vdW	0.123	0	N/A	4.44	0.26	
C ₈	PR vdW	0	-0.101	N/A	14.99	0.35	
C ₈	PR vdW	0.094	-0.02	N/A	5.37	0.12	
C ₈	PR MHV1	-100	60	0.88	5.77	0.54	
C ₈	PR MHV2	-160	310	0.64	7.34	0.71	
C ₈	PR HV NRTL	1140	5100	0.4	4.87	0.64	
C_8	$PR \; HV \; NRTL_{HV}$	-120	310	0.28	2.56	0.49	
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ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₈	SRK vdW	0.128	0	N/A	5.04	0.19
C ₈	SRK vdW	0	-0.109	N/A	16.09	0.42
C_8*	SRK vdW	0.111	-0.031	N/A	2.87	0.15
C_8	SRK MHV1	-110	60	0.76	5.21	0.42
C_8	SRK MHV2	-190	380	0.64	7.21	0.50
C_8	SRK HV NRTL	1070	6100	0.44	4.79	0.36
C ₈	SRK HV NRTL _{HV}	-90	300	0.32	2.53	35
C_8	PC-SAFT	0.067	N/A	N/A	1.93	0.45
C ₉	PR vdW	0.097	0	N/A	2.05	0.86
C ₉	PR vdW	0	-0.082	N/A	12.44	0.69
C ₉	PR vdW	0.097	0.0	N/A	2.05	0.86
C ₉	PR MHV1	200	-310	0.92	13.0	0.86
C ₉	PR MHV2	230	-340	0.72	16.56	0.72
C ₉	PR HV NRTL	1060	4000	0.52	8.25	1.19
C ₉	$PR \; HV \; NRTL_{HV}$	140	200	0.28	4.77	0.93
C ₉	SRK vdW	0.109	0	N/A	2.32	0.45
C ₉	SRK vdW	0	-0.09	N/A	13.35	0.54
C ₉ *	SRK vdW	0.101	-0.012	N/A	1.63	0.34
C ₉	SRK MHV1	270	-400	0.44	11.14	0.86
C ₉	SRK MHV2	-360	5130	0.24	16.62	1.29
C ₉	SRK HV NRTL	980	3850	0.56	7.75	0.79
C ₉	SRK HV NRTL _{HV}	-130	230	0.12	4.47	0.52
C ₉	PC-SAFT	0.044	N/A	N/A	3.51	0.96
C ₁₀	PR vdW	0.104	0	N/A	3.67	1.4
C ₁₀	PR vdW	0	-0.025	N/A	21.43	0.98
C ₁₀	PR vdW	0.082	-0.006	N/A	1.92	1.3
C ₁₀	PR MHV1	0	-300	0.5	16.52	1.58
C ₁₀	PR MHV2	170	-450	0.51	24.58	0.66
C ₁₀	PR HV NRTL	970	5500	0.51	14.28	1.7
C ₁₀	$PR \; HV \; NRTL_{HV}$	-370	290	0.12	6.35	1.25
C ₁₀	SRK vdW	0.109	0	N/A	4.64	1.05
C ₁₀	SRK vdW	0	-0.036	N/A	21.36	1.03
$C_{10}*$	SRK vdW	0.102	-0.017	N/A	2.78	0.96
C ₁₀	SRK MHV1	4080	-390	0.88	24.13	0.94
C ₁₀	SRK MHV2	5380	-390	0.8	28.57	1.26
C ₁₀	SRK HV NRTL	820	4660	0.52	14.44	0.15
C ₁₀	SRK HV NRTL _{HV}	-330	250	0.04	6.24	0.91
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Table A.3 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₁₀	PC-SAFT	0.05	N/A	N/A	3.38	2.05
C ₁₁	PR vdW	0.114	0	N/A	6.52	0.85
C ₁₁	PR vdW	0	0.001	N/A	31.58	0.71
C ₁₁ *	PR vdW	0.099	-0.019	N/A	3.93	0.36
C ₁₁	PR MHV1	100	-350	0.54	16.36	0.91
C ₁₁	PR MHV2	240	-430	0.51	27.35	0.67
C ₁₁	PR HV NRTL	1350	-110	0.36	11.64	1.43
C ₁₁	PR HV NRTL _{HV}	-200	290	0.24	5.7	0.73
C ₁₁	SRK vdW	0.114	0	N/A	8.32	0.69
C ₁₁	SRK vdW	0	-0.028	N/A	28.28	0.78
C ₁₁	SRK vdW	0.11	-0.023	N/A	4.46	0.38
C ₁₁	SRK MHV1	260	-400	0.8	18.14	0.65
C ₁₁	SRK MHV2	260	-420	0.92	31.49	0.68
C ₁₁	SRK HV NRTL	1250	-20	0.44	11.08	0.8
C ₁₁	SRK HV NRTL _{HV}	0	250	0.28	5.68	0.61
C ₁₁	PC-SAFT	0.061	N/A	N/A	4.7	0.84
C ₁₂	PR vdW	0.093	0	N/A	3.62	0.24
C ₁₂	PR vdW	0	-0.055	N/A	14.84	0.15
C ₁₂	PR vdW	0.09	-0.005	N/A	2.8	0.24
C ₁₂	PR MHV1	4280	-220	0.47	5.06	0.29
C ₁₂	PR MHV2	4270	2130	0.47	10.34	1.94
C ₁₂	PR HV NRTL	1970	20	0.34	4.7	0.25
C ₁₂	$PR \; HV \; NRTL_{HV}$	870	240	0.45	2.2	0.26
C ₁₂	SRK vdW	0.101	0	N/A	2.82	0.25
C ₁₂	SRK vdW	0	-0.058	N/A	15.52	0.15
C ₁₂	SRK vdW	0.102	-0.004	N/A	2.57	0.25
C_{12}^{*}	SRK MHV1	5230	-230	0.44	6.68	0.29
C ₁₂	SRK MHV2	-3020	5200	0.04	12.81	0.28
C ₁₂	SRK HV NRTL	1850	30	0.36	4.35	0.26
C ₁₂	SRK HV NRTL _{HV}	520	220	0.4	3.08	0.26
C ₁₂	PC-SAFT	0.062	N/A	N/A	4.57	0.26
C ₁₅	PR vdW	0.083	0	N/A	10.19	0.41
C ₁₅	PR vdW	0	-0.045	N/A	23.4	0.36
C ₁₅ *	PR vdW	0.085	0.006	N/A	10.75	0.40
C ₁₅	PR MHV1	5380	-460	0.47	32.0	0.58
C ₁₅	PR MHV2	4360	-400	0.55	52.94	0.42
C ₁₅	PR HV NRTL	2070	-80	0.3	20.86	1.15
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 Table A.3 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₁₅	PR HV NRTL _{HV}	3100	-10	0.0	14.42	0.57
C ₁₅	SRK vdW	0.098	0	N/A	9.54	0.38
C ₁₅	SRK vdW	0	-0.045	N/A	24.65	0.37
C ₁₅	SRK vdW	0.098	0.006	N/A	10.9	0.37
C ₁₅	SRK MHV1	290	-470	0.68	23.8	0.61
C ₁₅	SRK MHV2	-3000	5030	0.04	42.94	0.46
C ₁₅	SRK HV NRTL	1990	-210	0.28	21.15	0.12
C ₁₅	SRK HV NRTL _{HV}	-860	420	0.4	20.28	0.49
C ₁₅	PC-SAFT	0.054	N/A	N/A	14.94	0.41
C ₁₆	PR vdW	0.084	0	N/A	10.76	N/A
C ₁₆	PR vdW	0	0.349	N/A	53.7	N/A
C ₁₆	PR vdW	0.082	-0.013	N/A	8.31	N/A
C ₁₆	PR MHV1	2920	-310	0.63	23.38	N/A
C ₁₆	PR HV NRTL	2960	4700	0.27	16.59	N/A
C ₁₆	$PR \; HV \; NRTL_{HV}$	2960	4700	0.27	12.87	N/A
C ₁₆	SRK vdW	0.097	0	N/A	11.01	N/A
C ₁₆	SRK vdW	0	0.339	N/A	52.64	N/A
$C_{16}*$	SRK vdW	0.097	0.024	N/A	15.47	N/A
C ₁₆	SRK MHV1	75500	-420	0.36	29.62	N/A
C ₁₆	SRK MHV2	9590	-390	0.32	34.75	N/A
C ₁₆	SRK HV NRTL	3000	2700	0.28	17.28	N/A
C ₁₆	SRK HV NRTL _{HV}	10100	210	0.16	29.71	N/A
C ₁₆	PC-SAFT	0.067	N/A	N/A	19.19	N/A
C ₂₀	PR vdW	0.077	0	N/A	6.22	N/A
C ₂₀	PR vdW	0.078	0.003	N/A	7.52	N/A
C ₂₀	PR MHV1	4490	-590	0.55	33.24	N/A
C ₂₀	PR MHV2	4520	2910	0.49	41.18	N/A
C ₂₀	PR HV NRTL	-4410	1270	0.55	23.91	N/A
C ₂₀	$PR \; HV \; NRTL_{HV}$	1530	150	0.07	12.13	N/A
C ₂₀	SRK vdW	0.091	0	N/A	6.62	N/A
$C_{20}*$	SRK vdW	0.09	-0.002	N/A	6.30	N/A
C ₂₀	SRK MHV1	6050	-600	0.56	30.97	N/A
C ₂₀	SRK MHV2	6920	4910	0.44	44.57	N/A
C ₂₀	SRK HV NRTL	-4180	160	0.72	20.83	N/A
C ₂₀	SRK HV NRTL _{HV}	8840	240	0.24	13.58	N/A
C ₂₀	PC-SAFT	0.052	N/A	N/A	7.53	N/A
C ₂₄	PR vdW	0.078	0	N/A	14.51	0.07
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Table A.3 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
	DD vdW	0.00			0.60	
C_{24}	PK VUW	1800	0.017	N/A	9.09	0.08
C_{24}		680	1370	0.09	/8.1	0.00
C_{24}	PR MITV2 DD LIV NDTI	3060	-1370	0.31	40.1	0.03
C_{24}	DD LIV NDTI	2750	-380	0.29	10.53	0.08
C_{24}	SDK vdW	-2750	400	0.07 N/A	6.63	0.03
C_{24}	SRK vdW	0.009	0.044	N/A	10.86	0.07
	SRK VUW	6850	1140		10.00	0.06
C_{24}	SRK MHV2	6120	-000	0.44	49.75	0.00
	SRK WILVZ	5360	260	0.40	26.04	0.02
C_{24}	SRK HV NRTL	-3240	400	0.04	18 20	0.52
	PC-SAFT	0.05	-100 N/Δ	0.0 1 Ν/Δ	6 29	0.02
C 24		0.05			0.27	0.10
C ₂₈	PR vdW	0.081	0	N/A	22.7	0.03
C ₂₈	PR vdW	0.075	0.019	N/A	9.81	0.02
C ₂₈	PR MHV1	4840	-890	0.55	39.48	0.16
C ₂₈	PR MHV2	370	-1020	0.55	60.24	0.09
C ₂₈	PR HV NRTL	-5700	3020	0.54	21.06	0.19
C_{28}	PR HV NRTL _{HV}	3220	110	0.04	16.79	0.03
C ₂₈	SRK vdW	0.092	0	N/A	16.3	0.02
C ₂₈ *	SRK vdW	0.095	0.027	N/A	11.09	0.03
C ₂₈	SRK MHV1	8280	-1190	0.36	45.87	0.13
C ₂₈	SRK MHV2	270	-590	0.92	55.87	0.17
C ₂₈	SRK HV NRTL	5160	-320	0.24	33.92	0.39
C ₂₈	SRK HV NRTL _{HV}	-3410	390	0.04	15.82	0.03
C ₂₈	PC-SAFT	0.048	N/A	N/A	6.9	0.09
C ₃₆	PR vdW	0.059	0	N/A	23.01	N/A
C36*	PR vdW	0.068	0.023	N/A	8.16	N/A
C ₃₆	PR MHV1	130	-1150	0.44	37.26	N/A
C ₃₆	PR MHV2	800	-1310	0.55	63.81	N/A
C ₃₆	PR HV NRTL	3840	-310	0.43	38.59	N/A
C ₃₆	$PR \; HV \; NRTL_{HV}$	-2040	390	0.32	19.74	N/A
C ₃₆	SRK vdW	0.08	0	N/A	19.25	N/A
C ₃₆	SRK vdW	0.094	0.036	N/A	12.52	N/A
C ₃₆	SRK MHV1	90	-1220	0.4	40.31	N/A
C ₃₆	SRK MHV2	7430	-1050	0.44	66.31	N/A
C ₃₆	SRK HV NTRL	7230	-1030	0.16	42.22	N/A
C ₃₆	SRK HV NRTL _{HV}	-2240	380	0.28	21.35	N/A
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 Table A.3 – continued from previous page

Table A.5 – continued from previous page								
ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)		
C ₃₆	PC-SAFT	0.048	N/A	N/A	9.5	N/A		

Table A.3 – continued from previous page

Table A.4 Binary parameters and deviations for water binary pairs

ID2	Model	BIP1	BIP2	BIP3	Dev P (%)	Dev Y (%)
C ₁	PR vdW	0.442	0	N/A	100	13.79
C_1	PR vdW	0	0.124	N/A	41.40	51.72
C_1	PR vdW	0.598	0.368	N/A	41.43	15.41
C_1	PR MHV1	-980	3530	0.04	20.83	17.81
C_1	PR MHV2	-10	2370	0.04	12.14	22.15
C_1	PR HV NRTL	-840	3780	0.04	22.23	17.42
C_1	PR HV NRTL _{HV}	150	2700	0.12	18.72	16.93
C_1	SRK vdW	0.417	0	N/A	100	16.87
C_1	SRK vdW	0	0.14	N/A	41.86	50.10
C_1	SRK vdW	0.584	0.363	N/A	43.24	19.09
C_1	SRK MHV1	-40	2400	0.08	26.12	19.58
C_1	SRK MHV2	630	1780	0.08	11.98	25.38
C_1	SRK HV NRTL	-820	3780	0.04	23.15	16.20
C_1	SRK HV NRTL _{HV}	160	2750	0.12	19.68	15.95
C_1*	СРА	0.003	N/A	N/A	25.81	9.88
C ₁	PC-SAFT	-0.075	N/A	N/A	25.61	12.39
C ₂	PR vdW	0.455	0	N/A	99.1	18.12
C_2	PR vdW	0	0.318	N/A	100	47.96
C_2	PR vdW	0.669	0.318	N/A	53.26	19.68
C_2	PR MHV1	1920	2020	0.32	34.47	18.86
C_2	PR MHV2	2020	1880	0.28	15.62	27.16
C_2	PR HV NRTL	2320	2340	0.24	35.57	18.51
C_2	PR HV NRTL _{HV}	-600	3040	0.08	14.65	18.51
C_2	SRK vdW	0.462	0	N/A	99.1	18.12
C_2	SRK vdW	0	0.311	N/A	100	47.75
C_2	SRK vdW	0.677	0.37	N/A	55.26	25.23
C_2	SRK MHV1	1910	1970	0.32	35.08	21.23
C_2	SRK MHV2	2000	1850	0.28	15.44	29.19
C_2	SRK HV NTRL	2300	2270	0.24	36.36	21.21
C_2	SRK HV NRTL _{HV}	-580	2980	0.08	15.13	21.79
C_2	СРА	0.164	N/A	N/A	34.11	15.54
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ID2	Model	BIP1	BIP2	BIP3	Dev 2 in 1 (%)	Dev 1 in 2 (%)
C ₂ *	PC-SAFT	0.041	N/A	N/A	25.21	13.87
C ₃	PR vdW	0.509	0	N/A	86.76	8.95
C ₃	PR vdW	0.777	0.529	N/A	49.53	16.75
C ₃	PR MHV1	2310	2080	0.32	33.76	21.88
C ₃	PR MHV2	2190	790	0.08	40.60	28.95
C ₃	PR HV NRTL	3150	3800	0.2	36.77	64.9
C ₃ *	PR HV NRTL _{HV}	2500	2730	0.28	33.73	15.52
C ₃	SRK vdW	0.511	0	N/A	85.18	10.39
C ₃	SRK vdW	0.828	0.55	N/A	49.69	16.75
C ₃	SRK MHV1	2300	2030	0.32	33.98	22.54
C ₃	SRK MHV2	2800	2020	0.44	40.23	46.47
C ₃	SRK HV NRTL	3230	2690	0.24	36.51	24.69
C ₃	SRK HV NRTL _{HV}	2460	2700	0.2	34.93	16.39
C ₃	СРА	0.092	N/A	N/A	53.67	8.81
C ₃	PC-SAFT	0.014	N/A	N/A	54.29	8.01
C ₄	PR vdW	0.497	0	N/A	88.36	19.19
C_4	PR vdW	1.19	0.81	N/A	61.94	37.42
C_4	PR MHV1	2710	1590	0.24	47.31	33.76
C_4	PR MHV2	2840	1570	0.28	37.0	39.4
C_4	PR HV NRTL	3970	2280	0.2	51.66	37.56
C_4	PR HV NRTL _{HV}	1070	2350	0.16	38.05	31.18
C_4	SRK vdW	0.551	0	N/A	99.1	13.5
C_4	SRK vdW	1.06	0.71	N/A	62.9	35.4
C_4	SRK MHV1	2740	1580	0.24	47.46	35.14
C_4	SRK MHV2	2840	1550	0.28	37.74	40.79
C_4	SRK HV NTRL	3970	2210	0.2	52.43	39.18
C_4	SRK HV NRTL _{HV}	1060	2350	0.16	37.97	31.77
C_4*	CPA	0.106	N/A	N/A	42.25	12.37
C ₄	PC-SAFT	0.011	N/A	N/A	37.96	17.67
C ₅	PR vdW	0.099	0	N/A	55.38	100
C ₅	PR vdW	0.2	0.121	N/A	32.48	100
C ₅	PR MHV1	3310	3640	0.32	27.22	99.14
C ₅	PR MHV2	3450	20	0.16	27.72	100
C ₅	PR HV NRTL	4990	2920	0.2	41.38	25.23
C ₅	PR HV NRTL _{HV}	510	1460	0.12	24.27	100
C ₅	SRK vdW	0.063	0	N/A	38.96	100
C ₅	SRK vdW	0.177	0.07	N/A	32.58	100
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 Table A.4 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev 2 in 1 (%)	Dev 1 in 2 (%)
C ₅	SRK MHV1	3340	4080	0.32	25.92	100
C ₅	SRK MHV2	3400	100	0.16	28.71	100
C ₅	SRK HV NRTL	5020	2920	0.2	42.61	46.99
C_5*	SRK HV NRTL _{HV}	490	1470	0.12	24.04	100
C ₅	CPA	0.094	N/A	N/A	47.66	81.83
C ₅	PC-SAFT	-0.059	N/A	N/A	61.75	71.57
C ₆	PR vdW	0.181	0	N/A	52.49	100
C ₆	PR vdW	0.557	0.371	N/A	44.85	100
C ₆	PR MHV1	5560	5810	0.24	44.72	100
C ₆	PR MHV2	6480	4120	0.36	50.91	19.95
C ₆	PR HV NRTL	6980	6660	0.2	52.87	80.0
C ₆	PR HV NRTL _{HV}	450	1630	0.12	51.24	100
C ₆	SRK vdW	0.268	0	N/A	51.08	100
C ₆	SRK vdW	0.569	0.351	N/A	44.42	100
C ₆	SRK MHV1	5530	5830	0.24	45.58	100
C ₆	SRK MHV2	6480	3600	0.36	47.12	79.02
C ₆	SRK HV NTRL	7370	5770	0.2	54.86	20.0
C ₆	SRK HV NRTL _{HV}	580	1550	0.12	51.77	100
C ₆	CPA	-0.011	N/A	N/A	58.4	82.38
C ₆ *	PC-SAFT	-0.005	N/A	N/A	47.36	39.82
Bz	PR vdW	0.279	0	N/A	98.51	57.02
Bz	PR vdW	1.179	0.99	N/A	44.99	63.71
Bz	PR MHV1	2060	1460	0.32	34.72	62.08
Bz	PR MHV2	2140	420	0.08	35.01	71.24
Bz	PR HV NRTL	2940	1630	0.16	46.05	67.55
Bz	PR HV NRTL _{HV}	1880	2010	0.28	32.71	59.53
Bz	SRK vdW	0.282	0	N/A	97.93	60.09
Bz	SRK vdW	1.171	0.979	N/A	45.0	65.44
Bz	SRK MHV1	2080	1450	0.32	34.19	62.9
Bz	SRK MHV2	2730	-190	0.04	36.06	74.35
Bz	SRK HV NRTL	3200	1910	0.2	48.47	62.05
Bz	SRK HV NRTL _{HV}	1890	2050	0.28	38.33	58.21
Bz	СРА	-0.014	N/A	N/A	37.3	68.78
Bz	CPA solvation	0.033	0.079	N/A	34.94	50.18
Bz	PC-SAFT	0.001	N/A	N/A	43.94	65.59
Tol	PR vdW	0.297	0	N/A	100	44.34
Tol	PR vdW	1.433	1.203	N/A	35.74	74.64
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Table A.4 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev 2 in 1 (%)	Dev 1 in 2 (%)
Tol	PR MHV1	2560	1720	0.4	43.05	48.31
Tol	PR MHV2	2510	1520	0.28	27.7	59.93
Tol	PR HV NRTL	4230	1960	0.2	75.33	35.62
Tol*	PR HV NRTL _{HV}	2350	2120	0.28	26.13	41.17
Tol	SRK vdW	0.323	0	N/A	100	46.17
Tol	SRK vdW	1.46	1.22	N/A	36.39	73.16
Tol	SRK MHV1	2580	1720	0.4	42.26	48.11
Tol	SRK MHV2	2510	1510	0.28	28.95	58.5
Tol	SRK HV NTRL	4240	1950	0.2	75.86	33.48
Tol	SRK HV NRTL _{HV}	2310	2060	0.28	25.92	42.76
Tol	CPA	-0.027	N/A	N/A	30.41	64.83
Tol	CPA solvation	0.009	0.06	N/A	38.5	33.43
Tol	PC-SAFT	-0.006	N/A	N/A	72.9	28.4
C ₂ Bz	PR vdW	0.312	0	N/A	100	27.23
C_2Bz	PR vdW	1.136	1.061	N/A	94.43	0.0954
C_2Bz	PR MHV1	3260	5040	0.24	13.32	62.25
C_2Bz	PR MHV2	8070	-4230	0.04	26.77	95.44
C_2Bz	PR HV NRTL	4790	7500	0.16	28.88	91.25
C_2Bz	PR HV NRTL _{HV}	-830	2480	0.16	31.26	24.08
C_2Bz	SRK vdW	0.336	0	N/A	100	35.98
C_2Bz	SRK vdW	1.173	1.087	N/A	93.56	9.74
C_2Bz	SRK MHV1	3290	5020	0.24	28.89	91.45
C_2Bz	SRK MHV2	8150	-4270	0.04	28.98	95.5
C_2Bz	SRK HV NTRL	4870	8500	0.16	28.9	93.69
C_2Bz	SRK HV NRTL _{HV}	-830	2480	0.16	31.78	24.01
C_2Bz	СРА	-0.083	N/A	N/A	13.32	62.25
C_2Bz^*	CPA solvation	-0.054	0.051	N/A	11.47	22.71
C_2Bz	PC-SAFT	-0.084	N/A	N/A	18.35	53.49
CO ₂	PR vdW	0.175	0	N/A	86.24	9.54
CO_2	PR vdW	0.245	0.174	N/A	48.83	11.15
CO_2	PR MHV1	-1130	3000	0.04	17.0	20.02
CO_2	PR MHV2	670	1140	0.2	8.33	12.47
CO_2	PR HV NRTL	-1050	3240	0.04	18.6	22.07
CO_2*	PR HV NRTL _{HV}	-790	2500	0.08	10.47	11.43
CO_2	SRK vdW	0.158	0	N/A	84.38	13.31
CO_2	SRK vdW	0.233	0.169	N/A	51.26	16.58
CO_2	SRK MHV1	-1150	3030	0.04	12.76	42.93
CO_2	SRK MHV2	680	1110	0.2	11.81	27.54
			-	-	Continu	ued on next page

 Table A.4 – continued from previous page

ID2	Model	BIP1	BIP2	BIP3	Dev 2 in 1 (%)	Dev 1 in 2 (%)
CO_2	SRK HV NRTL	-1040	3220	0.04	12.94	45.49
CO_2	SRK HV NRTL _{HV}	-790	2490	0.08	11.62	30.29
CO_2	СРА	-0.009	N/A	N/A	15.03	38.91
CO_2	CPA solvation	0.097	0.1836	N/A	23.37	18.36
CO ₂	PC-SAFT	-0.017	N/A	N/A	14.06	37.63
H_2S	PR vdW	0.016	0	N/A	49.32	41.65
H_2S	PR vdW	0.3	0.214	N/A	30.45	27.33
H_2S	PR MHV1	560	920	0.32	16.46	22.21
H_2S	PR MHV2	480	730	0.04	6.81	23.37
H_2S	PR HV NRTL	530	1140	0.2	16.77	23.63
H_2S^*	PR HV NRTL _{HV}	-1710	2790	0.04	6.17	22.19
H_2S	SRK vdW	0.004	0	N/A	49.04	44.8
H_2S	SRK vdW	0.28	0.202	N/A	32.16	29.65
H_2S	SRK MHV1	510	900	0.28	16.27	25.97
H_2S	SRK MHV2	510	690	0.04	6.51	27.04
H_2S	SRK HV NTRL	680	1080	0.28	17.11	25.64
H_2S	SRK HV NRTL _{HV}	-1790	2900	0.04	5.96	26.11
H_2S	CPA	-0.022	0.0299	108.78	10.3	42.28
H_2S	CPA solvation	0.097	0.0624	108.67	8.93	35.87
H_2S	PC-SAFT	-0.014	N/A	N/A	9.85	36.85

Table A.4 – continued from previous page

Table A.5 Binary parameters and deviations for water binary pairs

	-								
ID2	Model	BIP1	BIP2	BIP3	Dev 2 in 1 (%)	Dev 1 in 2 (%)	Dev P (%)	Dev Y (%)	
C ₁₀	PR vdW	0.319	0	N/A	100	8.59	20.71	49.14	
C ₁₀	PR vdW	0.479	0.212	N/A	98.66	21.26	15.51	26.02	
C ₁₀	PR MHV1	7330	-840	0.12	81.47	38.3	11.8	40.19	
C ₁₀	PR MHV2	8750	-2940	0.12	39.22	39.56	60.2	65.3	
C_{10}	PR HV NRTL	10410	-3810	0.04	100	44.81	11.82	41.26	
C ₁₀	PR HV NRTL _{HV}	900	2090	0.12	95.83	39.71	8.86	28.16	
C ₁₀	SRK vdW	0.354	0	N/A	99.45	8.99	20.71	49.14	
C ₁₀	SRK vdW	0.504	0.188	N/A	98.57	19.71	15.69	28.05	
C ₁₀	SRK MHV1	8100	-840	0.12	90.04	41.59	13.87	35.74	
C ₁₀	SRK MHV2	5960	-600	0.16	86.4	36.76	12.5	33.78	
C ₁₀	SRK HV NRTL	10460	-600	0.08	92.54	40.03	12.33	35.35	
C ₁₀	SRK HV NRTL _{HV}	130	2140	0.12	92.5	50.15	7.89	21.66	
	Continued on next page								

ID2	Model	BIP1	BIP2	BIP3	Dev 2 in 1 (%)	Dev 1 in 2 (%)	Dev P (%)	Dev Y (%)
C ₁₀ *	СРА	-0.243	N/A	N/A	27.37	30.24	13.02	21.73
C_{10}	PC-SAFT	-0.09	N/A	N/A	13.77	31.28	30.39	25.33
C ₁₂	PR vdW	0.474	0	N/A	91.61	53.3	9.73	5.58
C ₁₂	PR vdW	1.34	1.253	N/A	51.15	65.73	30.99	17.72
C ₁₂	PR MHV1	12580	-3990	0.08	29.58	5.42	47.74	17.04
C ₁₂	PR MHV2	10000	-3010	0.12	49.19	17.71	53.01	17.26
C ₁₂	PR HV NRTL	13570	-1200	0.12	63.52	34.36	53.13	14.07
C ₁₂	PR HV NRTL _{HV}	270	2080	0.12	97.68	3.75	12.18	37.51
C ₁₂	SRK vdW	0.502	0	N/A	92.74	53.61	11.26	6.74
C ₁₂	SRK vdW	1.309	1.244	N/A	46.83	65.26	31.88	14.67
C ₁₂	SRK MHV1	12520	-3990	0.08	38.95	32.32	46.97	17.21
C ₁₂	SRK MHV2	9500	-2850	0.12	35.09	28.74	48.98	16.2
C ₁₂	SRK HV NTRL	13530	-1230	0.12	58.67	34.38	52.95	14.2
C ₁₂	SRK HV NRTL _{HV}	860	2000	0.16	93.45	45.1	7.58	13.61
C_{12}^{*}	CPA	-0.239	N/A	N/A	37.2	38.0	9.8	4.17
C ₁₂	PC-SAFT	-0.083	N/A	N/A	43.79	35.96	19.05	25.48

Table A.5 – continued from previous page

Appendix B

Description of examples used for flash calculations

A number of different mixtures were used to demonstrate the robustness and compare the computational cost of isenthalpic flash with isothermal flash. For examples 1,2,4,5 and 7 the ideal gas heat capacity equation for each component is:

$$\frac{C_p}{R} = C_1 + C_2 \times T + C_3 \times T^2 + C_4 \times T^3$$

For examples 3 the ideal gas heat capacity equation for each component is:

$$\frac{C_p}{R} = C_1 + C_2 \times T + C_3 \times T^2 + C_4 \times T^{-2}$$

For example 6 the ideal gas heat capacity equation for each component was taken from the DIPPR database using the equation

$$C_p = C_1 + C_2 \left(\frac{C_3}{T \sinh\left(\frac{C_3}{T}\right)}\right)^2 + C_4 \left(\frac{C_5}{T \cosh\left(\frac{C_5}{T}\right)}\right)^2$$

with units of J/(kmol K). The parameters used are from the DIPPR database.

Example 1,4,5 and 7 were modelled using the PR equation of state and examples 3 and 6 used the SRK equation of state.

Example 1 is a mixture of a heavy oil with water based on the real example described by [81] with the properties reported in tables B.1 and ideal gas parameters in table B.2.

Example 2 is an ideal solution example using correlations from [155] for the oleic phase fugacity of the form

$$\varphi_i^o = \frac{C_{1,i}}{P} \times \exp\left(\frac{C_{2,i}}{T - C_{3,i}}\right)$$

with parameters reported in table B.3. The ideal gas heat capacity parameters are given in table B.4. For the residual enthalpy a correlation was used for the enthalpy of vaporisation. This was of the form

$$\frac{H^{vap}}{R} = C_1 \times (1 - T_r)^{\left(C_2 + C_3 T_r + C_4 T_r^2\right)}$$

where $T_r = T/T_c$. If $T_r \ge 1$ then the enthalpy of vaporisation was set equal to zero. The parameters used are reported in table B.5.

The critical properties and ideal gas heat capacity parameters for examples 3,4,5 and 6 are given in tables B.6 - B.14. Note that though the same components are often given, their ideal gas heat capacity correlation parameters may differ, often these parameters were fitted pseudo-experimental data generated from the correlation from DIPPR for each component in each mixture. Example 6 uses the correlation from DIPPR directly, though its computational cost is not trivial. For example 8 both SRK and CPA was used to model the mixture. The critical properties are given in table B.15 with the SRK binary parameters given in table B.16 and the CPA parameters in table B.17. For CPA water was always considered as associating with a 4C scheme with $\epsilon/R = 2003K.248$ and $\beta = 0.0692$. In CPA1 model only water was considered as associating. In CPA2 model hydrogen sulphide was assumed to have a 3B scheme with the pure component parameters modified so that $\Gamma = 1590.102K$, b = 0.0292l/mol and $c_1 = 0.50222$ with $\epsilon/R = 654.271K$ and $\beta = 0.05832$. For CPA2 the cross association of water with hydrogen sulphide was given the values of $k_{ij} = 0.0991$, $\beta^{cross} = 0.0299$ and $\epsilon^{cross} = 1308.4K$ based on the values from [187]. The solvation of carbon dioxide in water was with binary parameters of $k_{ij} = 0.1145$, $\beta^{cross} = 0.0162$ and $\epsilon^{cross} = 1708K$ based on values from [186]. For example 9 the properties are given in table B.18.

Component	Zi	P _c (bar)	$T_{c}(K)$	ω	water k _{ij}
water	0.5	220.549	647.15	0.345	0
propane	0.0054	42.478	369.85	0.152	0.51
i-butane	0.005	36.48	408.15	0.177	0.5
n-butane	0.0228	37.962	425.05	0.2	0.5
i-pentane	0.0263	33.798	460.35	0.228	0.5
n-pentane	0.0349	33.701	469.75	0.252	0.5
hexane	0.0734	30.102	507.45	0.299	0.5
M-cyclo C ₅	0.0185	37.845	532.85	0.23	0.5
benzene	0.0083	48.953	562.05	0.21	0.5
cyclo C ₆	0.0109	40.748	553.55	0.212	0.5
M-cyclo C ₆	0.0049	34.715	572.25	0.235	0.5
toluene	0.0026	41.079	591.75	0.264	0.5
C ₂ -benzene	0.00068	36.087	617.15	0.304	0.5
m & p-xylene	0.0012	35.26	616.55	0.324	0.5
o-xylene	0.00042	37.321	630.35	0.31	0.5
C_7-C_{23}	0.0569	16.989	713.95	0.87	0.48
C_{24} - C_{31}	0.0569	14.513	816.55	1.129	0.44
C_{32} - C_{38}	0.0569	14.693	893.95	1.281	0.42
C_{39} - C_{49}	0.0569	15.775	976.55	1.361	0.4
C_{50} - C_{80}	0.0569	18.009	1123.75	1.207	0.38

Table B.1 Parameters for example 1, a 20 component heavy oil with water

Component	C_1	$C_2 \times 10^2 (K^{-1})$	$C_3 \times 10^5 (K^{-2})$	$C_4 \times 10^9 \ (K^{-3})$
water	3.952	-0.030	0.217	-0.868
propane	-0.506	3.707	-2.036	4.836
i-butane	-1.592	5.357	-3.352	9.090
n-butane	-0.320	4.833	2.709	6.469
i-pentane	-1.608	6.399	3.875	10.940
n-pentane	-0.876	6.050	-3.329	7.556
hexane	-2.303	7.861	-4.997	13.540
M-cyclo C ₅	-6.833	8.099	-5.025	12.600
benzene	-6.045	6.805	-5.333	16.840
cyclo C ₆	-3.426	5.704	-0.509	-10.720
M-cyclo C ₆	-8.341	9.807	-5.795	12.890
toluene	-4.798	7.221	-5.036	14.480
C ₂ -benzene	-6.203	9.029	-6.634	20.090
m & p-xylene	-4.912	8.261	-5.578	15.620
o-xylene	-2.779	7.615	-4.851	12.790
C_7-C_{23}	-0.022	3.118	-1.420	1.232
C_{24} - C_{31}	0.015	4.792	-2.107	1.243
C_{32} - C_{38}	0.121	5.870	-2.332	-0.547
C_{39} - C_{49}	0.011	6.887	-2.365	-3.694
C_{50} - C_{80}	0.047	8.563	-1.885	-12.587

Table B.2 Ideal gas heat capacity parameters for example 1

Table B.3 Oleic phase fugacity correlation parameters for example 2, a 7 component ideal solution mixture

Component	t zi	$C_1 \times 10^{-3}$ (bar)	$C_{2}(K)$	C ₃ (K)
water	0.5	119	-3816.4	46.13
methane	0.1	5.45	-879.8	7.16
ethane	0.05	8.46	-1511.4	17.16
n-butane	0.02	8.59	-2154.9	34.42
n-hexane	0.05	10.1	-2697.6	48.78
n-decane	0.05	12	-3456.8	78.67
n-eicosane	0.23	18.9	-4680.5	141.1

Component	C_1	$C_2 \times 10^3 (K^{-1})$	$C_3 \times 10^6 (K^{-2})$	$C_4 \times 10^9 (\mathrm{K}^{-3})$
water	3.89	0.017	1.71	-0.647
methane	2.43	4.87	4.440	-3.02
ethane	0.712	20.7	-7.210	0.477
n-butane	-0.646	49.8	-29.4	7.61
n-hexane	-3.05	81.6	-53.9	15.2
n-decane	-5.92	139	-95.9	27
n-eicosane	-8.94	267	-191	59.3

Table B.4 Ideal gas heat capacity parameters for example 2

Table B.5 Enthalpy of vaporisation correlation parameters for example 2

Component	$T_{c}(\mathbf{K})$	$C_1 \times 10^3$ (K)	C_2	C_3	C_4
water	647.15	6.26	0.32	-0.212	0.258
methane	190.56	1.23	0.261	-0.147	0.222
ethane	305.32	2.54	0.606	-0.555	0.328
n-butane	425.1	4.36	0.834	-0.823	0.396
n-hexane	507.6	5.36	0.39	0	0
n-decane	617.7	7.95	0.398	0	0
n-eicosane	768	15.5	0.504	0.33	-0.422

Table B.6 Properties of example 3, a 7 component natural gas mixture

Component	Zi	P _c (bar)	$T_{c}(K)$	ω	nitrogen k _{ij}
methane	0.943	45.99	190.564	0.0115	0.02
ethane	0.027	48.72	305.32	0.0995	0.06
propane	0.0074	42.479	369.83	0.1523	0.08
n-butane	0.0049	37.96	425.12	0.2002	0.08
n-pentane	0.0027	33.7	469.7	0.2515	0.08
n-hexane	0.001	30.25	507.6	0.3013	0.08
nitrogen	0.014	34	126.2	0.0377	0

Table B.7 Ideal gas heat capacity of example 3

Component	C_1	$C_2 \times 10^2 (K^{-1})$	$C_3 \times 10^5 (K^{-2})$	$C_4 (K^2)$
methane	1.702	0.9081	-0.2164	0
ethane	1.131	1.9225	-0.5561	0
propane	1.213	2.8785	-0.8824	0
n-butane	1.935	3.6915	-1.1402	0
n-pentane	2.464	4.535	-1.411	0
n-hexane	3.025	5.372	-1.679	0
nitrogen	3.631	-0.0649	0.0801	-949.1

Component	Zi	P _c (bar)	$T_{c}(K)$	ω
methane	0.99	45.99	190.564	0.0115
n-butane	0.01	37.96	425.12	0.2002

Table B.8 Parameters for example 4, C_1 with C_4

Table B.9 Ideal gas heat capacity parameters for example 4. Parameter C_4 is equal to zero for both components

Component	C_1	$C_2 \times 10^2 (K^{-1})$	$C_3 \times 10^5 (K^{-2})$
methane	1.702	0.9081	-0.2164
n-butane	1.935	3.6915	-1.1402

Table B.10 Properties of example 5, a 5-component mixture of water with oil

Component	Zi	P _c (bar)	$T_{c}(K)$	$ \omega $	water k _{ij}
Water	0.5	220.89	647.3	0.344	0
PC1	0.15	48.82	305.556	0.098	0.719
PC2	0.1	19.65	638.889	0.535	0.460
PC3	0.1	10.2	788.889	0.891	0.268
PC4	0.15	7.72	838.889	1.085	0.24166

Table B.11 Ideal gas heat capacity parameters for example 5

Component	C_1	$C_2 \times 10^4 (K^{-1})$	$C_3 \times 10^7 (K^{-2})$	$C_4 \times 10^{10} (K^{-3})$
Water	3.873	2.294	12.689	-4.325
PC1	-0.421	6.933	0.612	0
PC2	-0.0486	0.790	0.06507	0
PC3	-0.734	13.147	1.696	0
PC4	-0.541	9.681	1.251	0

Table B.12 Properties of 5 component mixture, example 6

Component	Zi	P _c (bar)	$T_{c}(K)$	ω	$\mathrm{CO}_2~\mathrm{k}_{\mathrm{ij}}$	$H_2S k_{ij}$
methane	0.66	45.99	190.56	0.0115	0.12	0.08
ethane	0.03	48.72	305.32	0.0995	0.15	0.07
propane	0.01	42.479	369.83	0.1523	0.15	0.07
CO_2	0.05	73.37	304.12	0.225	0.0	0.12
H_2S	0.25	90.0	373.1	0.10	0.12	0.0

Table B.13 Pro	perties of 2 co	mponent mixture,	exampl	e 7	7
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Component	Zi	P _c (bar)	$T_{c}(K)$	ω	water k_{ij}
n-butane	0.5	37.96	425.1	0.2002	0.535
water	0.5	220.64	647.29	0.345	0

Table B.14 Ideal gas heat capacity parameters for example 7

Component	C_1	$C_2 \times 10^4 (K^{-1})$	$C_3 \times 10^7 (K^{-2})$	$C_4 \times 10^{10} (K^{-3})$
Water	3.873	2.294	12.689	-4.325
n-butane	0.059	39.8	0133.2	-3.394

Table B.15 Properties of 17 component mixture, example 8 for 17 component mixture

Component	Zi	P _c (bar)	$T_{c}(K)$	ω
water	0.5	220.549	647.15	0.345
methane	0.03125	45.99	190.56	0 0.0115
ethane	0.03125	48.72	305.32	0.09949
propane	0.03125	42.48	369.83	0.1523
i-butane	0.03125	36.48	408.15	0.177
n-butane	0.03125	37.962	425.05	0.2
i-pentane	0.03125	33.798	460.35	0.228
n-pentane	0.03125	33.701	469.75	0.252
n-hexane	0.03125	30.25	507.6	0.3013
benzene	0.03125	48.97949175	562.16	0.21
n-heptane	0.03125	27.4	540.2	0.3495
n-decane	0.03125	21.1	617.7	0.4923
n-hexadecane	0.03125	14	723	0.7174
n-eicosane	0.03125	11.6	768	0.9069
nitrogen	0.03125	33.958	126.192	0.04
hydrogen sulphide	0.03125	89.4	373.2	0.081
carbon dioxide	0.03125	73.83	304.21	0.2236

Table B.16 SRK binary interaction parameters for example 8 (k_{ij})

Component	water	nitrogen	hydrogen sulphide	carbon dioxide
water	0	0.12	0.016	0.175
nitrogen	0.12	0	0.08	0.08
hydrogen sulphide	0.016	0.08	0	0.12
carbon dioxide	0.175	0.08	0.12	0
methane	0.51	0.02	0.08	0.1
ethane	0.5	0.0.06	0.07	0.1
other hydrocarbons	0.5	0.08	0.06	0.1

	1			L
Component	Zi	Γ(K)	b (l/mol)	c ₁
water	0.5	1017.338	0.014515	0.67359
methane	0.03125	959.028	0.0291	0.44718
ethane	0.03125	1544.548	0.0429	0.58463
propane	0.03125	1896.453	0.057834	0.6307
i-butane	0.03125	2078.622	0.0747	0.7021
n-butane	0.03125	2193.083	0.072081	0.70771
i-pentane	0.03125	2350.6	0.09038	0.7651
n-pentane	0.03125	2405.105	0.091008	0.79858
n-hexane	0.03125	2640.03	0.10789	0.8313
benzene	0.03125	2867.193	0.07499	0.7576
n-heptane	0.03125	2799.762	0.12535	0.9137
n-decane	0.03125	3190.542	0.17865	1.13243
n-hexadecane	0.03125	3855.51	0.2961	1.3728
n-eicosane	0.03125	4161.435	0.374384	1.53669
nitrogen	0.03125	634.07	0.02605	0.49855
hydrogen sulphide	0.03125	1878.146	0.0285	0.60265
carbon dioxide	0.03125	1551.222	0.0272	0.7602

Table B.17 CPA parameters for example 8

Table B.18 Properties of 3 component mixture, example 9. All $k_{ij} = 0$

Compon	ent z _i	P_{c} (bar)	$T_{c}(K)$	ω
methane	0.772	45.99	190.56	0.0115
ethane	0.218	48.72	305.32	0.0995
n-octane	0.01	24.90	568.7	0.3996

Appendix C

Vol-RAND equations for state function based flash specifications

For the (V, T), and (P, T) based flash specification the relevant equations from chapter 4 for the vol-RAND implementation are equation 4.84:

$$\Delta \boldsymbol{n}_{j} = \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \left(\boldsymbol{\mathcal{A}}^{T} \boldsymbol{\lambda} - \boldsymbol{A}_{\boldsymbol{n},j} - \boldsymbol{A}_{\boldsymbol{n},T,j} \Delta T \right) + \boldsymbol{\rho}_{j} \Delta V_{j}$$
(C.1)

along with the F equations 4.86:

$$\boldsymbol{\rho}_{j}^{T}\boldsymbol{\mathcal{A}}^{T}\boldsymbol{\lambda} + \frac{S_{j}}{V_{j}}\Delta T = \boldsymbol{\rho}_{j}^{T}\boldsymbol{\mu}_{j} + A_{V,j} + P^{*} \quad \forall j$$
(C.2)

and the E equations 4.88:

$$\mathcal{A}\left(\sum_{j=1}^{F} \mathbf{A}_{n,n,j}^{-1}\right) \mathcal{A}^{T} \boldsymbol{\lambda} + \mathcal{A} \mathbf{R} \Delta \boldsymbol{V} - \mathcal{A}\left(\sum_{j=1}^{F} \mathbf{A}_{n,n,j}^{-1} \mathbf{A}_{n,T,j}\right) \Delta T = \mathcal{A}\left(\sum_{j=1}^{F} \mathbf{A}_{n,n,j}^{-1} \boldsymbol{\mu}_{j}\right)$$
(C.3)

Solving for the equilibrium elemental potentials and the change in phase volume allows for the (V, T) and (P, T) flash to be solved as minimisations of suitable objective functions. For the remaining flash specifications it is necessary to introduce a number of additional constraints in a similar manner as was done in section 4.3.

$$S(T, V, \boldsymbol{n}) - S^{spec} = 0 \tag{C.4a}$$

$$U(T, V, \boldsymbol{n}) - U^{spec} = 0 \tag{C.4b}$$

and

$$H(T, V, \boldsymbol{n}) - H^{spec} \approx U(T, V, \boldsymbol{n}) + VP^{spec} - H^{spec} = 0$$
(C.4c)

and linearise around the variables of (T, V, n):

$$S - S^{spec} + \frac{C_v}{T} \Delta T + \sum_{j=1}^{F} \frac{\partial P_j}{\partial T} \Delta V_j - \sum_{j=1}^{F} \left(\frac{\partial \boldsymbol{\mu}_j}{\partial T}\right)^T \Delta \boldsymbol{n}_j = 0$$
(C.5a)

$$\frac{U - U^{spec}}{T} + \frac{C_v}{T}\Delta T + \sum_{j=1}^{F} \left(\frac{\partial P_j}{\partial T} - \frac{P_j}{T}\right) \Delta V_j - T \sum_{j=1}^{F} \left(\frac{\partial \frac{\mu_j}{T}}{\partial T}\right)^T \Delta \boldsymbol{n}_j = 0 \quad (C.5b)$$

and

$$\frac{U + VP^{spec} - H^{spec}}{T} + \frac{C_v}{T} \Delta T + \sum_{j=1}^{F} \left(\frac{\partial P_j}{\partial T} - \frac{P_j - P^{spec}}{T}\right) \Delta V_j - T \sum_{j=1}^{F} \left(\frac{\partial \frac{\mu_j}{T}}{\partial T}\right)^T \Delta \boldsymbol{n}_j = 0$$
(C.5c)

It is possible to make a number of simplifications. Following the same logic as in equation 4.59 we can replace

with

$$\frac{1}{T} \boldsymbol{A}_{\boldsymbol{n},T,j}$$

At this point it is necessary to divide the method into the two calculation types, one with a specified pressure (for (P, T), (P, S) and (P, H) flash) and one with a specified volume (for (V, T), (V, S) and (V, U) flash). In the case of the pressure specification equation C.5b is not relevant. The third term in equation C.5c can be simplified since at the solution $P_j - P^{spec} = 0$. It is then possible to replace equation C.5c and equation C.5a with a single equation:

$$r_{S,H} + \frac{C_v}{T} \Delta T - \sum_{j=1}^F A_{V,T,j} \Delta V_j - \sum_{j=1}^F \boldsymbol{A}_{\boldsymbol{n},T,j}^T \Delta \boldsymbol{n}_j = 0$$
(C.6)

where $r_{S,H} = S - S^{spec}$ for the (P, S) flash specification and $r_{S,H} = \frac{U - VP^{spec} - H^{spec}}{T}$ for the (P, H) flash specification. Substituting in the composition correction from equation

$$\frac{\partial \frac{\boldsymbol{\mu}_j}{T}}{\partial T}$$

C.1:

$$-\sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},T,j}^{T} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \boldsymbol{\mathcal{A}}^{T} \boldsymbol{\lambda} + \sum_{j=1}^{F} \frac{S_{j}}{V_{j}} \Delta V_{j} + \left(\frac{C_{v}}{T} + \sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},T,j}^{T} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \boldsymbol{A}_{\boldsymbol{n},T,j} \right) \Delta T = -\sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},T,j}^{T} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \boldsymbol{A}_{\boldsymbol{n},j} - r_{S,H}$$
(C.7)

When combined with equations C.2 and C.3 we obtain the system of equation (of size C + F + 1):

$$\begin{pmatrix} \boldsymbol{\mathcal{A}} \sum_{j=1}^{F} \boldsymbol{A}_{n,n,j}^{-1} \boldsymbol{\mathcal{A}}^{T} & \boldsymbol{\mathcal{A}} \boldsymbol{R} & \boldsymbol{t}_{v} \\ (\boldsymbol{\mathcal{A}} \boldsymbol{R})^{T} & \boldsymbol{0} & \frac{\boldsymbol{S}}{\boldsymbol{V}} \\ \boldsymbol{t}_{v}^{T} & \left(\frac{\boldsymbol{S}}{\boldsymbol{V}}\right)^{T} & \boldsymbol{C}_{v,x} \end{pmatrix} \begin{pmatrix} \boldsymbol{\lambda} \\ \Delta \boldsymbol{V} \\ \Delta T \end{pmatrix} = \begin{pmatrix} \boldsymbol{\mathcal{A}} \left(\sum_{j=1}^{F} \boldsymbol{A}_{n,n,j}^{-1} \boldsymbol{\mu}_{j} \right) \\ \boldsymbol{u}_{2,v} \\ -\sum_{j=1}^{F} \boldsymbol{A}_{n,T,j}^{T} \boldsymbol{A}_{n,n,j}^{-1} \boldsymbol{A}_{n,j} - \boldsymbol{r}_{S,H} \end{pmatrix}$$
(C.8)

where we have used:

$$\boldsymbol{t}_{v} = -\boldsymbol{\mathcal{A}}\left(\sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \boldsymbol{A}_{\boldsymbol{n},T,j}\right)$$
$$C_{v,x} = \frac{C_{v}}{T} + \sum_{j=1}^{F} \boldsymbol{A}_{\boldsymbol{n},T,j}^{T} \boldsymbol{A}_{\boldsymbol{n},\boldsymbol{n},j}^{-1} \boldsymbol{A}_{\boldsymbol{n},T,j}$$

and

$$u_{2,v,j} = \boldsymbol{\rho}_j^T \boldsymbol{\mu}_j + A_{V,j} + P^* \quad \forall j$$

For the remaining specifications (that is (V,T), (V,U) and (V,S)) we first define the volume of phase F as:

$$V_F = V^{spec} - \sum_{j=1}^{F-1} V_j$$
 (C.9)

Following linearisation of C.9 we obtain:

$$\Delta V_F = -\sum_{j=1}^{F-1} \Delta V_j \tag{C.10}$$

Substituting this into equation C.5a we find:

$$S - S^{spec} + \frac{C_v}{T} \Delta T + \sum_{j=1}^{F-1} \left(\frac{\partial P_j}{\partial T} - \frac{\partial P_F}{\partial T} \right) \Delta V_j - \sum_{j=1}^{F} \left(\frac{\partial \boldsymbol{\mu}_j}{\partial T} \right)^T \Delta \boldsymbol{n}_j = 0 \quad (C.11)$$

and into equation C.5b we find:

$$\frac{U - U^{spec}}{T} + \frac{C_v}{T}\Delta T + \sum_{j=1}^{F-1} \left(\frac{\partial P_j}{\partial T} - \frac{\partial P_F}{\partial T} - \frac{P_j - P_F}{T}\right) \Delta V_j - T \sum_{j=1}^{F} \left(\frac{\partial \frac{\mu_j}{T}}{\partial T}\right)^T \Delta \boldsymbol{n}_j = 0$$
(C.12)

Since P_F and P_j are the same at the solution it is possible to arrive at a single equation for both the (U, V) and the (V, S) flash specifications:

$$r_{S,U} + \frac{C_v}{T} \Delta T + \sum_{j=1}^{F-1} \left(A_{V,T,F} - A_{V,T,j} \right) \Delta V_j - \sum_{j=1}^F \boldsymbol{A}_{\boldsymbol{n},T,j}^T \Delta \boldsymbol{n}_j = 0$$
(C.13)

where $r_{S,U} = S - S^{spec}$ for the (V, S) flash specification and $r_{S,U} = \frac{U - U^{spec}}{T}$ for the (V, U) flash specification. Substituting in the composition correction we arrive at:

$$-\sum_{j=1}^{F} \boldsymbol{A}_{n,T,j}^{T} \boldsymbol{A}_{n,n,j}^{-1} \boldsymbol{\mathcal{A}}^{T} \boldsymbol{\lambda} + \sum_{j=1}^{F-1} \left(\frac{S_{j}}{V_{j}} - \frac{S_{F}}{V_{F}} \right) \Delta V_{j} + \left(\frac{C_{v}}{T} + \sum_{j=1}^{F} \boldsymbol{A}_{n,T,j}^{T} \boldsymbol{A}_{n,n,j}^{-1} \boldsymbol{A}_{n,T,j} \right) \Delta T = -\sum_{j=1}^{F} \boldsymbol{A}_{n,T,j}^{T} \boldsymbol{A}_{n,n,j}^{-1} \boldsymbol{A}_{n,j} - r_{S,H}$$
(C.14)

The resulting system of equations (size C + F) is then given by:

$$\begin{pmatrix} \mathcal{A} \sum_{j=1}^{F} \mathbf{A}_{n,n,j}^{-1} \mathcal{A}^{T} & \mathcal{A} \hat{\mathbf{R}} & \mathbf{t}_{v} \\ \begin{pmatrix} \left(\mathcal{A} \hat{\mathbf{R}} \right)^{T} & \mathbf{0} & \frac{\mathbf{S}}{\mathbf{V}} - \frac{S_{F}}{V_{F}} \\ \mathbf{t}_{v}^{T} & \left(\frac{\mathbf{S}}{\mathbf{V}} - \frac{S_{F}}{V_{F}} \right)^{T} & C_{v,x} \end{pmatrix} \begin{pmatrix} \boldsymbol{\lambda} \\ \Delta \mathbf{V} \\ \Delta T \end{pmatrix} = \begin{pmatrix} \mathcal{A} \left(\sum_{j=1}^{F} \mathbf{A}_{n,n,j}^{-1} \boldsymbol{\mu}_{j} \right) \\ \mathbf{u}_{3,v} \\ -\sum_{j=1}^{F} \mathbf{A}_{n,T,j}^{T} \mathbf{A}_{n,n,j}^{-1} \mathbf{A}_{n,j} - r_{S,U} \end{pmatrix}$$
(C.15)

with

$$m{R} = (m{
ho}_1 - m{
ho}_F, m{
ho}_2 - m{
ho}_F, ..., m{
ho}_{F-1} - m{
ho}_F)$$

and

$$u_{3,v,j} = (\boldsymbol{\rho}_j - \boldsymbol{\rho}_F)^T \, \boldsymbol{\mu}_j + A_{V,j} - A_{V,F} \quad \forall j$$

All other terms remain unchanged. The change in the volume of the remaining phase is found from equation C.9.