Master Thesis

ALMA MATER LEOBIENSIS

A Virtual PVT Cell

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Chair of Reservoir Engineering

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Betr.: **Thesis**

Leoben, am 12. Juli 2007

Sehr geehrte Herr Brunneder!

Das vom Lehrstuhl für Reservoir Engineering zur Verfügung gestellte Thema der Thesis mit dem Titel

A VIRTUAL PVT CELL

wurde Ihnen zur Ausarbeitung übertragen. Die Arbeiten werden von Ihnen zur Gänze am Department für Mineral Resources and Petroleum Engineering unter der Betreuung von Herrn Univ.Prof. Leonhard Ganzer durchgeführt.

Beginn: 1. August 2007

Dieses Schreiben wird nach Abschluss der Arbeit mit eingebunden.

Glück auf!

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Univ.Prof.Dipl.-Ing.Dr.mont. Leonhard Ganzer

EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre an Eides statt, dass ich diese Arbeit selbständig verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und mich auch sonst keiner unerlaubten Hilfsmittel bedient habe.

AFFIDAVIT

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

Datum	Unterschrift

Für meine Eltern, Leopoldine und Alois Brunneder, die mir das alles ermöglicht haben.

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I want to thank OMV for the allowance to take a look at their PVT laboratory and providing us with information.

And I also want to thank Horst Resch for the great photos used in the software.

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Zusammenfassung

Auf dem Weg von der Lagerstätte bis zum Tank treten teilweise erhebliche Druck- und Temperaturunterschiede auf. Das Wissen um das Phasenverhalten von Kohlenwasserstoffen in jedem Punkt auf diesem Weg ist entscheidend für eine effiziente Gewinnung, von der Dimensionierung der Bohrung über Lagerstättensimulationen bis zur Auslegung von Produktionsanlagen. Zur Erlangung dieser Daten sind teure und zeitaufwändige Analysen in einem sogenannten PVT (pressure, volume, temperature) Labor notwendig. Mittlerweile gibt es aber auch sehr gute mathematische Modelle die eine gute Übereinstimmung mit den Labordaten erzielen können und in Form kommerzieller Software zur Verfügung stehen.

Diese Master Thesis hat das Ziel ein freies Software Tool zu entwickeln, das für eine Mischung aus drei Komponenten ein realistisches Phasenverhalten errechnen kann und dem Anwender das Simulieren von einfachen PVT Experimenten ermöglicht. Besonderes Anliegen ist eine einfache Präsentation der Problematik, um auch fachfremde Benutzer anzusprechen, die das Programm ganz bequem von der Instituts-Hompage aus starten und verwenden können.

Fachliches Hauptaugenmerk liegt vor allem an der Erarbeitung und Aufbereitung von grundlegenden Berechnungsverfahren für die direkte Implementierung in einem Computer Programm. Es handelt sich dabei um sogenannte VLE (vapor-liquid equilibrium) Berechnungen, oder auch Two-Phase Split genannt, die in Verbindung mit einer Cubic EOS (equation of state), im konkreten Fall Peng-Robinson, es ermöglichen das Phasenverhalten zu modellieren.

In dieser Arbeit werden die verwendeten Gleichungen und Algorithmen, sowie Vergleiche der Ergebnisse mit Beispielen aus der Literatur als auch einer kommerziellen Software präsentiert.

Abstract

A reservoir fluid on it's way from downhole to the surface tank is exposed to large changes in temperature and pressure. To know the phase behavior of the hydrocarbon mixture in every point on it's path is essential for recovery efficiency, beginning from well planning, reservoir simulation and up to the dimensioning of facilities. To get this data, expensive and time consuming analysis in a PVT (pressure, volume, temperature) laboratory is necessary. Today good mathematical models exist that can predict phase behavior in accordance with experimental data and are available as commercial software.

This Master Thesis has the objective to develop a free software tool, that can predict realistic phase behavior of mixtures of up to three components and allows the user to perform basic PVT experiments. A main concern is an understandable presentation of the topic in order to be attractive for users who are not familiar with phase behavior yet. The application therefore can be launched from within the institute's homepage to be as convenient accessible as possible.

Main concern in a professional point of view is the formulation and preparation of the calculations to be suited for direct implementation in a computer program. These procedures are so called VLE (vapor-liquid equilibrium), also known as Two-Phase Split calculations, in combination with an EOS (equation of state), in case of this thesis Peng-Robinson, to model the phase behavior.

The thesis shows the used equations and algorithms as well as a comparison of results with literature and a commercial software.

Contents

List of Abbreviations

BIP's binary interaction parameters

EOS equation of state

GUI graphical user interface

Mathematica Cumputer algebra system from Wolfram Research

NIST National Institute of Standards and Technology

PVT pressure, volume, temperature

PVTP PVT software tool from Petroleum Experts

SOPE PVT demonstration tool from SHELL Laboratories Amsterdam, v5.1, 1989

SUREPVT PVT software tool from Seismic Micro Technology

TS trivial solution

VLE vapor-liquid equilibrium

VPC Virtual PVT Cell

List of Symbols

If not denoted otherwise the subscript v stands for vapor phase, L for liquid phase and i is the component index.

Ω_a EOS constant, 0.457 24

Ω_b EOS constant, 0.077 80

α_i correction term to constant A in EOS's

ϵ convergence criterion; error value

ω acentric factor

ϕ_i fugacity coefficient of component i

ϕ_l fugacity coefficient of liquid phase

ϕ_v fugacity coefficient of vapor phase

ρ volumetric density, kg·m^{-3}

A dimensionless EOS constant describing molecular attractive forces

A'_i coefficient for the fugacity coefficient ϕ_i

a_{ci} EOS constant of component i, Pa·m^6·mol^{-2}

a_T EOS constant describing molecular attractive forces, Pa·m^6·mol^{-2}

a_{Ti} EOS constant of component i, Pa·m^6·mol^{-2}

B dimensionless EOS constant describing molecular repulsive forces

b EOS constant describing molecular repulsive forces, m^3·mol^{-1}

B'_i coefficient for the fugacity coefficient ϕ_i

b_i EOS constant b for component i, m^3·mol^{-1}

C companion matrix

f_i fugacity of component i, Pa

f_{Li} fugacity of component i in liquid phase, Pa

F_v vapor fraction

f_{vi} fugacity of component i in vapor phase, Pa

F_{vmax} upper limit of F_v

F_{vmin} lower limit of F_v

f_{yi} second-phase fugacity of component i in the phase-stability-test, Pa

f_{zi} fugacity of component i in the overall mixture, Pa

g_L^* normalized Gibbs energy for liquid phase, Pa

g_{mix}^* normalized Gibbs energy for mixture, Pa

g_v^* normalized Gibbs energy for vapor phase, Pa

g_z^* feed composition normalized Gibbs energy (considered as a single phase), Pa

h Rachford-Rice function in phase-split calculation

K K value (equilibrium ratio)

K_i K value (equilibrium ratio) for component i

k_{ij} binary interaction parameter

K_{max} maximum K value

K_{min} minimum K value

M molar mass, kg·mol^{-1}

m correlation function in correction term α_i for EOS constant A

p pressure, all pressures are absolute if not stated otherwise, Pa

p_{ci} critical pressure of component i, Pa

p_{max} minimal allowed pressure, Pa

p_{min} minimal allowed pressure, Pa

p_{ri} reduced pressure of component i

R universal gas constant, $8.314\,472\,\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$

R_i fugacity-ratio correction for component i

S sum of mole numbers

T temperature, K

T_{ci} critical temperature of component i, K

T_{max} maximal allowed temperature, K

T_{min} minimum allowed temperature, K

T_{ri} reduced temperature of component i

V volume, $\mathrm{m^3}$

V_{act} actual volume, $\mathrm{m^3}$

V_m molar volume, $\mathrm{m^3{\cdot}mol^{-1}}$

x liquid phase composition

x_i mole fraction of component i in the liquid phase

y gas phase composition

Y_i component i mole number

y_i mole fraction of component i in the gas phase

Z gas deviation factor

z overall mixture composition

Z_L gas deviation factor for the liquid phase

Z_v gas deviation factor for the vapor phase

List of Figures

List of Tables

1. Requirements

1.1. Project Overview

1.1.1. Project Description

Currently there is no modern free software available to simulate simple pressure, volume, temperature (PVT) cell experiments, especially for educational and experimental use. Actually a program called "SOPE" (SHELL Laboratories Amsterdam, v5.1 from 1989) already provides most of the desired functionality but is an outdated MS-DOS software on the one hand and can only handle binary mixtures on the other.

Therefore the goal of this project is to create a modern application, that can simulate simple PVT cell laboratory experiments with mixtures consisting of up to three components and which is easy to use. A further objective is that the program can be started out of a web browser and is platform independent. The final version of Virtual PVT Cell (VPC) is then hosted on the institute's homepage (http://www.petroleumengineer.at) for free use.

1.1.2. Project Scope

Project Includes

- vapor-liquid equilibrium (VLE) calculations using existing equation of state (EOS) methods
- only consider liquid and vapor phase
- design
- implementation
- testing
- online manual
- thesis paper

Project Excludes

- implementation of standard PVT experiments (CCE, DLE, ...)
- arrange and setup web hosting

1.1.3. Project Life Cycle

The project starts from scratch and includes planning, implementation of the software and deliver a Master Thesis paper. It ends, when the source code, binaries and the paper are submitted to the supervisor and approved by him.

1.2. Requirement Definition

1.2.1. Functional Requirements

The software should simulate PVT experiments in a laboratory PVT cell and deliver realistic phase behavior. The user specifies a fluid composition of up to three components and can change pressure, temperature and composition as listed in Table 1.1 on page 21. The program calculates the vapor and liquid phase composition as well as various fluid parameters.

1.2.2. Software Functionality

Besides performing the experiments, the program should provide the following functionality:

- EOS: Peng-Robinson
- provide built-in component library
- provide built-in binary interaction parameters (BIP's)
- online manual
- platform independency
- can run in a web browser

Table 1.1.: Possible Experiments

Changed parameter	**Constant parameter**	**Calculated parameter**
A) Fixed PVT cell volume		
1) p	V, z	T
2) T	V, z	p
B) Variable PVT cell volume		
1) p	T, z	V
Additionally the following parameters are calculated		
ρ_L, ρ_v, F_v, $K_i{}^{1)}$, M_L, M_v, V_L, V_v, V_{mL}, V_{mv}, $x_i{}^{1)}$, $y_i{}^{1)}$, $Z_L{}^{1)}$, $Z_v{}^{1)}$		

$^{1)}$ not available in single component system

where p is the pressure [Pa], V is the volume [m^3], z is the overall mixture composition [-], T is the temperature [K], ρ is the volumetric density [kg·m^{-3}], F_v is the vapor fraction [-], K is the K value (equilibrium ratio), M is the molar mass [kg·mol^{-1}], V_m is the molar volume [m^3·mol^{-1}], x is the liquid phase composition [-], y is the gas phase composition [-], Z is the gas deviation factor [-].

1.2.3. Interface Requirements

1.2.3.1. Graphical User Interface

A state-of-the-art graphical user interface (GUI) is mandatory which provides an easy handling and a self explaining structure. The language of the user interface is English. As this is a software mainly targeted to users from the oil industry, the input and output should be possible in different metric and field units to be comfortable to use.

1.2.3.2. Application Programming Interface

To provide a flexible base for reuse and enhancements, the "physics" should be completely separated from the GUI. Therefore an interface is needed which defines the communication between core application and presentation layer.

2. Calculations

2.1. The Equation of State

For the VPC the Peng-Robinson EOS is used, as it is one of the most widespread one EOS and should deliver acceptable results for vapor and liquid phase. Another aspect is it's availability in almost every commercial PVT software for result comparison.

2.1.1. Peng-Robinson

From [5]. See the Peng-Robinson EOS applied in a Mathematica example in Appendix C.2 on page 110.

$$p = \frac{RT}{V_m - b} - \frac{a_T}{V_m(V_m + b) + b(V_m - b)} \tag{2.1}$$

where p is the pressure [Pa], $R = 8.314\,472$ is the universal gas constant [J·mol^{-1}·K^{-1}], T is the temperature [K], V_m is the molar volume [m^3·mol^{-1}], b is an EOS constant describing molecular repulsive forces [m^3·mol^{-1}] and a_T is an EOS constant describing molecular attractive forces [Pa·m^6·mol^{-2}].

$$a_{ci} = \Omega_a \frac{R^2 T_{ci}^2}{p_{ci}} \tag{2.2}$$

where a_{ci} is an EOS constant of component i [Pa·m^6·mol^{-2}], $\Omega_a = 0.457\,24$ is an EOS constant [-], T_{ci} is the critical temperature of component i [K] and p_{ci} is the critical pressure of component i [Pa].

$$b = \Omega_b \frac{R T_{ci}}{p_{ci}} \tag{2.3}$$

where $\Omega_b = 0.077\,80$ is an EOS constant [-].

$$\alpha_i = [1 + m(1 - \sqrt{T_{ri}})]^2 \tag{2.4}$$

$$T_{ri} = \frac{T}{T_{ci}} \tag{2.5}$$

$$a_{Ti} = a_{ci}\alpha_i \tag{2.6}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{2.7}$$

where α_i is a correction term to constant A for component i [-], m is the correlation function in correction term α_i [-], T_{ri} is the reduced temperature of component i [-], a_{Ti} is an EOS constant of component i [Pa·m^6·mol^{-2}] and ω is the acentric factor [-].

Modified Peng-Robinson for $\omega > 0.49$

$$m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3 \tag{2.8}$$

Mixing Rules

$$b = \sum_{i=1}^{N} y_i b_i \tag{2.9}$$

where y_i is the mole fraction of component i in the gas phase [-] and b_i is the EOS constant b for component i [m^3·mol^{-1}].

$$a_T = \sum_{i=1}^{N}\sum_{j=1}^{N} y_i y_j a_{Tij} \tag{2.10}$$

$$a_{Tij} = (1 - k_{ij})\sqrt{(a_{Ti}a_{Tj})} \tag{2.11}$$

where k_{ij} is the binary interaction parameter between component pair i-j [-].

Peng-Robinson in terms of Z-factor

Substitution of the real gas law

$$V_m = \frac{V}{n} = \frac{ZRT}{p} \tag{2.12}$$

into (2.1) and rearranging yields

$$Z^3 - (1 - B)Z^2 + \left(A - 2B - 3B^2\right)Z - \left(AB - B^2 - B^3\right) = 0 \tag{2.13}$$

$$A = \frac{a_T p}{(RT)^2} \tag{2.14}$$

$$B = \frac{bp}{RT} \tag{2.15}$$

where Z is the gas deviation factor [-],A is a dimensionless EOS constant describing molecular attractive forces [-] and B is a dimensionless EOS constant describing molecular repulsive forces [-].

Fugacity expression is given by

$$\ln \phi_i = -\ln(Z - B) + (Z - 1)B'_i - \frac{A}{2\sqrt{2}B}(A'_i - B'_i)\ln[\frac{Z + (1 + \sqrt{2})B}{Z - (1 - \sqrt{2})B}] \tag{2.16}$$

$$A'_i = \frac{1}{a_T}[2\sqrt{a_{Tj}}\sum_{j=1}^{N} y_j\sqrt{a_{Tj}}(1 - k_{ij})] \tag{2.17}$$

$$B'_i = \frac{b_i}{b} \tag{2.18}$$

where ϕ_i is the fugacity coefficient of component i [-], A'_i is a coefficient for the fugacity coefficient ϕ_i [-] and B'_i is a coefficient for the fugacity coefficient ϕ_i [-].

$$f_i = y_i p \phi_i \tag{2.19}$$

where f_i is the fugacity of component i [Pa].

2.1.2. Solving the Z-Factor Equation

The EOS equations (2.1 to 2.19) are straight forward to program, but the first problem occurs in (2.16) when the Z-factor is needed which requires that the polynomial (2.13) is solved with respect to Z.

In VPC the popular "companion matrix method" (see C.1 on page 109 for an outlined Mathematica example) was chosen as a general approach for finding all roots of a polynomial of the form

$$a(x) = a_0 + a_1 x + ... + a_{n-1}x^{n-1} + x^n \tag{2.20}$$

The first step is to setup the polynomial in a special form, the so called companion matrix [6].

$$C = \begin{bmatrix} 0 & 0 & \cdots & 0 & -a_0 \\ 1 & 0 & \cdots & 0 & -a_1 \\ 0 & 1 & \cdots & 0 & -a_2 \\ \vdots & \vdots & \ddots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 & -a_n \end{bmatrix} \tag{2.21}$$

The second step is to calculate the eigenvalues for the companion matrix C by a numerical method of choice. In case of VPC the third-party library ojAlgo (v21)was selected for this task.

2.2. Single Component System: Solve for Volume

The first application problem that needs to be solved is the phase behavior of a single component under the specified PVT conditions. The procedure used in VPC follows [4] (Ch. 15, “Pure Substances”). Please see C.2 on page 110 for a calculated Mathematica example. Although [4] states a two-phase condition for a pure substance this is only of theoretical interest.

Here is the procedure outline to solve for the volume:

1. Calculate the Z-factors according (2.13)
2. If $T \geq T_c$ and $p \geq p_c$ then the fluid is supercritical; select the first Z-factor; finished
3. Else if number of Z-factors == 1 then we are in single phase state →apply criterion (2.23)
4. Else if number of Z-factors == 3
   a) The Z-factor for liquid phase Z_L =smallest Z-factor; calculate fugacity coefficient for liquid phase ϕ_l (2.16) with Z_L
   b) The Z-factor for vapor phase Z_v =largest Z-factor; calculate fugacity coefficient for vapor phase ϕ_v with Z_v
   c) If $\phi_l < \phi_v$ then the phase state is liquid, else vapor
5. Calculate parameters like V, V_m with the real gas law (2.12) or the density

$$\rho = \frac{M}{V_m} \tag{2.22}$$

where ρ is the volumetric density [kg·m^{-3}] and M is the molar mass [kg·mol^{-1}].

Distinguish Vapor and Liquid Telling whether the fluid is present in liquid or vapor phase is apparent in an experiment. Unfortunately there is no mathematical model that can predict the phase state without a doubt. For VPC the following criterion is used:

$$phase\,state = \begin{cases} liquid & \text{if } \frac{V_m}{b} \leq 1.7 \\ vapor & \text{else} \end{cases} \tag{2.23}$$

where V_m is the molar volume [$\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$] and b is an EOS constant describing molecular repulsive forces [$\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$].

2.3. Vapor-Liquid Equilibrium Calculation

2.3.1. Introduction

The traditional approach [1] of VLE calculation assumes that the equilibrium ratio

$$K_i = \frac{y_i}{x_i} \tag{2.24}$$

where K_i is the K value (equilibrium ratio) for component i [-], y_i is the mole fraction of component i in the gas phase [-] and x_i is the mole fraction of component i in the liquid phase [-],

is known from charts or experiments. As the K value is a function of temperature, pressure and composition, this solution method is not suitable for implementation in a program because this would require an improper number of charts and the use of interpolation/extrapolation.

The solution method chosen for this software is a combination of methods described by [7] and [4].

> Phase equilibria are calculated with an EOS by satisfying the condition of chemical equilibrium. For a two-phase system to be in equilibrium, the chemical potential of each component in the liquid phase $\mu_i(x_i)$ must be equal to the chemical potential of the component in the vapor phase $\mu_i(y_i)$, $\mu_i(x_i) = \mu_i(y_i)$. Chemical potential is usually expressed in terms of fugacity, f_i, where $\mu_i = RT \ln f_i + \lambda_i(T)$ and $\lambda_i(T)$ are constant terms that drop out in most problems. It is readily shown that the condition $\mu_i(x_i) = \mu_i(y_i)$ is satisfied by the equal-fugacity constraint, $f_{li} = f_{vi}$, where fugacity is given by
>
> $$\ln \phi_i = \ln \frac{f_i}{y_i p} = \frac{1}{RT} \int_V^\infty \left(\frac{\partial p}{\partial n_i} - \frac{RT}{V}\right) \mathrm{d}V - \ln Z. \tag{2.25}$$

2.3.2. Multi-Component Mixture: Solve for the Volume

Calculation procedure for the two-phase VLE for mixtures:

1. Estimate initial K values with (2.33) (see 2.3.2.1 on the next page) or start with K values from previously converged calculation
2. Solve the Rachford-Rice phase-split calculation (see 2.3.2.2 on page 29). If $F_v < 0$ or $F_v > 1$ or a trivial solution is approached, perform a phase stability test (2.3.2.3) to confirm it.
3. Calculate phase composition for liquid phase x and vapor phase y where

   $$x_i = \frac{z_i}{F_v(K_i - 1) + 1} \tag{2.26}$$

   and

   $$y_i = \frac{z_i K_i}{F_v(K_i - 1) + 1} = K_i x_i \tag{2.27}$$

4. Calculate phase Z-factors Z_L and Z_v from the EOS (2.13). If multiple roots occur during iterations it may be necessary to perform up to four flash calculations.
   a) Select roots according Table 2.1 on page 28.
   b) Converge the flash calculation with a consistent selection of roots
   c) If necessary, converge also a 2^{nd}, 3^{rd} and 4^{th} flash
   d) Finally, select the flash solution with the lowest mixture Gibbs energy g^*_{mix}

   $$g^*_L = \sum_{i=1}^{N} x_i \ln f_{Li} \tag{2.28}$$

   where g^*_L is the normalized Gibbs energy for liquid phase [Pa] and f_{Li} is the fugacity of component i in liquid phase [Pa]

   $$g^*_v = \sum_{i=1}^{N} y_i \ln f_{vi} \tag{2.29}$$

   where g^*_v is the normalized Gibbs energy for vapor phase [Pa] and f_{vi} is the fugacity of component i in vapor phase [Pa]

   $$g^*_{mix} = F_v g^*_v + (1 - F_v) g^*_L \tag{2.30}$$

Table 2.1.: Sequence of Flash Calculations to Ensure Correct Solution with Multiple Z-factor Roots [7]

	Liquid Z-factor		Vapor Z-factor	
Possible Order of Multiple Flash Calculations	Smallest	Largest	Smallest	Largest
1	x			x
2		x		x
3		x	x	
4	x		x	

where g^*_{mix} is the normalized Gibbs energy for the mixture [Pa].

5. Calculate fugacity coefficients ϕ_L, ϕ_v 2.16

6. Calculate new K values and check if convergence is achieved [4]

$$K_i^{(n+1)} = \frac{\phi_{Li}}{\phi_{vi}} \tag{2.31}$$

with a convergence criterion

$$\frac{(K_i^{(n)} - K_i^{(n+1)})}{K_i^{(n)} K_i^{(n+1)}} < \epsilon \tag{2.32}$$

where the index n stands for the trial K value and $n+1$ is the new K value. In VPC $\epsilon = 1 \times 10^{-10} K_i^n$.

   a) If convergence is not reached return to step 2.
   b) If convergence is reached stop.
   c) Check for convergence to a trivial solution ($K \to 1$) with (2.49).

2.3.2.1. Estimate initial K values

To get a initialization value for the VLE iterative calculation the Wilson equation [8] is used.

$$K_i = \frac{\exp^{[5.37(1+\omega_i)(1-\frac{1}{T_{ri}})]}}{p_{ri}} \tag{2.33}$$

$$p_{ri} = \frac{p}{p_{ci}} \tag{2.34}$$

where p_{ri} is the reduced pressure of component i [-].

2.3.2.2. Rachford-Rice Equation

From [7].

$$h(F_v) = \sum_{i=1}^{N}(y_i - x_i) = \sum_{i=1}^{N} \frac{z_i(K_i - 1)}{1 + F_v(K_i - 1)} = 0 \tag{2.35}$$

where h is the Rachford-Rice function in phase-split calculation [-], F_v is the vapor fraction [-]

$$h'(F_v) = \frac{\mathrm{d}h}{\mathrm{d}F_v} = \sum_{i=1}^{N} \frac{z_i(K_i - 1)^2}{[1 + F_v(K_i - 1)]^2} = 0 \tag{2.36}$$

Equation (2.36) is solved numerically for F_v with the Newton method. A numerical library (Michael Thomas Flanagan's Java Scientific Library, Version 20. April 2008 by Dr Michael Thomas Flanagan) used but the algorithm is also presented in Appendix C.3 on page 114.

$$F_v^{(n+1)} = F_v^{(n)} - \frac{h(F_v^{(n)})}{h'(F_v^{(n)})} \tag{2.37}$$

Figure 2.1 on page 30 shows a plot of the Rachford-Rice function (2.35) for a three component mixture. As [7] states, the only physical meaningful solution lies in the region $F_{vmin} < F_v < F_{vmax}$ whith the consequence that at least one K value is < 1 and one is > 1.

$$F_{vmin} = \frac{1}{1 - K_{max}} \tag{2.38}$$

where F_{vmin} is the lower limit of F_v [-] and K_{max} is the maximum K value [-],

$$F_{vmax} = \frac{1}{1 - K_{min}} \tag{2.39}$$

where F_{vmax} is the upper limit of F_v [-] and K_{min} is the minimum K value [-].

For an example please see Appendix C.3 on page 114.

Three types of converged solutions can be obtained [7]:

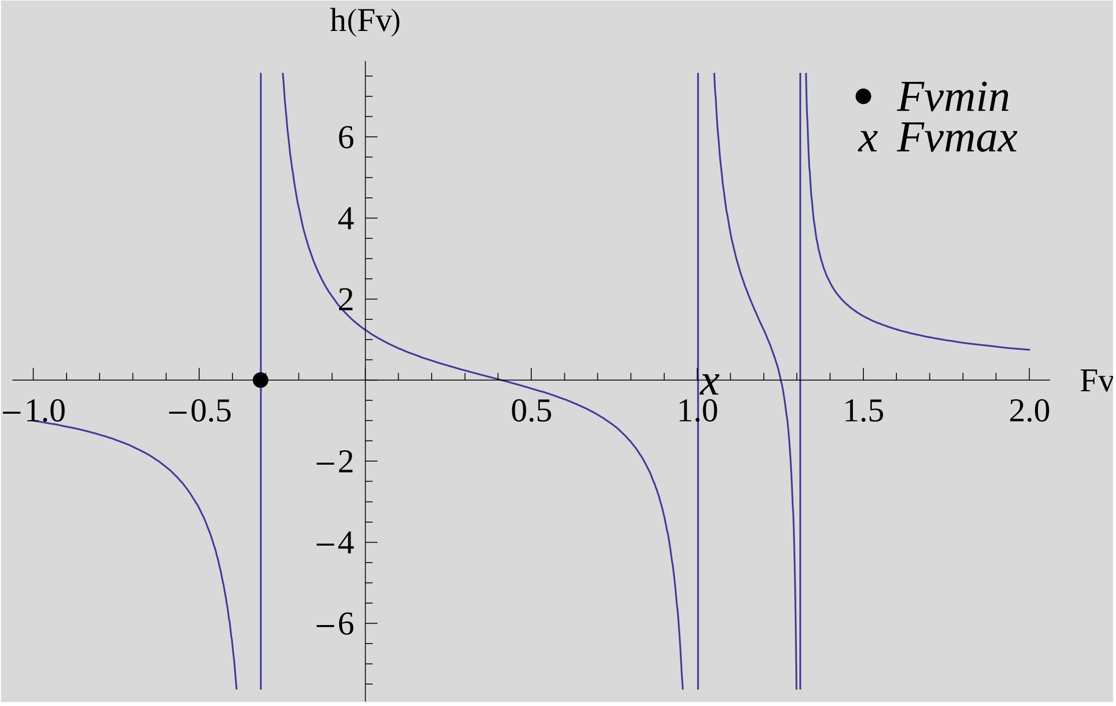

Figure 2.1.: Example Rachford-Rice Function for a Three Component Mixture

1. A physically acceptable solution is found with $0 \leq F_v \leq 1$, where $F_v = 0$ corresponds to a bubblepoint condition, $F_v = 1$ to a dewpoint condition and $0 < F_v < 1$ indicates a two-phase condition.
2. A physically unacceptable solution is found with $F_v < 0$ or $F_v > 1$. It indicates that the mixture is thermodynamically stable as a single phase.
3. A so called trivial solution is found where the calculated phase compositions are identical to the mixture composition and K values equal one ($x_i = y_i = z_i$).

2.3.2.3. Phase Stability Test

> One of the most difficult aspects of making VLE calculations with an EOS is knowing whether a mixture will actually split into two (or more) phases at the specified pressure and temperature. Phase stability deals with the question of weather a mixture can attain a lower energy by splitting into two or more phases [7].

This is the phase stability test procedure as outlined in [7]. First, a vapor-like search is performed and then a liquid-like search. On the results of both searches a decision is made.

1. Calculate the mixture fugacities, f_{zi} (2.19); with multiple Z-factor roots, choose the root with the lowest normalized Gibbs energy

$$g_z^* \sum_{i=1}^{N} z_i \ln f_{zi} \tag{2.40}$$

   where g_z^* is the feed composition normalized Gibbs energy (considered as a single phase) [Pa] and f_{zi} is the fugacity of component i in the overall mixture [Pa].

2. Use the Wilson equation (2.33) to estimate initial K values

3. Calculate second-phase mole numbers, Y_i, using the mixture composition z_i and the present Kvalue estimates

$$(Y_i)_v = z_i(K_i)_v \tag{2.41}$$

   or

$$(Y_i)_L = \frac{z_i}{(K_i)_L} \tag{2.42}$$

   where Y_i is the component i mole number.

4. Sum the mole numbers.

$$S = \sum_{i=1}^{N} Y_i \tag{2.43}$$

   where S is the sum of mole number.

5. Normalize the second-phase mole numbers to get mole fractions, y_i.

$$y_i = \frac{Y_i}{S} \tag{2.44}$$

6. Calculate the second-phase fugacities $(f_{yi})_v$ or $(f_{yi})_L$ from the EOS; with multiple Z-factor roots choose the root with the lowest Gibbs energy g_z^*.

7. Calculate the fugacity-ratio corrections for successive-substitution update of the K values.

Table 2.2.: Possible Two-Phase Phase-Stability-Test Results

Second Phase	
Vapor-Like	**Liquid-Like**
$S_v > 1$	TS
TS	$S_L > 1$
$S_v > 1$	$S_L > 1$

trivial solution (TS).

$$(R_i)_v^{(n)} = \frac{f_{zi}}{(f_{yi})_v} \frac{1}{S} \tag{2.45}$$

or

$$(R_i)_L^{(n)} = \frac{(f_{yi})_L}{f_{zi}} S \tag{2.46}$$

where R_i is the fugacity-ratio correction for component i [-].

8. Check whether convergence is achieved (e.g. $\epsilon < 1 \times 10^{-12}$)

$$\sum_{i=1}^{N} (R_i^{(n)} - 1)^2 < \epsilon \tag{2.47}$$

9. If convergence is not obtained, update the K values.

$$K_i^{(n+1)} = K_i^{(n)} R_i^{(n)} \tag{2.48}$$

10. Check whether a trivial solution is approached using the criterion

$$\sum_{i=1}^{N} (\ln K_i^{(n+1)})^2 < 1 \times 10^{-4} \tag{2.49}$$

11. If a trivial solution is not indicated, go to Step 3 for another iteration.

After the both searches are finished decide according Table 2.2 on page 32 if the mixture will be will split into two phases. As the VPC does not deal with tree-phase conditions, a single-phase state is assumed otherwise.

Decide Whether Single Phase is Liquid or Vapor State

1. Calculate Z-factor roots for the overall mixture z; with multiple Z-factor roots choose the root with the lowest normalized Gibbs energy g_z^* (2.40).
2. Apply criterion (2.23).

2.4. Solve VLE for the Pressure

In order to simulate PVT experiments the VPC also has to provide the possibility to calculate the VLE out of a given volume and temperature $(T, V_{target}, n \rightarrow p)$. Unfortunately the procedures for calculating the volume cannot be rearranged to yield the pressure, therefore in VPC a simple numerical solution procedure was applied.

As it is the case in reality, the PVT equipment is specified for a certain pressure range between p_{min} and p_{max}. Therefore an interval bisection method can be applied to look for the pressure that causes the fluid to occupy the given volume under the given temperature.

The following procedure applies to single component cases as well as to mixtures.

1. An initial value for the pressure is needed
    a) From a previous solution
    b) If not available
    $$p = \frac{p_{max} - p_{min}}{2} \tag{2.50}$$
2. Calculate the actual volume V_{act} with the current pressure (2.2 on page 25 or 2.3.2 on page 27)
3. Check for convergence and stop if converged
    $$|V_{target} - V_{act}| < 1 \times 10^{-10} V \tag{2.51}$$
4. If not converged assume a new pressure.
    a) If $V_{act} > V_{target}$ we have to increase the pressure to reduce the volume
    $$p_{min} = p \tag{2.52}$$
    b) If $V_{act} < V_{target}$ we have to decrease the pressure to increase the volume
    $$p_{max} = p \tag{2.53}$$

   c) Update pressure

$$p = p_{min} + \frac{p_{max} - p_{min}}{2} \tag{2.54}$$

   d) Return to step 2.

2.5. Solve VLE for the Temperature

This calculation is analogous to Section 2.4. Again the temperature range is bounded by a predefined T_{min} and a T_{max}.

1. An initial value for the temperature is needed
    a) From a previous solution
    b) If not available

$$T = \frac{T_{max} - T_{min}}{2} \tag{2.55}$$

2. Calculate the actual volume V_{act} with the current pressure (2.2 on page 25 or 2.3.2 on page 27)
3. Check for convergence (2.51) and stop if converged.
4. If not converged assume a new temperature
    a) If $V_{act} > V_{target}$ we have to decrease the temperature to reduce the volume

$$T_{max} = T \tag{2.56}$$

    b) If $V_{act} < V_{target}$ we have to increase the temperature to increase the volume

$$T_{min} = T \tag{2.57}$$

    c) Update temperature

$$T = T_{min} + \frac{T_{max} - T_{min}}{2} \tag{2.58}$$

    d) Return to step 2.

3. Results

To evaluate the quality of the results from VPC several tests[1] were cunducted. First, single component systems (3.1) are compared against a literature source to check the quality of the Peng-Robinson EOS results. Despite Peng-Robinson's known weakness in predicting liquid densities, the data are in good agreement with the reference data.

Further a binary (3.2 on page 62) and two ternary mixtures (3.3 on page 75) are tested against other software packages that uses the Peng-Robinson EOS. The pressure and temperature conditions were selected to reflect typical surface conditions (1.013 25 bar, 293.15 K) up to reservoir conditions of 301.013 25 bar and 493.15 K. Again the data are in good agreement with the reference except for some differences in the decision about the phase state.

The reader has to be aware that this is an EOS program comparison and evaluates the quality of the calculation procedure and does not necessarily mean that the results agree with "reality".

3.1. Single Component Systems

The results from VPC for single component systems for Methane, n-Butane and n-Decane are compared against a literature source, which is the National Institute of Standards and Technology (NIST) Chemistry WebBook available online [3][2]. As the key parameter and for comparison the density was selected. The selected pressure range for fixed temperature comparison is 1.013 25 bar to 301.013 25 bar. The temperature range for fixed pressure comparison was the minimum and maximum available value from the literature source.

3.1.1. Fixed Temperature

3.1.1.1. Methane

Figure 3.1 on page 37 shows the results for Methane and it can be seen that there is a good match over all temperatures and pressures and the density differences is at maximum

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[1] The tests were executed as a so called unit test and not with the GUI

[2] The uncertainties in density are 0.03% for pressures below 12 MPa and temperatures below 350 K and up to 0.07% for pressures less than 50 MPa

3.8 % (refer to Table 3.1 on page 38, Table 3.2 on page 39, Table 3.3 on page 40), the phase state prediction is identical. There is an indication for a general trend that the difference increases with increasing pressure.

3.1.1.2. n-Butane

Figure 3.2 on page 41 shows that as soon as n-Butane is present in the liquid phase, the predicted density is off by roughly 5 % to 7 % (refer to Table 3.4 on page 42, Table 3.5 on page 43, Table 3.6 on page 44). This is due to the weakness of Peng-Robinson to predict accurate liquid densities. At 493.15 K the phase state is vapor and supercritical and the densities are more accurate. Again there is an indication for a general trend that the difference increases with increasing pressure.

3.1.1.3. n-Decane

In 3.3 can be seen that there is an almost constant difference of about 8 % at 293.15 K. With increasing temperature and pressure there is a trend of decreasing difference in density, falling below 5 % at 393.15 K and 31 bar (refer to Table 3.7 on page 46, Table 3.8 on page 47, Table 3.9 on page 48).

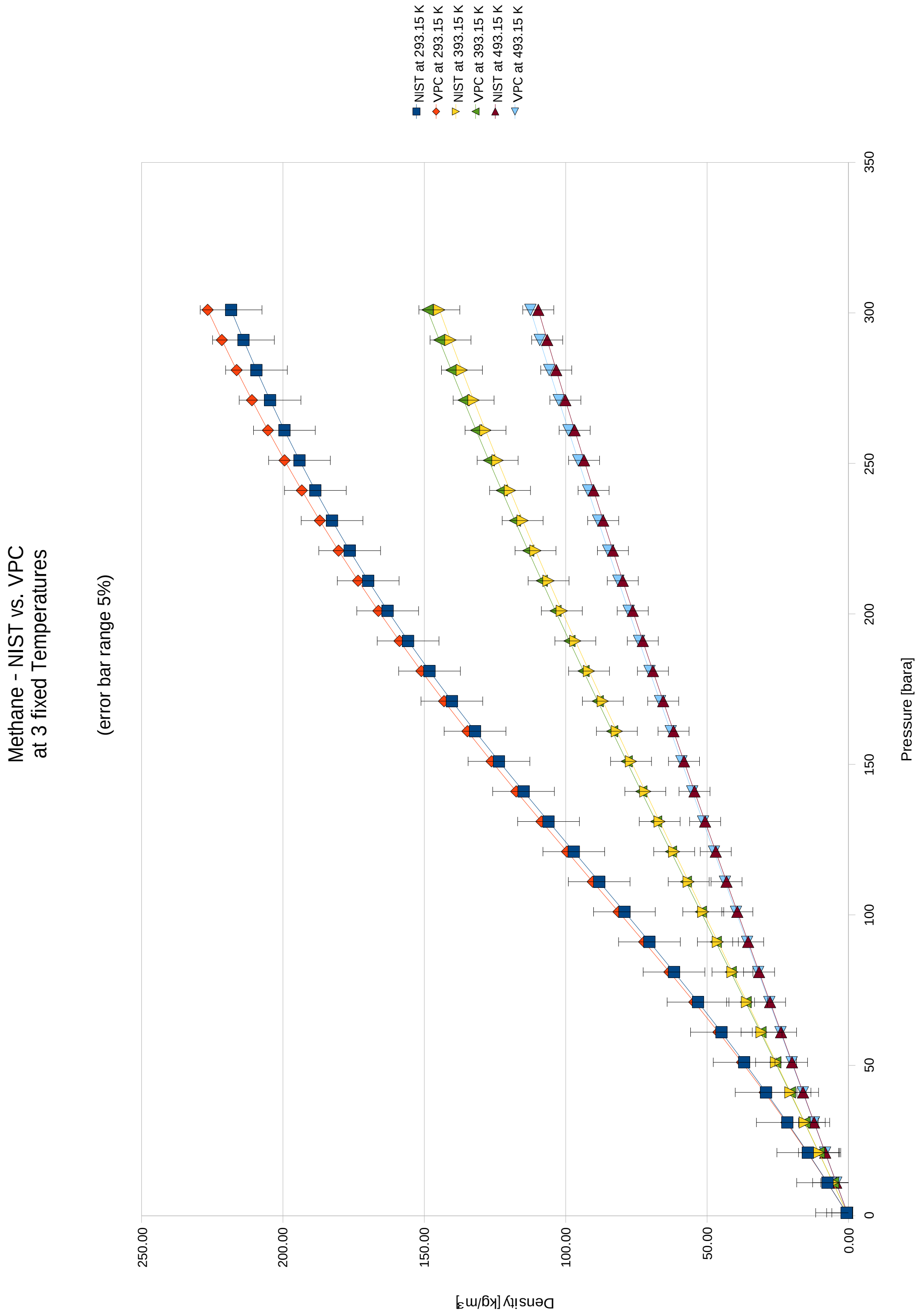


Figure 3.1.: Comparison of Methane at 3 fixed temperatures

Table 3.1.: Comparison of Methane at 293.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	0.67	0.67	0.05%	VAP	VAP
11.01	7.40	7.44	0.54%	VAP	VAP
21.01	14.38	14.52	0.99%	VAP	VAP
31.01	21.62	21.93	1.41%	VAP	VAP
41.01	29.13	29.64	1.78%	VAP	VAP
51.01	36.90	37.67	2.09%	SC	SC
61.01	44.92	45.97	2.34%	SC	SC
71.01	53.20	54.54	2.52%	SC	SC
81.01	61.70	63.32	2.63%	SC	SC
91.01	70.39	72.27	2.67%	SC	SC
101.01	79.22	81.33	2.66%	SC	SC
111.01	88.16	90.44	2.59%	SC	SC
121.01	97.13	99.55	2.49%	SC	SC
131.01	106.07	108.58	2.37%	SC	SC
141.01	114.91	117.49	2.25%	SC	SC
151.01	123.60	126.23	2.13%	SC	SC
161.01	132.06	134.75	2.04%	SC	SC
171.01	140.26	143.03	1.98%	SC	SC
181.01	148.16	151.05	1.95%	SC	SC
191.01	155.73	158.79	1.97%	SC	SC
201.01	162.96	166.25	2.02%	SC	SC
211.01	169.85	173.43	2.11%	SC	SC
221.01	176.40	180.33	2.23%	SC	SC
231.01	182.63	186.96	2.37%	SC	SC
241.01	188.54	193.32	2.54%	SC	SC
251.01	194.15	199.44	2.72%	SC	SC
261.01	199.48	205.31	2.92%	SC	SC
271.01	204.55	210.96	3.13%	SC	SC
281.01	209.37	216.39	3.35%	SC	SC
291.01	213.96	221.61	3.57%	SC	SC
301.01	218.34	226.64	3.80%	SC	SC

Table 3.2.: Comparison of Methane at 393.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	0.50	0.50	0.02%	VAP	VAP
11.01	5.43	5.45	0.28%	VAP	VAP
21.01	10.42	10.47	0.51%	VAP	VAP
31.01	15.45	15.56	0.73%	VAP	VAP
41.01	20.51	20.70	0.92%	VAP	VAP
51.01	25.60	25.88	1.10%	SC	SC
61.01	30.72	31.11	1.26%	SC	SC
71.01	35.87	36.37	1.39%	SC	SC
81.01	41.02	41.64	1.51%	SC	SC
91.01	46.18	46.93	1.62%	SC	SC
101.01	51.35	52.22	1.71%	SC	SC
111.01	56.50	57.51	1.79%	SC	SC
121.01	61.64	62.78	1.85%	SC	SC
131.01	66.76	68.03	1.91%	SC	SC
141.01	71.84	73.25	1.96%	SC	SC
151.01	76.89	78.44	2.01%	SC	SC
161.01	81.90	83.58	2.06%	SC	SC
171.01	86.85	88.68	2.10%	SC	SC
181.01	91.75	93.72	2.14%	SC	SC
191.01	96.59	98.70	2.19%	SC	SC
201.01	101.36	103.62	2.23%	SC	SC
211.01	106.06	108.48	2.28%	SC	SC
221.01	110.68	113.26	2.33%	SC	SC
231.01	115.23	117.98	2.39%	SC	SC
241.01	119.69	122.62	2.45%	SC	SC
251.01	124.07	127.19	2.52%	SC	SC
261.01	128.36	131.69	2.59%	SC	SC
271.01	132.57	136.10	2.67%	SC	SC
281.01	136.69	140.45	2.75%	SC	SC
291.01	140.73	144.71	2.83%	SC	SC
301.01	144.68	148.90	2.92%	SC	SC

Table 3.3.: Comparison of Methane at 493.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	0.40	0.40	0.01%	VAP	VAP
11.01	4.31	4.32	0.17%	VAP	VAP
21.01	8.23	8.25	0.32%	VAP	VAP
31.01	12.14	12.19	0.46%	VAP	VAP
41.01	16.05	16.14	0.58%	VAP	VAP
51.01	19.95	20.09	0.70%	SC	SC
61.01	23.85	24.04	0.81%	SC	SC
71.01	27.73	27.99	0.92%	SC	SC
81.01	31.61	31.93	1.02%	SC	SC
91.01	35.46	35.86	1.11%	SC	SC
101.01	39.30	39.77	1.19%	SC	SC
111.01	43.12	43.67	1.27%	SC	SC
121.01	46.92	47.55	1.35%	SC	SC
131.01	50.70	51.42	1.42%	SC	SC
141.01	54.44	55.26	1.49%	SC	SC
151.01	58.17	59.07	1.56%	SC	SC
161.01	61.86	62.86	1.63%	SC	SC
171.01	65.52	66.63	1.69%	SC	SC
181.01	69.14	70.36	1.76%	SC	SC
191.01	72.74	74.06	1.82%	SC	SC
201.01	76.30	77.73	1.88%	SC	SC
211.01	79.82	81.37	1.94%	SC	SC
221.01	83.30	84.97	2.01%	SC	SC
231.01	86.74	88.54	2.07%	SC	SC
241.01	90.15	92.07	2.14%	SC	SC
251.01	93.51	95.57	2.20%	SC	SC
261.01	96.83	99.03	2.27%	SC	SC
271.01	100.11	102.45	2.33%	SC	SC
281.01	103.35	105.83	2.40%	SC	SC
291.01	106.54	109.18	2.48%	SC	SC
301.01	109.69	112.49	2.55%	SC	SC

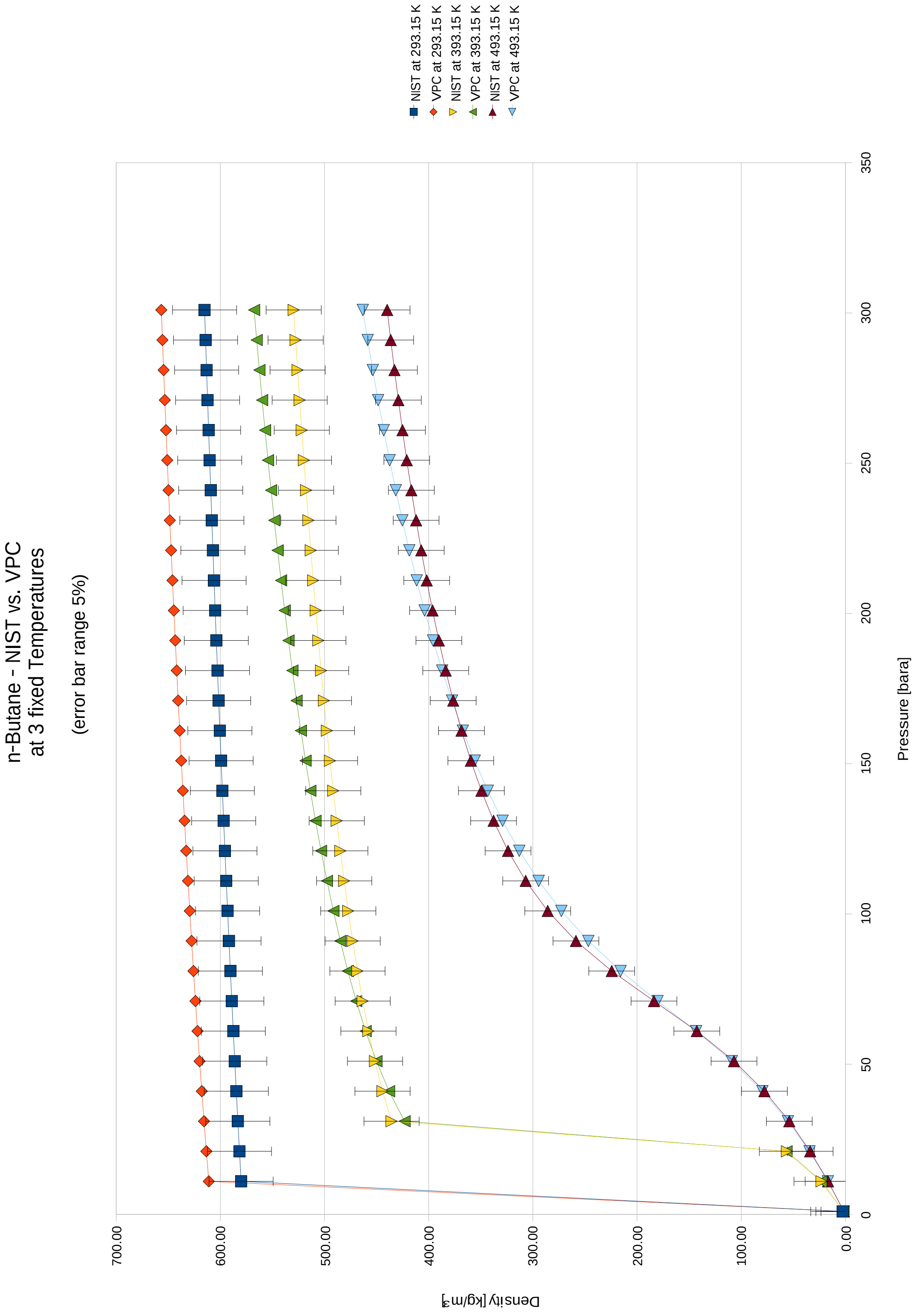


Figure 3.2.: Comparison of n-Butane at Three Fixed Temperatures

Table 3.4.: Comparison of n-Butane at 293.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	2.50	2.49	-0.25%	VAP	VAP
11.01	580.04	611.05	5.35%	LIQ	LIQ
21.01	581.63	613.38	5.46%	LIQ	LIQ
31.01	583.17	615.63	5.57%	LIQ	LIQ
41.01	584.68	617.79	5.66%	LIQ	LIQ
51.01	586.15	619.88	5.75%	LIQ	LIQ
61.01	587.58	621.89	5.84%	LIQ	LIQ
71.01	588.99	623.84	5.92%	LIQ	LIQ
81.01	590.36	625.72	5.99%	LIQ	LIQ
91.01	591.70	627.55	6.06%	LIQ	LIQ
101.01	593.02	629.32	6.12%	LIQ	LIQ
111.01	594.32	631.04	6.18%	LIQ	LIQ
121.01	595.58	632.71	6.23%	LIQ	LIQ
131.01	596.83	634.33	6.28%	LIQ	LIQ
141.01	598.05	635.91	6.33%	LIQ	LIQ
151.01	599.25	637.45	6.37%	LIQ	LIQ
161.01	600.43	638.95	6.42%	LIQ	LIQ
171.01	601.58	640.41	6.45%	LIQ	LIQ
181.01	602.72	641.83	6.49%	LIQ	LIQ
191.01	603.84	643.22	6.52%	LIQ	LIQ
201.01	604.95	644.58	6.55%	LIQ	LIQ
211.01	606.04	645.90	6.58%	LIQ	LIQ
221.01	607.11	647.20	6.60%	LIQ	LIQ
231.01	608.16	648.46	6.63%	LIQ	LIQ
241.01	609.20	649.70	6.65%	LIQ	LIQ
251.01	610.22	650.91	6.67%	LIQ	LIQ
261.01	611.23	652.10	6.69%	LIQ	LIQ
271.01	612.23	653.26	6.70%	LIQ	LIQ
281.01	613.21	654.40	6.72%	LIQ	LIQ
291.01	614.18	655.51	6.73%	LIQ	LIQ
301.01	615.14	656.61	6.74%	LIQ	LIQ

Table 3.5.: Comparison of n-Butane at 393.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	1.82	1.83	0.11%	VAP	VAP
11.01	22.87	23.10	1.03%	VAP	VAP
21.01	56.10	56.49	0.69%	VAP	VAP
31.01	435.62	423.12	-2.87%	LIQ	VAP
41.01	444.30	438.00	-1.42%	LIQ	VAP
51.01	451.53	450.14	-0.31%	LIQ	VAP
61.01	457.79	460.47	0.59%	LIQ	VAP
71.01	463.34	469.50	1.33%	LIQ	VAP
81.01	468.36	477.56	1.96%	LIQ	LIQ
91.01	472.94	484.83	2.51%	LIQ	LIQ
101.01	477.18	491.48	3.00%	LIQ	LIQ
111.01	481.12	497.60	3.43%	LIQ	LIQ
121.01	484.81	503.28	3.81%	LIQ	LIQ
131.01	488.29	508.58	4.15%	LIQ	LIQ
141.01	491.58	513.54	4.47%	LIQ	LIQ
151.01	494.71	518.22	4.75%	LIQ	LIQ
161.01	497.69	522.63	5.01%	LIQ	LIQ
171.01	500.53	526.82	5.25%	LIQ	LIQ
181.01	503.26	530.80	5.47%	LIQ	LIQ
191.01	505.88	534.59	5.68%	LIQ	LIQ
201.01	508.40	538.21	5.86%	LIQ	LIQ
211.01	510.83	541.68	6.04%	LIQ	LIQ
221.01	513.17	545.00	6.20%	LIQ	LIQ
231.01	515.44	548.19	6.35%	LIQ	LIQ
241.01	517.64	551.26	6.50%	LIQ	LIQ
251.01	519.77	554.22	6.63%	LIQ	LIQ
261.01	521.83	557.07	6.75%	LIQ	LIQ
271.01	523.84	559.82	6.87%	LIQ	LIQ
281.01	525.80	562.48	6.98%	LIQ	LIQ
291.01	527.70	565.06	7.08%	LIQ	LIQ
301.01	529.56	567.55	7.17%	LIQ	LIQ

Table 3.6.: Comparison of n-Butane at 493.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	1.44	1.45	0.10%	VAP	VAP
11.01	16.61	16.79	1.05%	VAP	VAP
21.01	33.84	34.45	1.83%	VAP	VAP
31.01	53.85	55.11	2.36%	VAP	VAP
41.01	77.72	79.64	2.47%	SC	SC
51.01	106.89	108.95	1.93%	SC	SC
61.01	142.61	143.22	0.43%	SC	SC
71.01	183.71	180.30	-1.86%	SC	SC
81.01	224.29	215.82	-3.78%	SC	SC
91.01	258.65	246.73	-4.61%	SC	SC
101.01	285.72	272.65	-4.57%	SC	SC
111.01	306.88	294.42	-4.06%	SC	SC
121.01	323.79	312.98	-3.34%	SC	SC
131.01	337.68	329.07	-2.55%	SC	SC
141.01	349.42	343.22	-1.77%	SC	SC
151.01	359.56	355.84	-1.04%	SC	SC
161.01	368.48	367.21	-0.34%	SC	SC
171.01	376.45	377.55	0.29%	SC	SC
181.01	383.65	387.03	0.88%	SC	SC
191.01	390.23	395.78	1.42%	SC	SC
201.01	396.28	403.90	1.92%	SC	SC
211.01	401.89	411.48	2.39%	SC	SC
221.01	407.12	418.57	2.81%	SC	SC
231.01	412.03	425.25	3.21%	SC	SC
241.01	416.64	431.54	3.58%	SC	SC
251.01	421.01	437.50	3.92%	SC	SC
261.01	425.14	443.15	4.24%	SC	SC
271.01	429.08	448.53	4.53%	SC	SC
281.01	432.83	453.65	4.81%	SC	SC
291.01	436.42	458.55	5.07%	SC	SC
301.01	439.86	463.24	5.31%	SC	SC

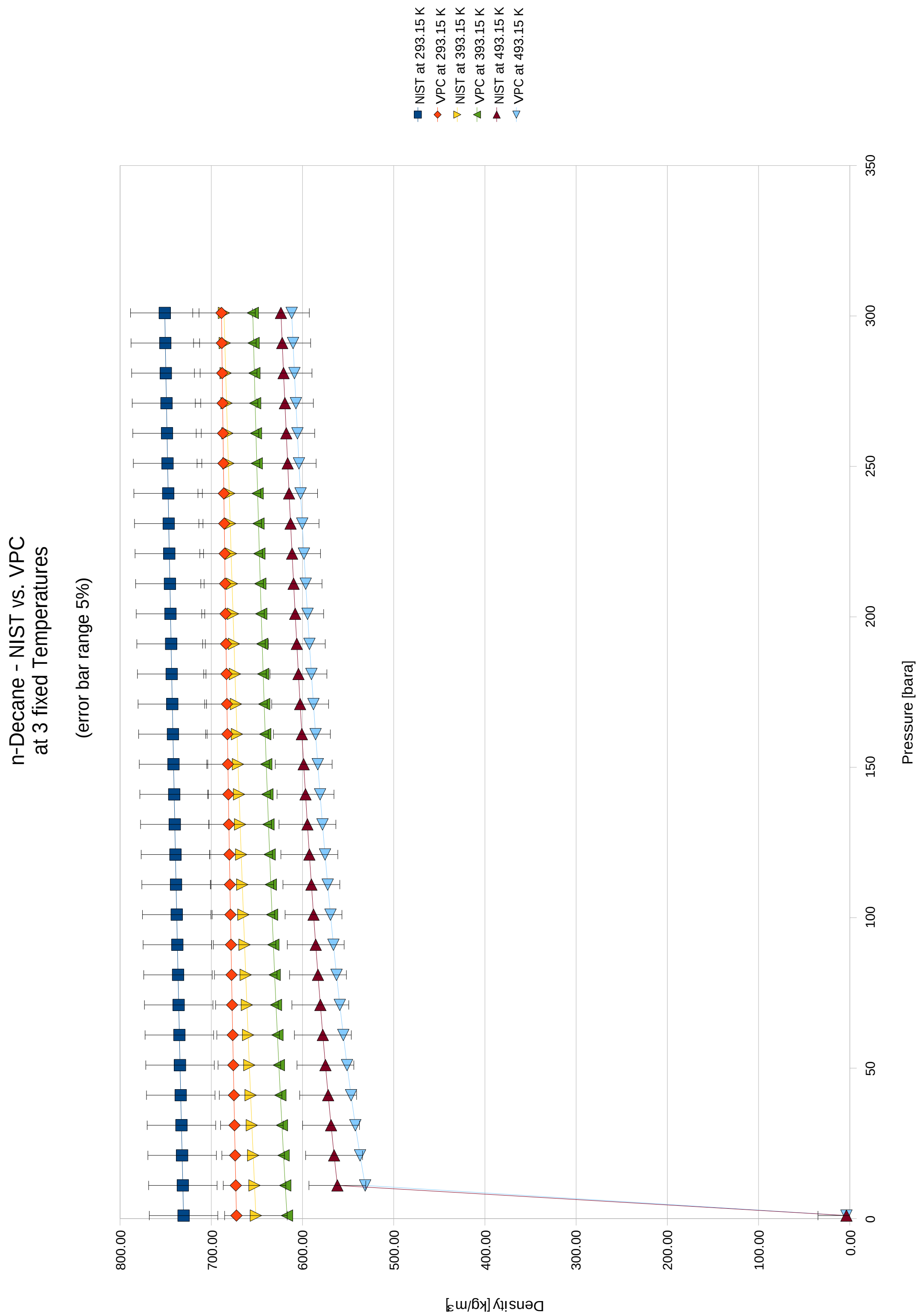


Figure 3.3.: Comparison of n-Decane at Three Fixed Temperatures

Table 3.7.: Comparison of n-Decane at 293.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	730.41	672.37	-7.95%	LIQ	LIQ
11.01	731.19	673.10	-7.94%	LIQ	LIQ
21.01	731.97	673.81	-7.95%	LIQ	LIQ
31.01	732.74	674.50	-7.95%	LIQ	LIQ
41.01	733.50	675.18	-7.95%	LIQ	LIQ
51.01	734.25	675.85	-7.95%	LIQ	LIQ
61.01	735.00	676.50	-7.96%	LIQ	LIQ
71.01	735.73	677.13	-7.96%	LIQ	LIQ
81.01	736.47	677.75	-7.97%	LIQ	LIQ
91.01	737.19	678.36	-7.98%	LIQ	LIQ
101.01	737.91	678.96	-7.99%	LIQ	LIQ
111.01	738.61	679.54	-8.00%	LIQ	LIQ
121.01	739.32	680.12	-8.01%	LIQ	LIQ
131.01	740.01	680.68	-8.02%	LIQ	LIQ
141.01	740.71	681.23	-8.03%	LIQ	LIQ
151.01	741.39	681.77	-8.04%	LIQ	LIQ
161.01	742.07	682.30	-8.05%	LIQ	LIQ
171.01	742.74	682.82	-8.07%	LIQ	LIQ
181.01	743.41	683.33	-8.08%	LIQ	LIQ
191.01	744.07	683.83	-8.10%	LIQ	LIQ
201.01	744.72	684.33	-8.11%	LIQ	LIQ
211.01	745.37	684.81	-8.12%	LIQ	LIQ
221.01	746.02	685.29	-8.14%	LIQ	LIQ
231.01	746.66	685.75	-8.16%	LIQ	LIQ
241.01	747.29	686.21	-8.17%	LIQ	LIQ
251.01	747.92	686.67	-8.19%	LIQ	LIQ
261.01	748.54	687.11	-8.21%	LIQ	LIQ
271.01	749.16	687.55	-8.22%	LIQ	LIQ
281.01	749.78	687.98	-8.24%	LIQ	LIQ
291.01	750.39	688.40	-8.26%	LIQ	LIQ
301.01	750.99	688.82	-8.28%	LIQ	LIQ

Table 3.8.: Comparison of n-Decane at 393.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	651.10	616.98	-5.24%	LIQ	LIQ
11.01	652.60	618.91	-5.16%	LIQ	LIQ
21.01	654.07	620.76	-5.09%	LIQ	LIQ
31.01	655.50	622.54	-5.03%	LIQ	LIQ
41.01	656.91	624.25	-4.97%	LIQ	LIQ
51.01	658.28	625.90	-4.92%	LIQ	LIQ
61.01	659.63	627.49	-4.87%	LIQ	LIQ
71.01	660.95	629.03	-4.83%	LIQ	LIQ
81.01	662.25	630.51	-4.79%	LIQ	LIQ
91.01	663.52	631.95	-4.76%	LIQ	LIQ
101.01	664.77	633.34	-4.73%	LIQ	LIQ
111.01	665.99	634.69	-4.70%	LIQ	LIQ
121.01	667.20	636.00	-4.68%	LIQ	LIQ
131.01	668.39	637.27	-4.66%	LIQ	LIQ
141.01	669.55	638.50	-4.64%	LIQ	LIQ
151.01	670.70	639.70	-4.62%	LIQ	LIQ
161.01	671.83	640.87	-4.61%	LIQ	LIQ
171.01	672.94	642.00	-4.60%	LIQ	LIQ
181.01	674.04	643.11	-4.59%	LIQ	LIQ
191.01	675.12	644.18	-4.58%	LIQ	LIQ
201.01	676.18	645.23	-4.58%	LIQ	LIQ
211.01	677.23	646.26	-4.57%	LIQ	LIQ
221.01	678.26	647.25	-4.57%	LIQ	LIQ
231.01	679.29	648.23	-4.57%	LIQ	LIQ
241.01	680.29	649.18	-4.57%	LIQ	LIQ
251.01	681.29	650.11	-4.58%	LIQ	LIQ
261.01	682.27	651.02	-4.58%	LIQ	LIQ
271.01	683.23	651.91	-4.58%	LIQ	LIQ
281.01	684.19	652.78	-4.59%	LIQ	LIQ
291.01	685.14	653.63	-4.60%	LIQ	LIQ
301.01	686.07	654.46	-4.61%	LIQ	LIQ

Table 3.9.: Comparison of n-Decane at 493.15 K

	Density [kg/m^3]			**Phase state**	
Pressure [bara]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
1.01	3.67	3.66	-0.34%	VAP	VAP
11.01	561.77	531.29	-5.43%	LIQ	LIQ
21.01	565.35	536.91	-5.03%	LIQ	LIQ
31.01	568.70	542.05	-4.69%	LIQ	LIQ
41.01	571.87	546.78	-4.39%	LIQ	LIQ
51.01	574.86	551.16	-4.12%	LIQ	LIQ
61.01	577.71	555.26	-3.89%	LIQ	LIQ
71.01	580.43	559.09	-3.68%	LIQ	LIQ
81.01	583.03	562.69	-3.49%	LIQ	LIQ
91.01	585.52	566.09	-3.32%	LIQ	LIQ
101.01	587.92	569.31	-3.17%	LIQ	LIQ
111.01	590.23	572.36	-3.03%	LIQ	LIQ
121.01	592.46	575.27	-2.90%	LIQ	LIQ
131.01	594.61	578.04	-2.79%	LIQ	LIQ
141.01	596.70	580.69	-2.68%	LIQ	LIQ
151.01	598.72	583.22	-2.59%	LIQ	LIQ
161.01	600.69	585.65	-2.50%	LIQ	LIQ
171.01	602.60	587.98	-2.43%	LIQ	LIQ
181.01	604.46	590.22	-2.36%	LIQ	LIQ
191.01	606.27	592.38	-2.29%	LIQ	LIQ
201.01	608.03	594.46	-2.23%	LIQ	LIQ
211.01	609.76	596.46	-2.18%	LIQ	LIQ
221.01	611.44	598.40	-2.13%	LIQ	LIQ
231.01	613.08	600.27	-2.09%	LIQ	LIQ
241.01	614.69	602.09	-2.05%	LIQ	LIQ
251.01	616.26	603.84	-2.01%	LIQ	LIQ
261.01	617.80	605.55	-1.98%	LIQ	LIQ
271.01	619.31	607.20	-1.96%	LIQ	LIQ
281.01	620.79	608.80	-1.93%	LIQ	LIQ
291.01	622.25	610.36	-1.91%	LIQ	LIQ
301.01	623.67	611.87	-1.89%	LIQ	LIQ

3.1.2. Fixed Pressure

3.1.2.1. Methane

For Methane at atmospheric pressure there is almost perfect agreement with the literature as long as it is present in vapor phase (see Figure 3.4 on page 50). There is an indication for decreasing differences with increasing temperature. An mentionable fact is that the prediction of the liquid density is worse than for heavier components an ranges from about 5 % to over 12 %.

Above 530 K at 201 bar VPC cannot calculate reliable results anymore.

3.1.2.2. n-Butane

For the case of atmospheric pressure and vapor phase the VPC prediction matches (Figure 3.5 on page 54). Otherwise a moderate difference up to 6 % is occurring (refer to Table 3.13 on page 55, Table 3.14 on page 56, Table 3.15 on page 57).

3.1.2.3. n-Decane

No general trend can be seen in Figure 3.6 on page 58 and Table 3.16 on page 59, Table 3.17 on page 60 and Table 3.18 on page 61. For the vapor phase a good match can be expected but the VPC density prediction for liquid and supercritical phase state is basically too low by a few percent.

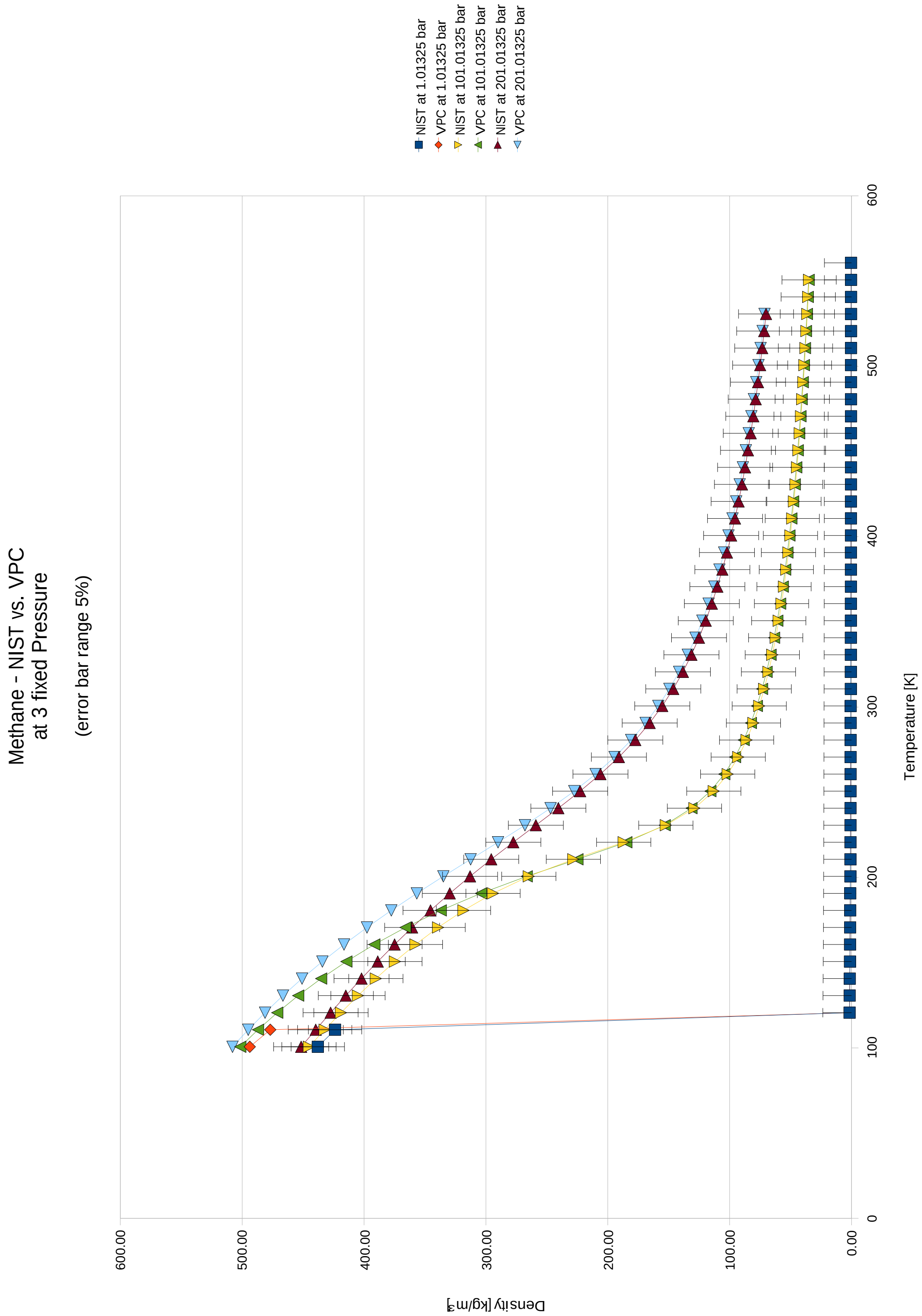


Figure 3.4.: Comparison of Methane at Three Fixed Pressures

Table 3.10.: Comparison of Methane at 1.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
100.69	437.98	493.78	12.74%	LIQ	LIQ
110.69	423.78	476.95	12.55%	LIQ	LIQ
120.69	1.67	1.67	-0.12%	VAP	VAP
130.69	1.53	1.53	0.00%	VAP	VAP
140.69	1.42	1.42	0.05%	VAP	VAP
150.69	1.32	1.32	0.08%	VAP	VAP
160.69	1.23	1.23	0.10%	VAP	VAP
170.69	1.16	1.16	0.10%	VAP	VAP
180.69	1.09	1.09	0.10%	VAP	VAP
190.69	1.03	1.03	0.10%	VAP	VAP
200.69	0.98	0.98	0.09%	VAP	VAP
210.69	0.93	0.93	0.09%	VAP	VAP
220.69	0.89	0.89	0.08%	VAP	VAP
230.69	0.85	0.85	0.08%	VAP	VAP
240.69	0.82	0.82	0.07%	VAP	VAP
250.69	0.78	0.78	0.07%	VAP	VAP
260.69	0.75	0.75	0.06%	VAP	VAP
270.69	0.72	0.72	0.06%	VAP	VAP
280.69	0.70	0.70	0.05%	VAP	VAP
290.69	0.67	0.67	0.05%	VAP	VAP
300.69	0.65	0.65	0.05%	VAP	VAP
310.69	0.63	0.63	0.04%	VAP	VAP
320.69	0.61	0.61	0.04%	VAP	VAP
330.69	0.59	0.59	0.04%	VAP	VAP
340.69	0.57	0.57	0.03%	VAP	VAP
350.69	0.56	0.56	0.03%	VAP	VAP
360.69	0.54	0.54	0.03%	VAP	VAP
370.69	0.53	0.53	0.03%	VAP	VAP
380.69	0.51	0.51	0.03%	VAP	VAP
390.69	0.50	0.50	0.02%	VAP	VAP
400.69	0.49	0.49	0.02%	VAP	VAP
410.69	0.48	0.48	0.02%	VAP	VAP
420.69	0.46	0.46	0.02%	VAP	VAP
430.69	0.45	0.45	0.02%	VAP	VAP
440.69	0.44	0.44	0.02%	VAP	VAP
450.69	0.43	0.43	0.02%	VAP	VAP
460.69	0.42	0.42	0.01%	VAP	VAP
470.69	0.42	0.42	0.02%	VAP	VAP
480.69	0.41	0.41	0.01%	VAP	VAP
490.69	0.40	0.40	0.01%	VAP	VAP
500.69	0.39	0.39	0.01%	VAP	VAP
510.69	0.38	0.38	0.01%	VAP	VAP
520.69	0.38	0.38	0.01%	VAP	VAP
530.69	0.37	0.37	0.01%	VAP	VAP
540.69	0.36	0.36	0.01%	VAP	VAP
550.69	0.35	0.36	0.01%	VAP	VAP
560.69	0.35	0.35	0.01%	VAP	VAP

Table 3.11.: Comparison of Methane at 101.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
100.69	445.20	501.57	12.66%	LIQ	LIQ
110.69	432.30	487.03	12.66%	LIQ	LIQ
120.69	418.94	471.24	12.48%	LIQ	LIQ
130.69	404.99	454.04	12.11%	LIQ	LIQ
140.69	390.31	435.23	11.51%	LIQ	LIQ
150.69	374.67	414.53	10.64%	LIQ	LIQ
160.69	357.79	391.60	9.45%	LIQ	LIQ
170.69	339.25	365.98	7.88%	LIQ	LIQ
180.69	318.39	337.07	5.87%	LIQ	VAP
190.69	294.16	304.13	3.39%	SC	SC
200.69	264.82	266.49	0.63%	SC	SC
210.69	228.25	224.95	-1.45%	SC	SC
220.69	186.96	184.79	-1.16%	SC	SC
230.69	152.37	153.31	0.62%	SC	SC
240.69	128.87	131.33	1.91%	SC	SC
250.69	113.01	115.85	2.51%	SC	SC
260.69	101.62	104.41	2.75%	SC	SC
270.69	92.96	95.57	2.80%	SC	SC
280.69	86.09	88.47	2.77%	SC	SC
290.69	80.46	82.62	2.68%	SC	SC
300.69	75.72	77.68	2.58%	SC	SC
310.69	71.66	73.43	2.47%	SC	SC
320.69	68.12	69.74	2.37%	SC	SC
330.69	65.00	66.47	2.26%	SC	SC
340.69	62.22	63.57	2.16%	SC	SC
350.69	59.72	60.95	2.06%	SC	SC
360.69	57.46	58.59	1.97%	SC	SC
370.69	55.39	56.44	1.88%	SC	SC
380.69	53.50	54.46	1.80%	SC	SC
390.69	51.75	52.65	1.73%	SC	SC
400.69	50.14	50.97	1.66%	SC	SC
410.69	48.64	49.41	1.59%	SC	SC
420.69	47.24	47.96	1.53%	SC	SC
430.69	45.93	46.60	1.47%	SC	SC
440.69	44.70	45.33	1.42%	SC	SC
450.69	43.54	44.14	1.37%	SC	SC
460.69	42.45	43.01	1.32%	SC	SC
470.69	41.42	41.95	1.28%	SC	SC
480.69	40.45	40.95	1.24%	SC	SC
490.69	39.52	40.00	1.20%	SC	SC
500.69	38.64	39.09	1.17%	SC	SC
510.69	37.81	38.24	1.13%	SC	SC
520.69	37.01	37.42	1.10%	SC	SC
530.69	36.25	36.64	1.07%	SC	SC
540.69	35.52	35.89	1.04%	SC	SC
550.69	34.83	35.18	1.02%	SC	SC

Table 3.12.: Comparison of Methane at 201.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
100.69	451.61	507.96	12.48%	LIQ	LIQ
110.69	439.66	495.05	12.60%	LIQ	LIQ
120.69	427.47	481.27	12.58%	LIQ	LIQ
130.69	414.96	466.57	12.44%	LIQ	LIQ
140.69	402.08	450.90	12.14%	LIQ	LIQ
150.69	388.77	434.21	11.69%	LIQ	LIQ
160.69	374.96	416.45	11.06%	LIQ	LIQ
170.69	360.55	397.60	10.27%	LIQ	LIQ
180.69	345.47	377.66	9.32%	LIQ	LIQ
190.69	329.65	356.72	8.21%	SC	SC
200.69	313.03	334.92	6.99%	SC	SC
210.69	295.63	312.56	5.73%	SC	SC
220.69	277.53	290.06	4.51%	SC	SC
230.69	259.03	268.00	3.46%	SC	SC
240.69	240.55	246.97	2.67%	SC	SC
250.69	222.70	227.52	2.17%	SC	SC
260.69	206.02	209.98	1.92%	SC	SC
270.69	190.88	194.44	1.86%	SC	SC
280.69	177.43	180.82	1.91%	SC	SC
290.69	165.62	168.94	2.00%	SC	SC
300.69	155.31	158.56	2.09%	SC	SC
310.69	146.28	149.47	2.18%	SC	SC
320.69	138.36	141.46	2.24%	SC	SC
330.69	131.37	134.37	2.28%	SC	SC
340.69	125.16	128.05	2.31%	SC	SC
350.69	119.61	122.38	2.31%	SC	SC
360.69	114.62	117.26	2.31%	SC	SC
370.69	110.10	112.63	2.29%	SC	SC
380.69	105.99	108.40	2.27%	SC	SC
390.69	102.23	104.52	2.24%	SC	SC
400.69	98.78	100.96	2.21%	SC	SC
410.69	95.60	97.67	2.18%	SC	SC
420.69	92.65	94.63	2.14%	SC	SC
430.69	89.90	91.79	2.10%	SC	SC
440.69	87.35	89.15	2.07%	SC	SC
450.69	84.96	86.68	2.03%	SC	SC
460.69	82.71	84.36	1.99%	SC	SC
470.69	80.60	82.18	1.96%	SC	SC
480.69	78.62	80.13	1.92%	SC	SC
490.69	76.74	78.19	1.89%	SC	SC
500.69	74.96	76.36	1.86%	SC	SC
510.69	73.28	74.62	1.83%	SC	SC
520.69	71.68	72.97	1.79%	SC	SC
530.69	70.16	71.40	1.77%	SC	SC

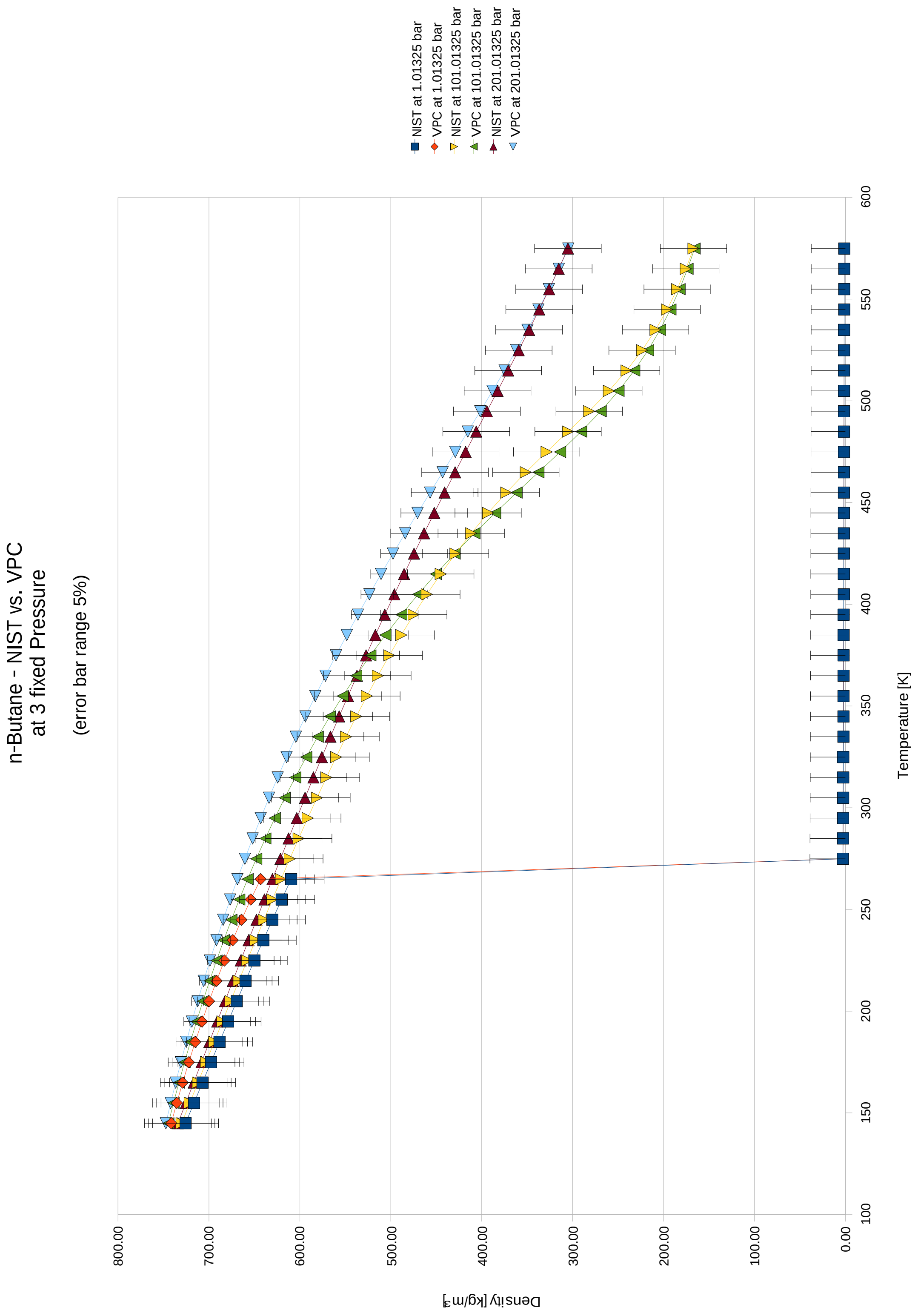


Figure 3.5.: Comparison of n-Butane at Three Fixed Pressures

Table 3.13.: Comparison of n-Butane at 1.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
144.89	725.68	741.45	2.17%	LIQ	LIQ
154.89	716.37	735.32	2.64%	LIQ	LIQ
164.89	707.05	728.88	3.09%	LIQ	LIQ
174.89	697.72	722.13	3.50%	LIQ	LIQ
184.89	688.34	715.05	3.88%	LIQ	LIQ
194.89	678.90	707.61	4.23%	LIQ	LIQ
204.89	669.40	699.79	4.54%	LIQ	LIQ
214.89	659.79	691.56	4.82%	LIQ	LIQ
224.89	650.08	682.90	5.05%	LIQ	LIQ
234.89	640.22	673.77	5.24%	LIQ	LIQ
244.89	630.21	664.13	5.38%	LIQ	LIQ
254.89	619.99	653.93	5.47%	LIQ	LIQ
264.89	609.55	643.12	5.51%	LIQ	LIQ
274.89	2.68	2.67	-0.51%	VAP	VAP
284.89	2.58	2.57	-0.35%	VAP	VAP
294.89	2.48	2.47	-0.23%	VAP	VAP
304.89	2.39	2.39	-0.14%	VAP	VAP
314.89	2.31	2.31	-0.07%	VAP	VAP
324.89	2.23	2.23	-0.02%	VAP	VAP
334.89	2.16	2.16	0.02%	VAP	VAP
344.89	2.09	2.09	0.05%	VAP	VAP
354.89	2.03	2.03	0.07%	VAP	VAP
364.89	1.97	1.97	0.09%	VAP	VAP
374.89	1.92	1.92	0.10%	VAP	VAP
384.89	1.86	1.87	0.10%	VAP	VAP
394.89	1.81	1.82	0.11%	VAP	VAP
404.89	1.77	1.77	0.11%	VAP	VAP
414.89	1.72	1.73	0.11%	VAP	VAP
424.89	1.68	1.68	0.11%	VAP	VAP
434.89	1.64	1.64	0.11%	VAP	VAP
444.89	1.60	1.61	0.11%	VAP	VAP
454.89	1.57	1.57	0.11%	VAP	VAP
464.89	1.53	1.54	0.11%	VAP	VAP
474.89	1.50	1.50	0.11%	VAP	VAP
484.89	1.47	1.47	0.10%	VAP	VAP
494.89	1.44	1.44	0.10%	VAP	VAP
504.89	1.41	1.41	0.10%	VAP	VAP
514.89	1.38	1.38	0.09%	VAP	VAP
524.89	1.36	1.36	0.09%	VAP	VAP
534.89	1.33	1.33	0.08%	VAP	VAP
544.89	1.30	1.31	0.08%	VAP	VAP
554.89	1.28	1.28	0.08%	VAP	VAP
564.89	1.26	1.26	0.08%	VAP	VAP
574.89	1.24	1.24	0.07%	VAP	VAP

Table 3.14.: Comparison of n-Butane at 101.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
144.89	729.99	744.56	2.00%	LIQ	LIQ
154.89	721.01	738.88	2.48%	LIQ	LIQ
164.89	712.04	732.96	2.94%	LIQ	LIQ
174.89	703.08	726.77	3.37%	LIQ	LIQ
184.89	694.11	720.33	3.78%	LIQ	LIQ
194.89	685.13	713.60	4.16%	LIQ	LIQ
204.89	676.11	706.58	4.51%	LIQ	LIQ
214.89	667.05	699.25	4.83%	LIQ	LIQ
224.89	657.93	691.60	5.12%	LIQ	LIQ
234.89	648.75	683.61	5.37%	LIQ	LIQ
244.89	639.48	675.27	5.60%	LIQ	LIQ
254.89	630.11	666.55	5.78%	LIQ	LIQ
264.89	620.63	657.44	5.93%	LIQ	LIQ
274.89	611.00	647.90	6.04%	LIQ	LIQ
284.89	601.23	637.92	6.10%	LIQ	LIQ
294.89	591.27	627.47	6.12%	LIQ	LIQ
304.89	581.11	616.51	6.09%	LIQ	LIQ
314.89	570.73	605.01	6.01%	LIQ	LIQ
324.89	560.08	592.94	5.87%	LIQ	LIQ
334.89	549.14	580.25	5.67%	LIQ	LIQ
344.89	537.86	566.90	5.40%	LIQ	LIQ
354.89	526.21	552.84	5.06%	LIQ	LIQ
364.89	514.13	538.02	4.65%	LIQ	LIQ
374.89	501.57	522.37	4.15%	LIQ	LIQ
384.89	488.47	505.84	3.56%	LIQ	LIQ
394.89	474.73	488.37	2.87%	LIQ	LIQ
404.89	460.28	469.88	2.09%	LIQ	VAP
414.89	445.01	450.32	1.19%	LIQ	VAP
424.89	428.79	429.67	0.21%	LIQ	VAP
434.89	411.48	407.92	-0.86%	SC	SC
444.89	392.91	385.16	-1.97%	SC	SC
454.89	372.91	361.59	-3.03%	SC	SC
464.89	351.40	337.58	-3.93%	SC	SC
474.89	328.54	313.68	-4.52%	SC	SC
484.89	304.96	290.60	-4.71%	SC	SC
494.89	281.75	269.03	-4.51%	SC	SC
504.89	260.06	249.48	-4.07%	SC	SC
514.89	240.59	232.15	-3.51%	SC	SC
524.89	223.54	217.00	-2.93%	SC	SC
534.89	208.77	203.83	-2.37%	SC	SC
544.89	196.02	192.37	-1.86%	SC	SC
554.89	185.00	182.35	-1.43%	SC	SC
564.89	175.41	173.55	-1.06%	SC	SC
574.89	167.00	165.75	-0.75%	SC	SC

Table 3.15.: Comparison of n-Butane at 201.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
144.89	734.09	747.33	1.80%	LIQ	LIQ
154.89	725.39	742.04	2.29%	LIQ	LIQ
164.89	716.73	736.54	2.76%	LIQ	LIQ
174.89	708.10	730.83	3.21%	LIQ	LIQ
184.89	699.49	724.89	3.63%	LIQ	LIQ
194.89	690.88	718.74	4.03%	LIQ	LIQ
204.89	682.27	712.35	4.41%	LIQ	LIQ
214.89	673.66	705.71	4.76%	LIQ	LIQ
224.89	665.02	698.83	5.08%	LIQ	LIQ
234.89	656.37	691.70	5.38%	LIQ	LIQ
244.89	647.67	684.29	5.65%	LIQ	LIQ
254.89	638.94	676.62	5.90%	LIQ	LIQ
264.89	630.15	668.66	6.11%	LIQ	LIQ
274.89	621.30	660.42	6.30%	LIQ	LIQ
284.89	612.38	651.87	6.45%	LIQ	LIQ
294.89	603.37	643.02	6.57%	LIQ	LIQ
304.89	594.27	633.84	6.66%	LIQ	LIQ
314.89	585.07	624.35	6.71%	LIQ	LIQ
324.89	575.76	614.52	6.73%	LIQ	LIQ
334.89	566.32	604.35	6.72%	LIQ	LIQ
344.89	556.75	593.84	6.66%	LIQ	LIQ
354.89	547.03	582.98	6.57%	LIQ	LIQ
364.89	537.17	571.77	6.44%	LIQ	LIQ
374.89	527.14	560.21	6.27%	LIQ	LIQ
384.89	516.94	548.30	6.07%	LIQ	LIQ
394.89	506.58	536.06	5.82%	LIQ	LIQ
404.89	496.03	523.50	5.54%	LIQ	LIQ
414.89	485.31	510.63	5.22%	LIQ	LIQ
424.89	474.42	497.48	4.86%	LIQ	LIQ
434.89	463.35	484.08	4.47%	SC	SC
444.89	452.13	470.49	4.06%	SC	SC
454.89	440.75	456.74	3.63%	SC	SC
464.89	429.25	442.90	3.18%	SC	SC
474.89	417.64	429.04	2.73%	SC	SC
484.89	405.96	415.22	2.28%	SC	SC
494.89	394.23	401.54	1.85%	SC	SC
504.89	382.50	388.05	1.45%	SC	SC
514.89	370.83	374.85	1.08%	SC	SC
524.89	359.26	362.00	0.76%	SC	SC
534.89	347.86	349.56	0.49%	SC	SC
544.89	336.69	337.58	0.26%	SC	SC
554.89	325.82	326.11	0.09%	SC	SC
564.89	315.28	315.16	-0.04%	SC	SC
574.89	305.14	304.75	-0.13%	SC	SC

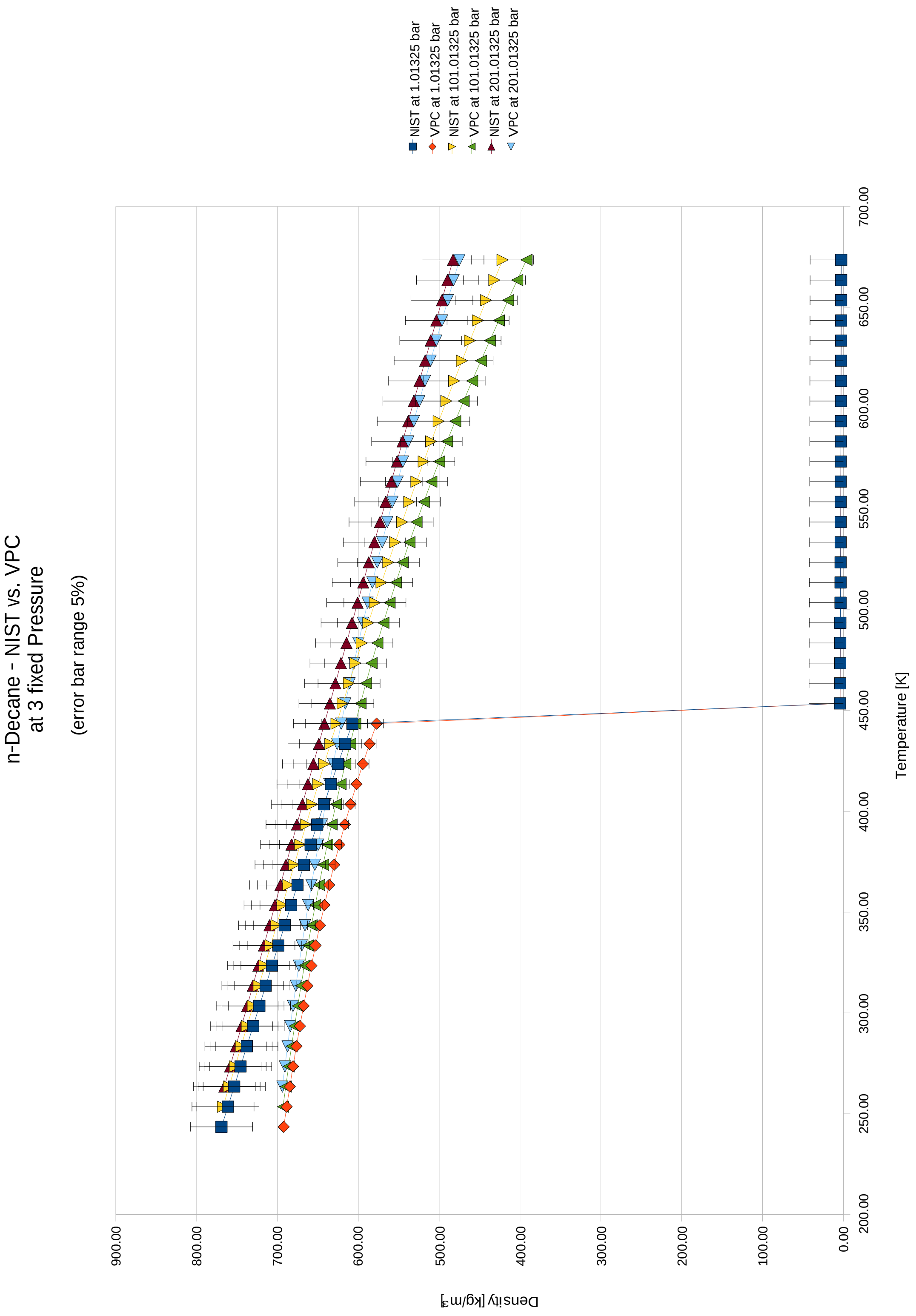


Figure 3.6.: Comparison of n-Decane at Three Fixed Pressures

Table 3.16.: Comparison of n-Decane at 1.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
243.50	769.29	692.34	-10.00%	LIQ	LIQ
253.50	761.38	688.63	-9.55%	LIQ	LIQ
263.50	753.52	684.77	-9.12%	LIQ	LIQ
273.50	745.70	680.76	-8.71%	LIQ	LIQ
283.50	737.91	676.57	-8.31%	LIQ	LIQ
293.50	730.14	672.22	-7.93%	LIQ	LIQ
303.50	722.37	667.68	-7.57%	LIQ	LIQ
313.50	714.60	662.95	-7.23%	LIQ	LIQ
323.50	706.80	658.02	-6.90%	LIQ	LIQ
333.50	698.98	652.88	-6.60%	LIQ	LIQ
343.50	691.12	647.51	-6.31%	LIQ	LIQ
353.50	683.21	641.90	-6.05%	LIQ	LIQ
363.50	675.24	636.04	-5.81%	LIQ	LIQ
373.50	667.19	629.90	-5.59%	LIQ	LIQ
383.50	659.05	623.47	-5.40%	LIQ	LIQ
393.50	650.81	616.74	-5.24%	LIQ	LIQ
403.50	642.44	609.66	-5.10%	LIQ	LIQ
413.50	633.94	602.23	-5.00%	LIQ	LIQ
423.50	625.27	594.40	-4.94%	LIQ	LIQ
433.50	616.43	586.15	-4.91%	LIQ	LIQ
443.50	607.37	577.42	-4.93%	LIQ	LIQ
453.50	4.07	4.03	-0.94%	VAP	VAP
463.50	3.96	3.93	-0.74%	VAP	VAP
473.50	3.86	3.83	-0.58%	VAP	VAP
483.50	3.76	3.74	-0.45%	VAP	VAP
493.50	3.67	3.66	-0.34%	VAP	VAP
503.50	3.58	3.58	-0.25%	VAP	VAP
513.50	3.50	3.50	-0.17%	VAP	VAP
523.50	3.43	3.42	-0.11%	VAP	VAP
533.50	3.35	3.35	-0.06%	VAP	VAP
543.50	3.28	3.28	-0.02%	VAP	VAP
553.50	3.22	3.22	0.01%	VAP	VAP
563.50	3.16	3.16	0.04%	VAP	VAP
573.50	3.10	3.10	0.06%	VAP	VAP
583.50	3.04	3.04	0.08%	VAP	VAP
593.50	2.98	2.98	0.09%	VAP	VAP
603.50	2.93	2.93	0.10%	VAP	VAP
613.50	2.88	2.88	0.11%	VAP	VAP
623.50	2.83	2.83	0.11%	VAP	VAP
633.50	2.78	2.78	0.11%	VAP	VAP
643.50	2.73	2.74	0.12%	VAP	VAP
653.50	2.69	2.69	0.11%	VAP	VAP
663.50	2.65	2.65	0.11%	VAP	VAP
673.50	2.61	2.61	0.11%	VAP	VAP

Table 3.17.: Comparison of n-Decane at 101.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
253.50	767.41	693.18	-9.67%	LIQ	LIQ
263.50	759.88	689.77	-9.23%	LIQ	LIQ
273.50	752.42	686.24	-8.80%	LIQ	LIQ
283.50	745.01	682.60	-8.38%	LIQ	LIQ
293.50	737.65	678.82	-7.97%	LIQ	LIQ
303.50	730.31	674.92	-7.58%	LIQ	LIQ
313.50	723.00	670.88	-7.21%	LIQ	LIQ
323.50	715.71	666.70	-6.85%	LIQ	LIQ
333.50	708.42	662.38	-6.50%	LIQ	LIQ
343.50	701.14	657.91	-6.16%	LIQ	LIQ
353.50	693.85	653.29	-5.85%	LIQ	LIQ
363.50	686.55	648.51	-5.54%	LIQ	LIQ
373.50	679.23	643.56	-5.25%	LIQ	LIQ
383.50	671.89	638.44	-4.98%	LIQ	LIQ
393.50	664.51	633.15	-4.72%	LIQ	LIQ
403.50	657.10	627.67	-4.48%	LIQ	LIQ
413.50	649.64	622.01	-4.25%	LIQ	LIQ
423.50	642.13	616.15	-4.05%	LIQ	LIQ
433.50	634.57	610.08	-3.86%	LIQ	LIQ
443.50	626.94	603.81	-3.69%	LIQ	LIQ
453.50	619.24	597.32	-3.54%	LIQ	LIQ
463.50	611.47	590.60	-3.41%	LIQ	LIQ
473.50	603.62	583.66	-3.31%	LIQ	LIQ
483.50	595.67	576.47	-3.22%	LIQ	LIQ
493.50	587.63	569.05	-3.16%	LIQ	LIQ
503.50	579.49	561.36	-3.13%	LIQ	LIQ
513.50	571.24	553.42	-3.12%	LIQ	LIQ
523.50	562.87	545.22	-3.14%	LIQ	LIQ
533.50	554.37	536.75	-3.18%	LIQ	LIQ
543.50	545.75	528.00	-3.25%	LIQ	LIQ
553.50	536.99	518.98	-3.35%	LIQ	LIQ
563.50	528.09	509.68	-3.49%	LIQ	LIQ
573.50	519.04	500.10	-3.65%	LIQ	LIQ
583.50	509.86	490.25	-3.85%	LIQ	LIQ
593.50	500.52	480.14	-4.07%	LIQ	LIQ
603.50	491.05	469.77	-4.33%	LIQ	LIQ
613.50	481.43	459.16	-4.63%	LIQ	LIQ
623.50	471.69	448.33	-4.95%	SC	SC
633.50	461.83	437.31	-5.31%	SC	SC
643.50	451.87	426.13	-5.70%	SC	SC
653.50	441.82	414.82	-6.11%	SC	SC
663.50	431.70	403.43	-6.55%	SC	SC
673.50	421.54	392.01	-7.00%	SC	SC

Table 3.18.: Comparison of n-Decane at 201.013 25 bar

	Density [kg/m^3]			**Phase**	
Temperature [K]	**NIST**	**VPC**	**Difference (base is NIST) [%]**	**NIST**	**VPC**
263.50	765.76	693.94	-9.38%	LIQ	LIQ
273.50	758.60	690.79	-8.94%	LIQ	LIQ
283.50	751.51	687.55	-8.51%	LIQ	LIQ
293.50	744.48	684.21	-8.10%	LIQ	LIQ
303.50	737.50	680.77	-7.69%	LIQ	LIQ
313.50	730.56	677.23	-7.30%	LIQ	LIQ
323.50	723.65	673.59	-6.92%	LIQ	LIQ
333.50	716.78	669.85	-6.55%	LIQ	LIQ
343.50	709.94	666.00	-6.19%	LIQ	LIQ
353.50	703.12	662.04	-5.84%	LIQ	LIQ
363.50	696.31	657.97	-5.51%	LIQ	LIQ
373.50	689.51	653.78	-5.18%	LIQ	LIQ
383.50	682.73	649.49	-4.87%	LIQ	LIQ
393.50	675.94	645.08	-4.57%	LIQ	LIQ
403.50	669.16	640.54	-4.28%	LIQ	LIQ
413.50	662.38	635.89	-4.00%	LIQ	LIQ
423.50	655.59	631.12	-3.73%	LIQ	LIQ
433.50	648.80	626.23	-3.48%	LIQ	LIQ
443.50	642.00	621.21	-3.24%	LIQ	LIQ
453.50	635.19	616.07	-3.01%	LIQ	LIQ
463.50	628.36	610.81	-2.79%	LIQ	LIQ
473.50	621.52	605.42	-2.59%	LIQ	LIQ
483.50	614.66	599.90	-2.40%	LIQ	LIQ
493.50	607.79	594.26	-2.23%	LIQ	LIQ
503.50	600.91	588.49	-2.07%	LIQ	LIQ
513.50	594.00	582.60	-1.92%	LIQ	LIQ
523.50	587.08	576.59	-1.79%	LIQ	LIQ
533.50	580.15	570.46	-1.67%	LIQ	LIQ
543.50	573.20	564.21	-1.57%	LIQ	LIQ
553.50	566.24	557.85	-1.48%	LIQ	LIQ
563.50	559.27	551.39	-1.41%	LIQ	LIQ
573.50	552.29	544.81	-1.35%	LIQ	LIQ
583.50	545.30	538.14	-1.31%	LIQ	LIQ
593.50	538.31	531.38	-1.29%	LIQ	LIQ
603.50	531.33	524.53	-1.28%	LIQ	LIQ
613.50	524.35	517.61	-1.29%	LIQ	LIQ
623.50	517.39	510.62	-1.31%	SC	SC
633.50	510.44	503.56	-1.35%	SC	SC
643.50	503.51	496.46	-1.40%	SC	SC
653.50	496.62	489.33	-1.47%	SC	SC
663.50	489.75	482.16	-1.55%	SC	SC
673.50	482.93	474.98	-1.65%	SC	SC

3.2. Two Component Mixtures

The Z-factor of a mixture with two components is compared against SUREPVT (v5.4). The setup is as follows:

- Methane (90 mol%)
- Ethane (10 mol%)

SUREPVT settings:

- Peng-Robinson (mod.)
- all BIP's where set to 0
- volume shift set to 0

For the presented case VPC and SUREPVT predict identical Z-factors and phase states.

3.2.1. Fixed Temperature

The selected temperatures are 293.15 K, 393.15 K and 493.15 K. For the pressure a range of 1.013 25 bar to 301.013 25 bar was selected. See Figure 3.7 on page 63 to Figure 3.9 on page 67 and Table 3.19 on page 64 to Table 3.21 on page 68.

3.2.2. Fixed Pressure

For the pressure the values 1.013 25 bar, 101.013 25 bar and 201.013 25 bar were selected and the temperature ranges from 200 K to 580 K. See Figure 3.10 on page 69 to Figure 3.12 on page 73 and Table 3.22 on page 70 to Table 3.24 on page 74.

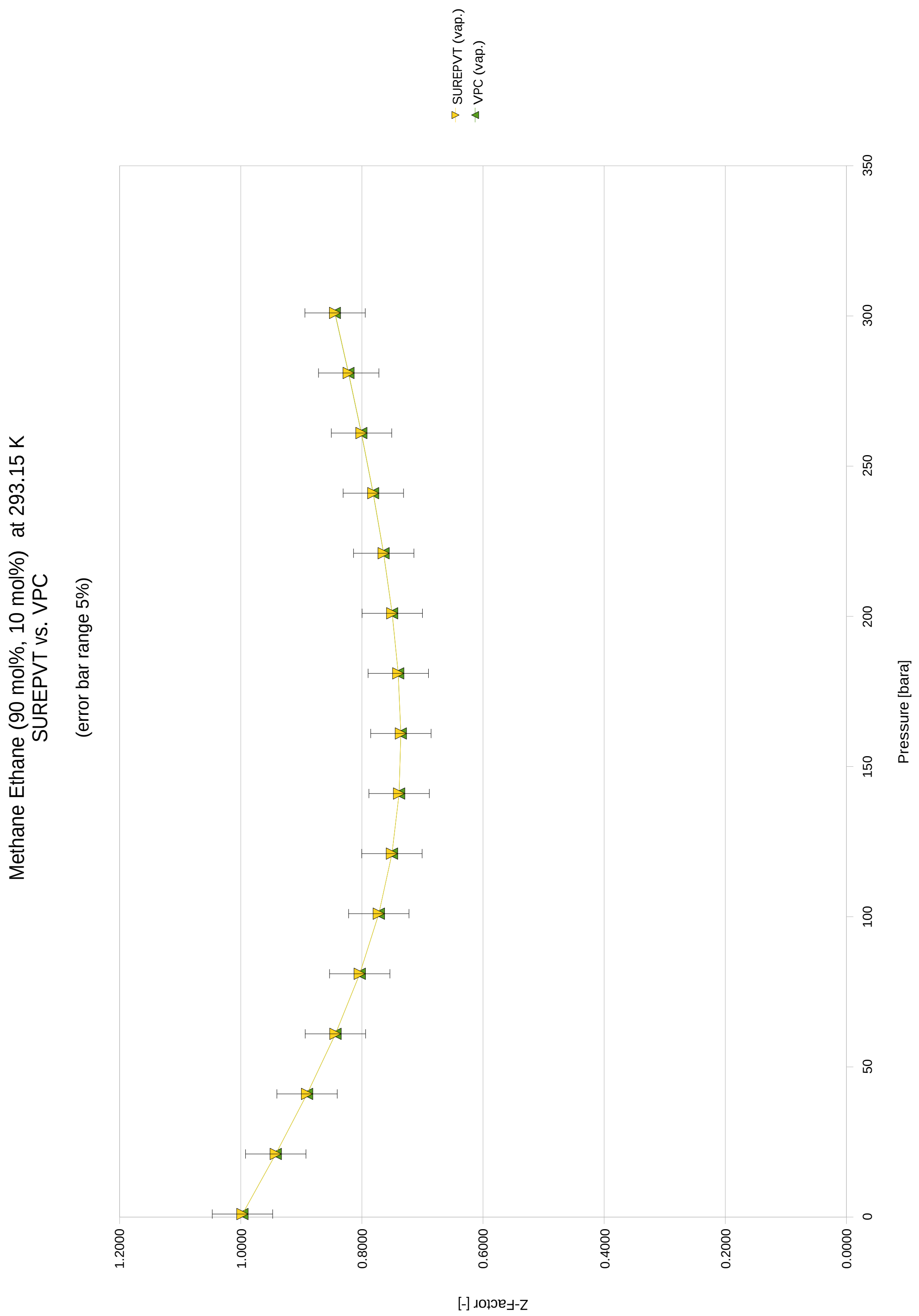


Figure 3.7.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 293.15 K

Table 3.19.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 293.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
1.01				0.9972	0.9971	0.00%
21.01				0.9422	0.9421	-0.01%
41.01				0.8905	0.8904	-0.01%
61.01				0.8437	0.8436	-0.01%
81.01				0.8036	0.8035	-0.01%
101.01				0.7721	0.7720	-0.01%
121.01				0.7504	0.7503	0.00%
141.01				0.7385	0.7386	0.00%
161.01				0.7356	0.7357	0.01%
181.01				0.7399	0.7401	0.02%
201.01				0.7498	0.7501	0.03%
221.01				0.7639	0.7642	0.04%
241.01				0.7811	0.7815	0.05%
261.01				0.8006	0.8010	0.05%
281.01				0.8218	0.8222	0.05%
301.01				0.8442	0.8447	0.06%

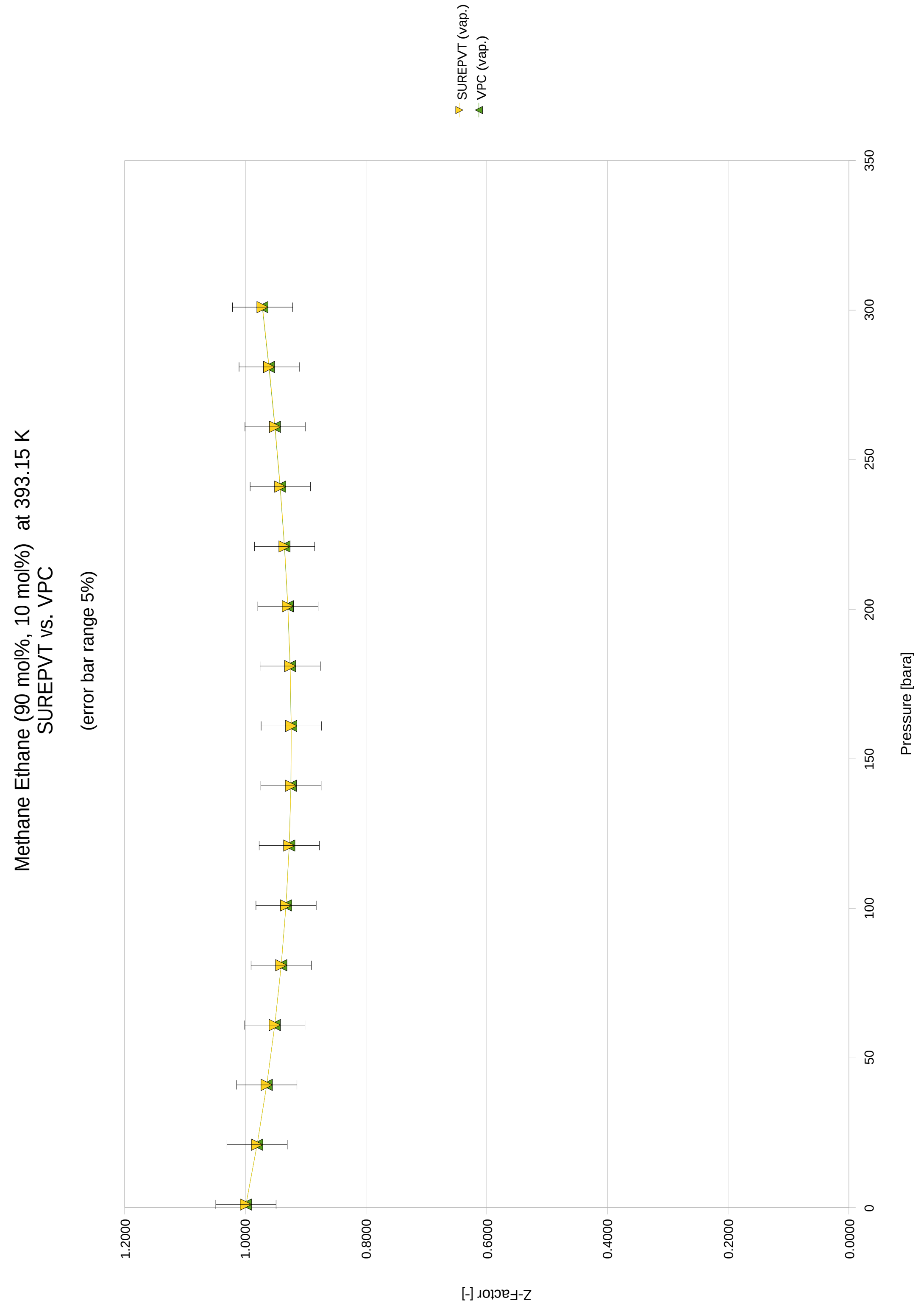


Figure 3.8.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 393.15 K

Table 3.20.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 393.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
1.01				0.9990	0.9990	0.00%
21.01				0.9805	0.9805	0.00%
41.01				0.9645	0.9646	0.00%
61.01				0.9512	0.9512	0.01%
81.01				0.9405	0.9406	0.01%
101.01				0.9325	0.9326	0.01%
121.01				0.9272	0.9273	0.02%
141.01				0.9244	0.9245	0.02%
161.01				0.9239	0.9241	0.02%
181.01				0.9257	0.9259	0.03%
201.01				0.9294	0.9297	0.03%
221.01				0.9350	0.9353	0.04%
241.01				0.9421	0.9425	0.04%
261.01				0.9507	0.9511	0.04%
281.01				0.9605	0.9610	0.05%
301.01				0.9714	0.9719	0.05%

Figure 3.9.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 493.15 K

Table 3.21.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 493.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
1.01				0.9997	0.9997	0.00%
21.01				0.9943	0.9943	0.00%
41.01				0.9902	0.9903	0.01%
61.01				0.9875	0.9876	0.01%
81.01				0.9861	0.9862	0.01%
101.01				0.9859	0.9860	0.02%
121.01				0.9868	0.9870	0.02%
141.01				0.9889	0.9891	0.02%
161.01				0.9919	0.9922	0.02%
181.01				0.9960	0.9962	0.03%
201.01				1.0009	1.0012	0.03%
221.01				1.0066	1.0069	0.03%
241.01				1.0130	1.0134	0.04%
261.01				1.0202	1.0206	0.04%
281.01				1.0280	1.0284	0.04%
301.01				1.0363	1.0368	0.04%

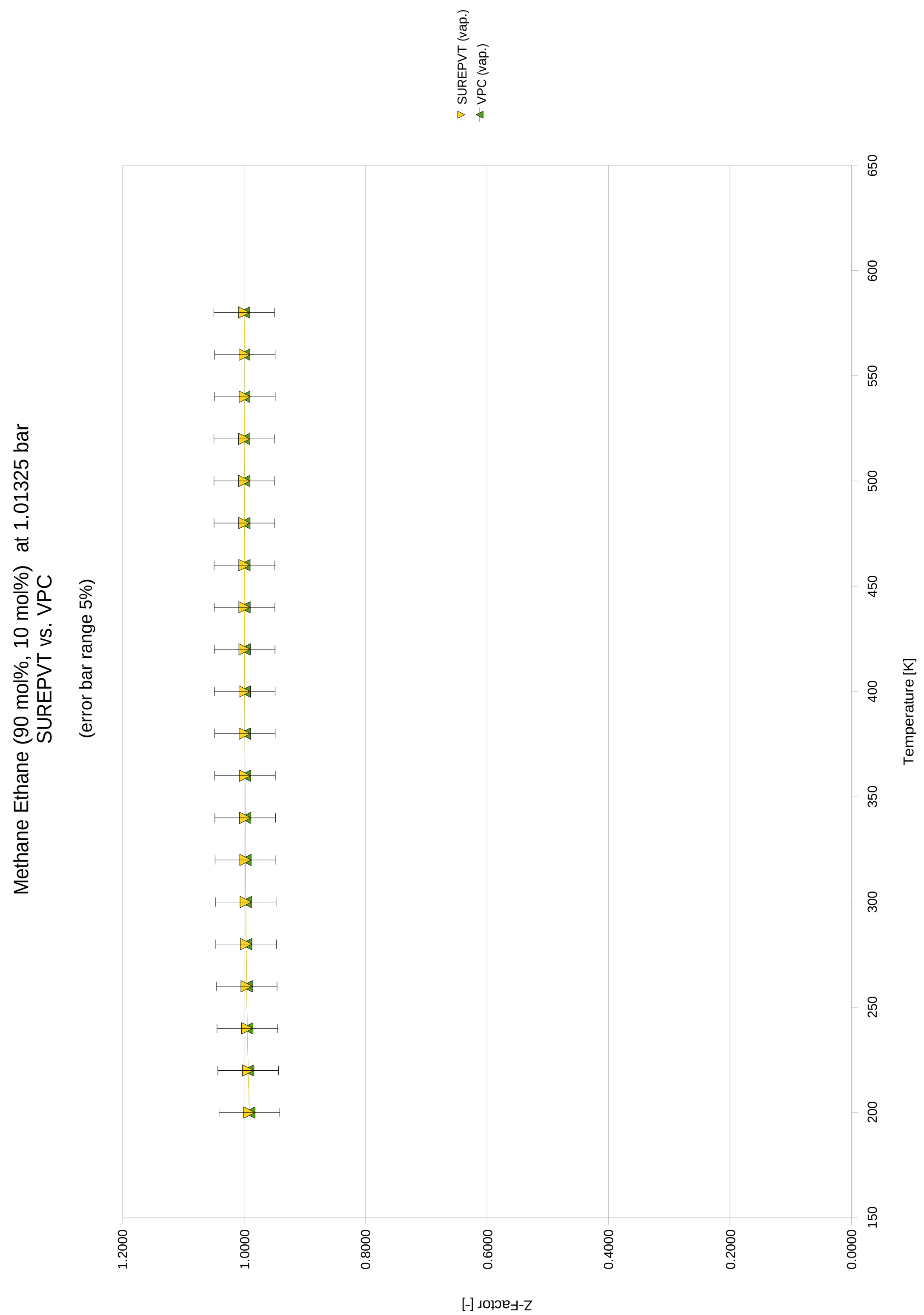


Figure 3.10.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 1.013 25 bar

Table 3.22.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 1.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
200				0.9914	0.9914	0.00%
220				0.9934	0.9933	0.00%
240				0.9948	0.9948	0.00%
260				0.9959	0.9959	0.00%
280				0.9967	0.9967	0.00%
300				0.9974	0.9974	0.00%
320				0.9979	0.9979	0.00%
340				0.9983	0.9983	0.00%
360				0.9986	0.9986	0.00%
380				0.9989	0.9989	0.00%
400				0.9991	0.9991	0.00%
420				0.9993	0.9992	0.00%
440				0.9994	0.9994	0.00%
460				0.9995	0.9995	0.00%
480				0.9996	0.9996	0.00%
500				0.9997	0.9997	0.00%
520				0.9998	0.9998	0.00%
540				0.9988	0.9999	0.10%
560				0.9990	0.9999	0.09%
580				1.0000	1.0000	0.00%

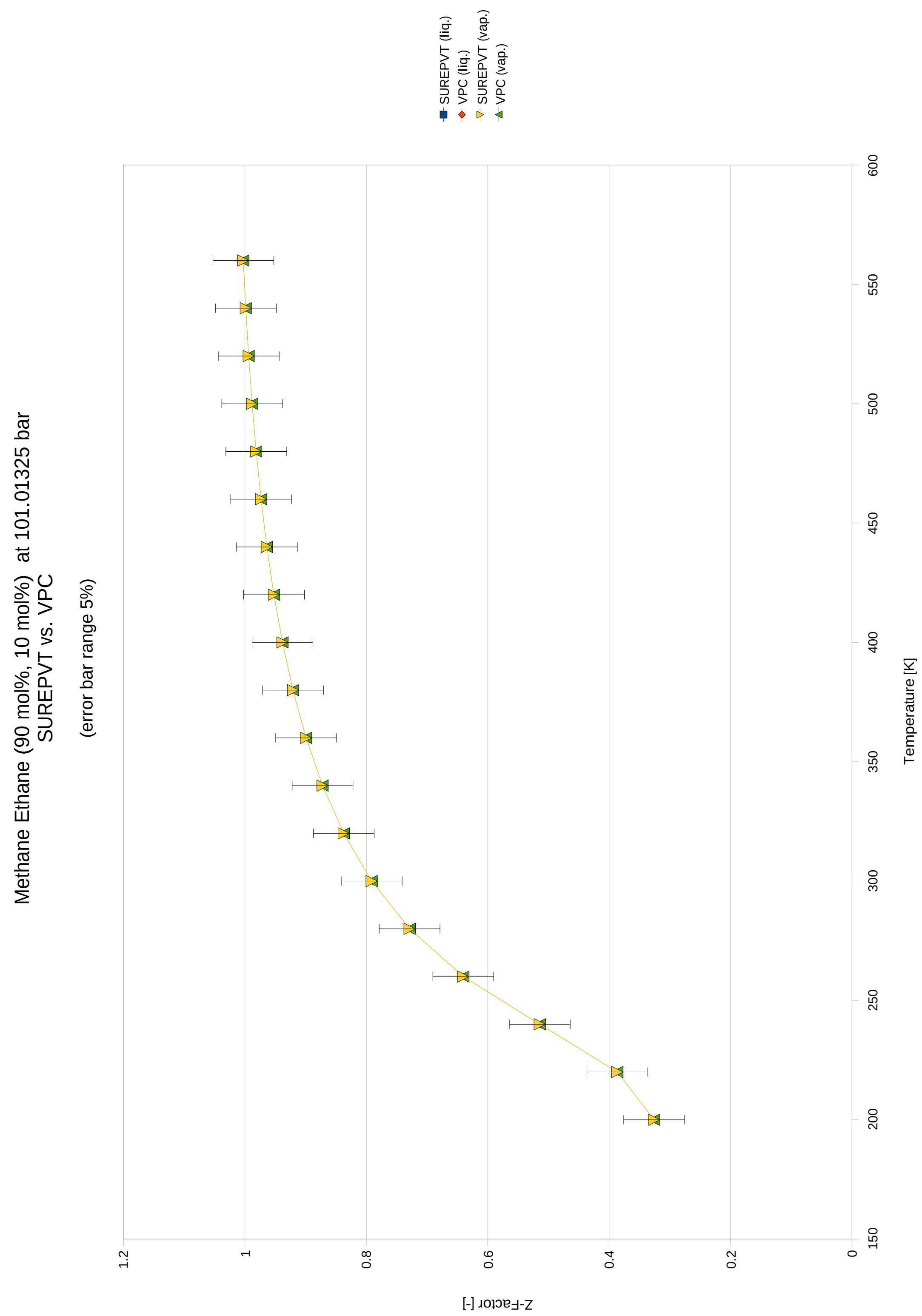


Figure 3.11.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 101.013 25 bar

Table 3.23.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 101.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
200				0.3259	0.3259	0.03%
220				0.3865	0.3864	-0.03%
240				0.5143	0.5139	-0.07%
260				0.6404	0.6401	-0.04%
280				0.7288	0.7286	-0.02%
300				0.7912	0.7912	-0.01%
320				0.8372	0.8372	0.00%
340				0.8721	0.8721	0.01%
360				0.8992	0.8993	0.01%
380				0.9207	0.9208	0.01%
400				0.9381	0.9382	0.01%
420				0.9521	0.9523	0.01%
440				0.9637	0.9639	0.01%
460				0.9733	0.9735	0.01%
480				0.9813	0.9815	0.01%
500				0.9880	0.9882	0.02%
520				0.9937	0.9938	0.01%
540				0.9985	0.9986	0.01%
560				1.0026	1.0027	0.01%

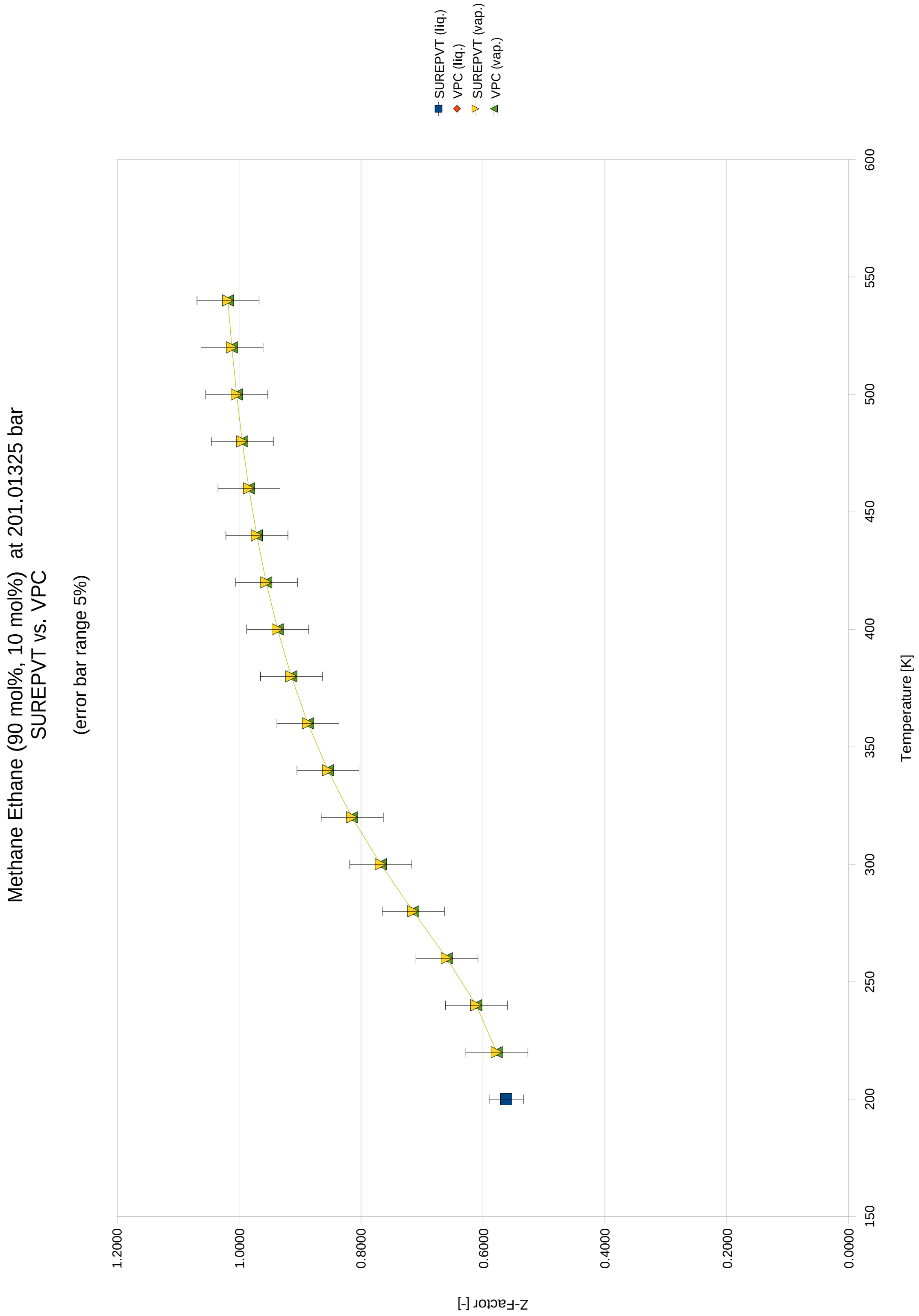


Figure 3.12.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 201.013 25 bar

Table 3.24.: Comparison of Methane - Ethane (90 mol%, 10 mol%) at 201.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
200	0.5617	0.5621	0.06%			
220				0.5772	0.5775	0.05%
240				0.6107	0.6110	0.05%
260				0.6591	0.6594	0.04%
280				0.7142	0.7145	0.03%
300				0.7675	0.7677	0.03%
320				0.8145	0.8147	0.03%
340				0.8541	0.8544	0.03%
360				0.8870	0.8873	0.03%
380				0.9142	0.9145	0.03%
400				0.9366	0.9369	0.03%
420				0.9553	0.9556	0.03%
440				0.9708	0.9711	0.03%
460				0.9838	0.9841	0.03%
480				0.9946	0.9949	0.03%
500				1.0038	1.0041	0.03%
520				1.0116	1.0119	0.03%
540				1.0182	1.0184	0.03%

3.3. Three Component Mixtures

The first mixture contains only hydrocarbons and is compared against SUREPVT (v5.4). The setup is as follows:

Mixture:

- Methane (40 mol%)
- n-Butane (30 mol%)
- n-Decane (30 mol%)

SUREPVT settings:

- Peng-Robinson (mod.)
- all BIP's where set to 0
- volume shift set to 0
- VLE experiment

For the presented case VPC and PVT software tool from Seismic Micro Technology (SUREPVT) predict identical Z-factors and phase states.

The second mixture contains CO_2 as a non-hydrocarbon component and is compared against PVT software tool from Petroleum Experts (PVTP).

- Carbon dioxide (10 mol%)
- Methane (10 mol%)
- n-Decane (80 mol%)

PVTP settings:

- Peng-Robinson
- no volume shift
- CCE experiment

Also for the second mixture VPC predicts Z-factors identical to PVTP. There are only some qualitative differences in the determination of the phase state.

Table 3.25.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 293.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
1.01	0.0079	0.0079	-0.23%	0.9911	0.9911	0.00%
21.01	0.1237	0.1236	-0.14%	0.9352	0.9354	0.02%
41.01	0.2225	0.2222	-0.12%	0.8883	0.8885	0.02%
61.01	0.3075	0.3071	-0.11%	0.8445	0.8447	0.03%
81.01	0.3811	0.3807	-0.11%	0.8049	0.8052	0.04%
101.01	0.4657	0.4654	-0.07%			
121.01	0.5548	0.5544	-0.07%			
141.01	0.6432	0.6427	-0.08%			
161.01	0.7309	0.7303	-0.08%			
181.01	0.8180	0.8173	-0.08%			
201.01	0.9044	0.9037	-0.08%			
221.01	0.9904	0.9896	-0.08%			
241.01	1.0758	1.0749	-0.08%			
261.01	1.1608	1.1599	-0.08%			
281.01	1.2454	1.2443	-0.08%			
301.01	1.3296	1.3284	-0.08%			

3.3.1. Fixed Temperature

The selected temperatures are 293.15 K, 393.15 K and 493.15 K. For the pressure a range of 1.013 25 bar to 301.013 25 bar was selected.

3.3.1.1. Methane - n-Butane - n-Decane

Figure 3.13 on page 77 to Figure 3.15 on page 80 and Table 3.25 on page 76 to Table 3.27 on page 81.

3.3.1.2. Carbon dioxide - Methane - n-Decane

Figure 3.16 on page 82 to Figure 3.18 on page 86 and Table 3.28 on page 83 to Table 3.30 on page 87.

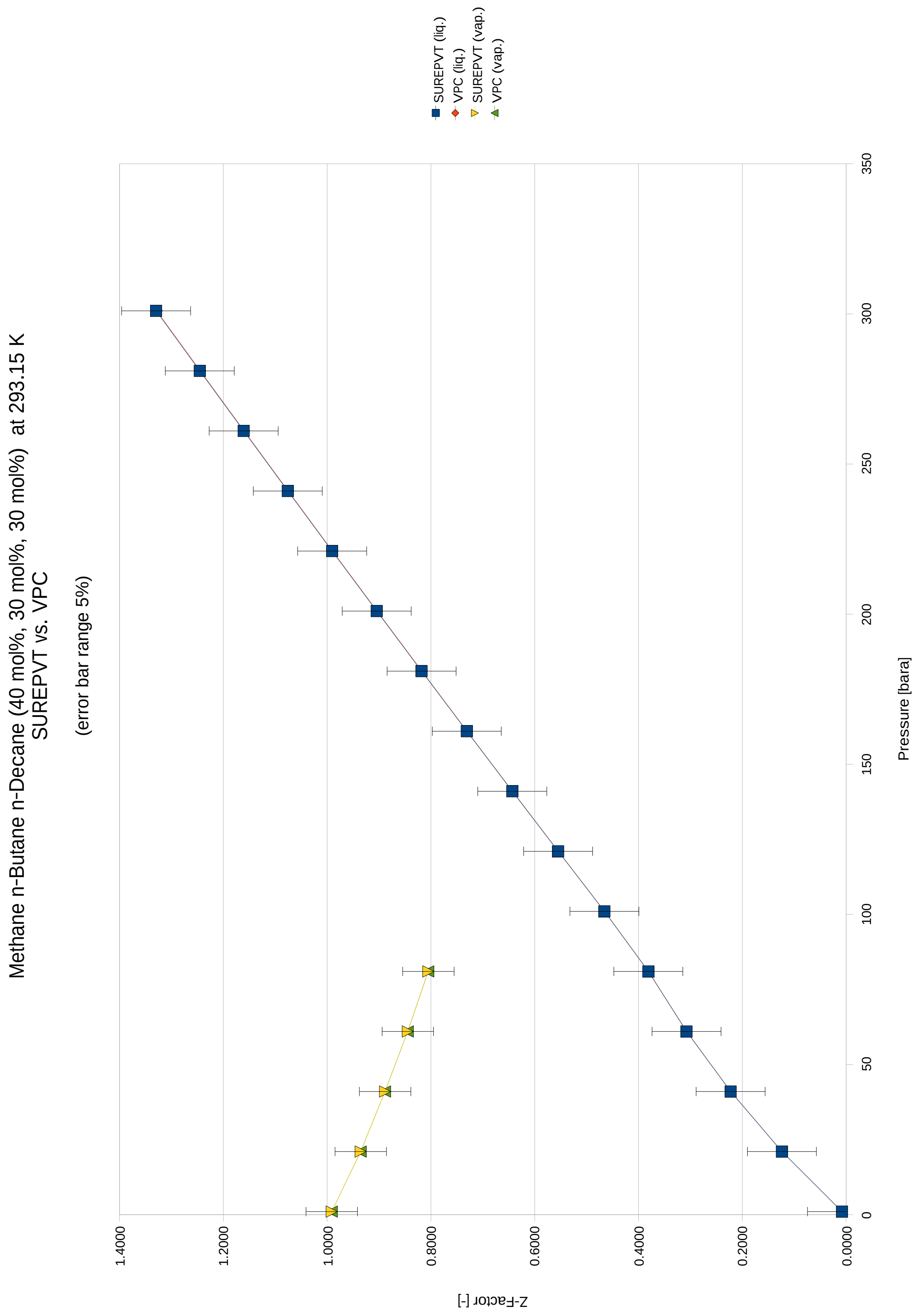


Figure 3.13.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 293.15 K

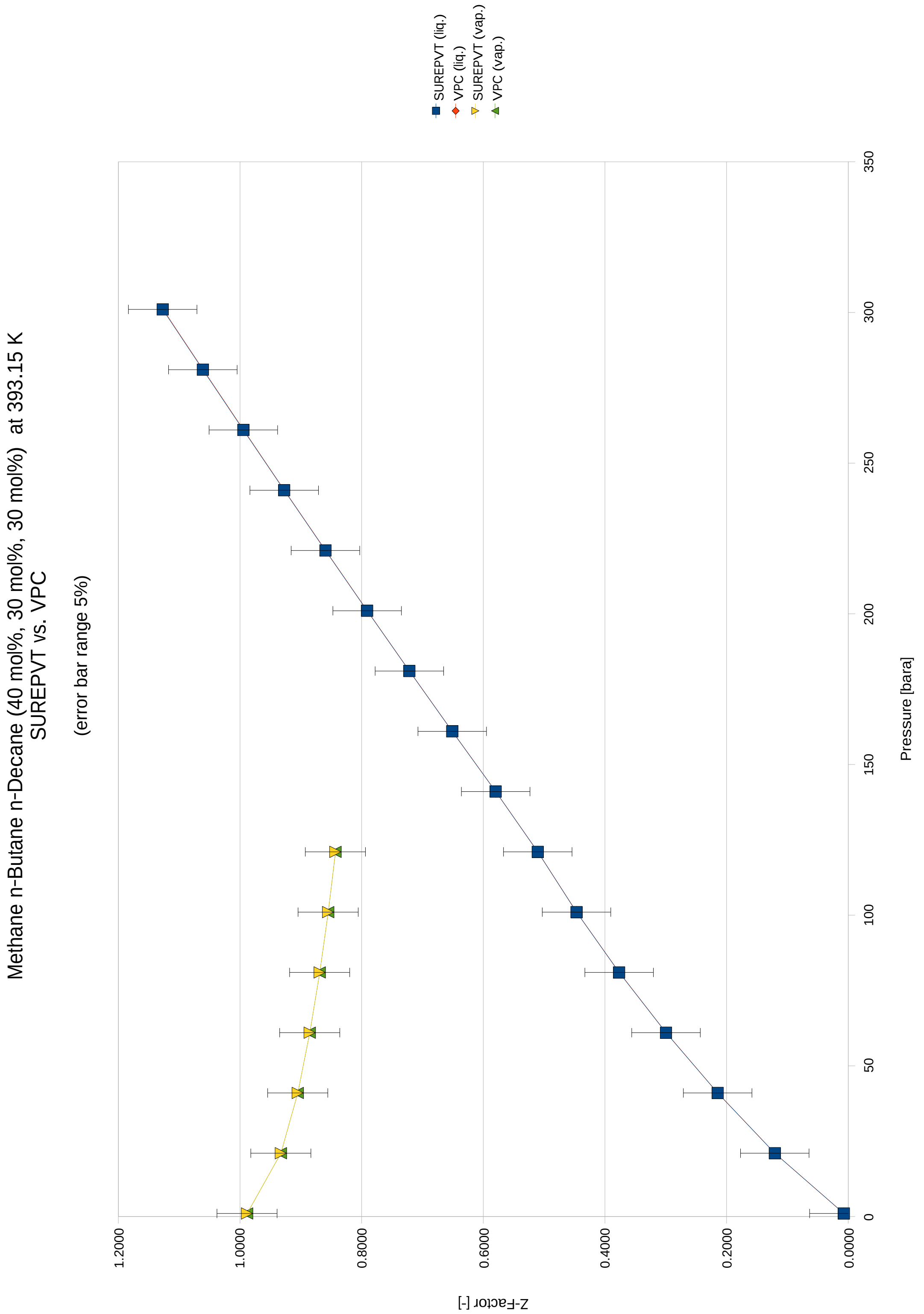


Figure 3.14.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 393.15 K

Table 3.26.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 393.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
1.01	0.0071	0.0071	-0.18%	0.9885	0.9883	-0.02%
21.01	0.1207	0.1206	-0.11%	0.9329	0.9327	-0.01%
41.01	0.2147	0.2145	-0.09%	0.9051	0.9050	-0.01%
61.01	0.2995	0.2993	-0.08%	0.8854	0.8853	-0.01%
81.01	0.3766	0.3764	-0.07%	0.8691	0.8689	-0.02%
101.01	0.4467	0.4464	-0.06%	0.8551	0.8549	-0.02%
121.01	0.5104	0.5102	-0.06%	0.8432	0.8429	-0.03%
141.01	0.5796	0.5794	-0.03%			
161.01	0.6511	0.6509	-0.04%			
181.01	0.7215	0.7212	-0.04%			
201.01	0.7910	0.7906	-0.05%			
221.01	0.8595	0.8591	-0.05%			
241.01	0.9274	0.9269	-0.05%			
261.01	0.9946	0.9940	-0.06%			
281.01	1.0611	1.0605	-0.06%			
301.01	1.1272	1.1265	-0.06%			

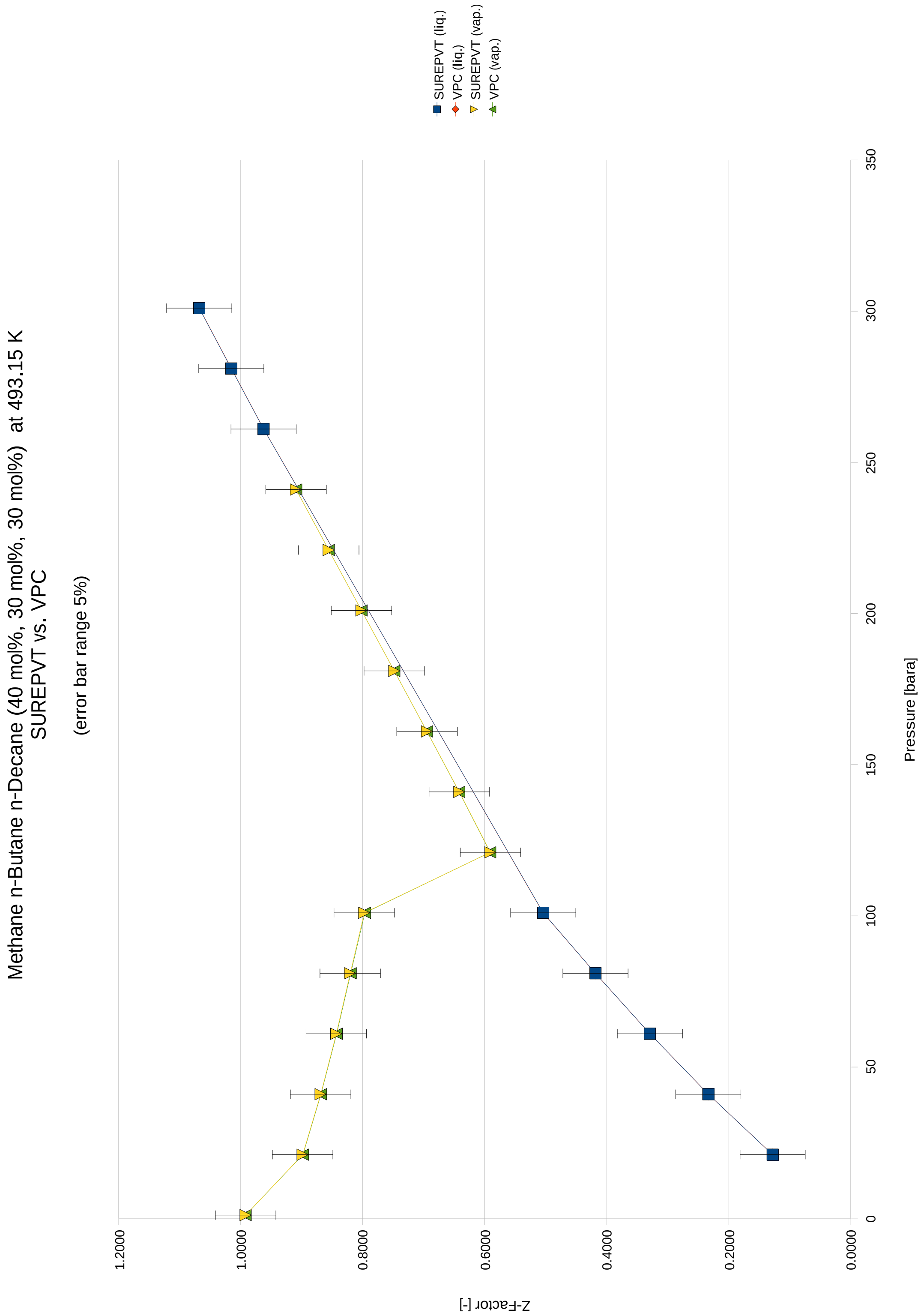


Figure 3.15.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 493.15 K

Table 3.27.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 493.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
1.01				0.9920	0.9920	0.00%
21.01	0.1281	0.1280	-0.05%	0.8986	0.8981	-0.05%
41.01	0.2336	0.2336	-0.02%	0.8690	0.8685	-0.06%
61.01	0.3293	0.3293	0.01%	0.8434	0.8428	-0.07%
81.01	0.4186	0.4187	0.03%	0.8206	0.8198	-0.10%
101.01	0.5042	0.5045	0.07%	0.7975	0.7965	-0.13%
121.01				0.5907	0.5912	0.08%
141.01				0.6417	0.6420	0.05%
161.01				0.6947	0.6948	0.03%
181.01				0.7483	0.7484	0.01%
201.01				0.8021	0.8021	0.00%
221.01				0.8558	0.8557	-0.01%
241.01				0.9093	0.9092	-0.02%
261.01	0.9625	0.9623	-0.02%			
281.01	1.0155	1.0152	-0.03%			
301.01	1.0681	1.0678	-0.03%			

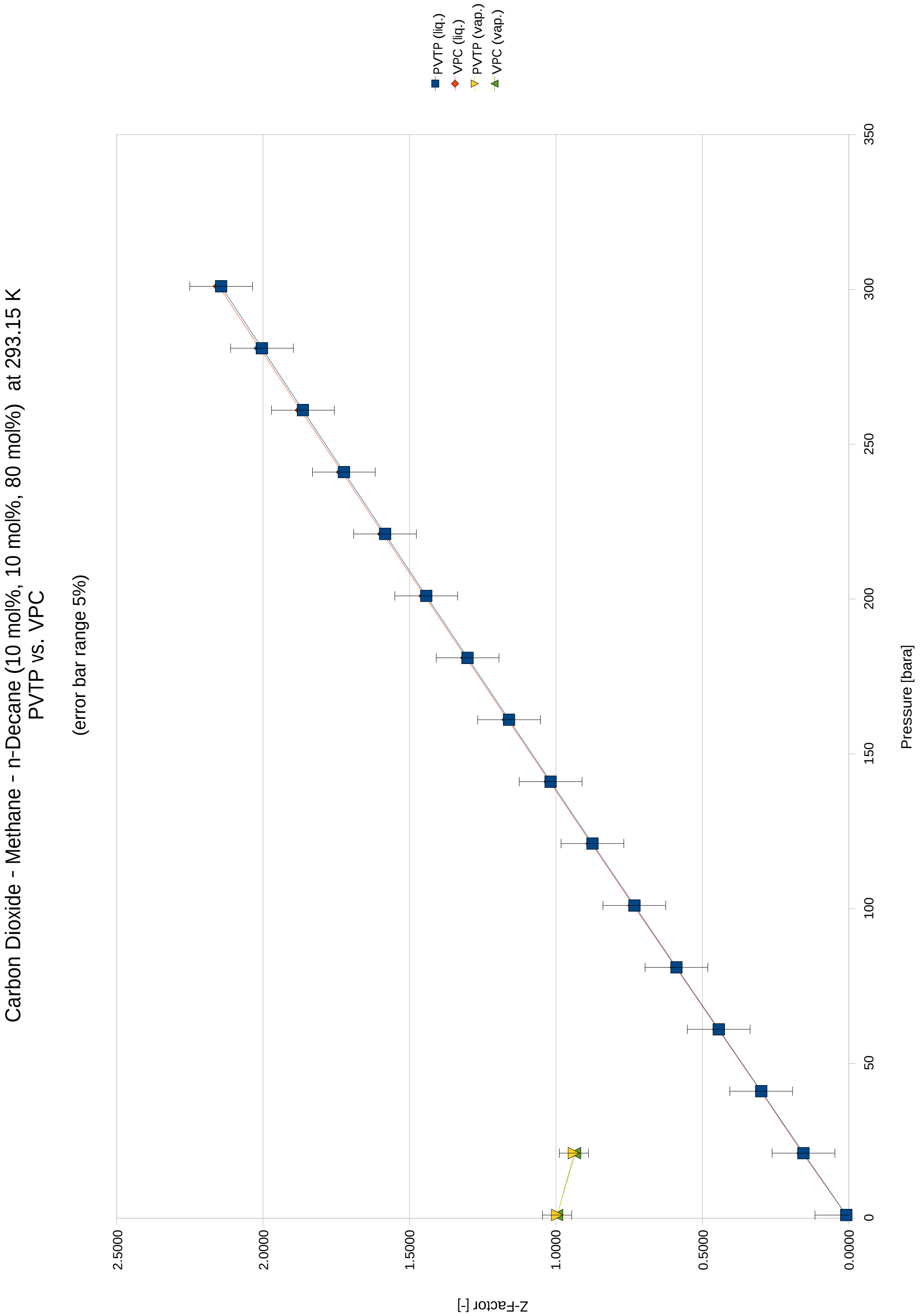


Figure 3.16.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 293.15 K

Table 3.28.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 293.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	PVTP	**VPC**	**Difference (base is PVTP) [%]**	**PVTP**	**VPC**	**Difference (base is PVTP) [%]**
1.01	0.0087	0.0087	0.76%	0.9961	0.9963	0.02%
21.01	0.1548	0.1584	2.28%	0.9388	0.9348	-0.43%
41.01	0.2995	0.3008	0.43%			
61.01	0.4444	0.4463	0.42%			
81.01	0.5887	0.5912	0.42%			
101.01	0.7324	0.7354	0.41%			
121.01	0.8755	0.8790	0.41%			
141.01	1.0181	1.0221	0.40%			
161.01	1.1602	1.1647	0.40%			
181.01	1.3018	1.3069	0.39%			
201.01	1.4429	1.4486	0.39%			
221.01	1.5837	1.5898	0.39%			
241.01	1.7241	1.7307	0.38%			
261.01	1.8641	1.8712	0.38%			
281.01	2.0038	2.0113	0.38%			
301.01	2.1431	2.1511	0.37%			

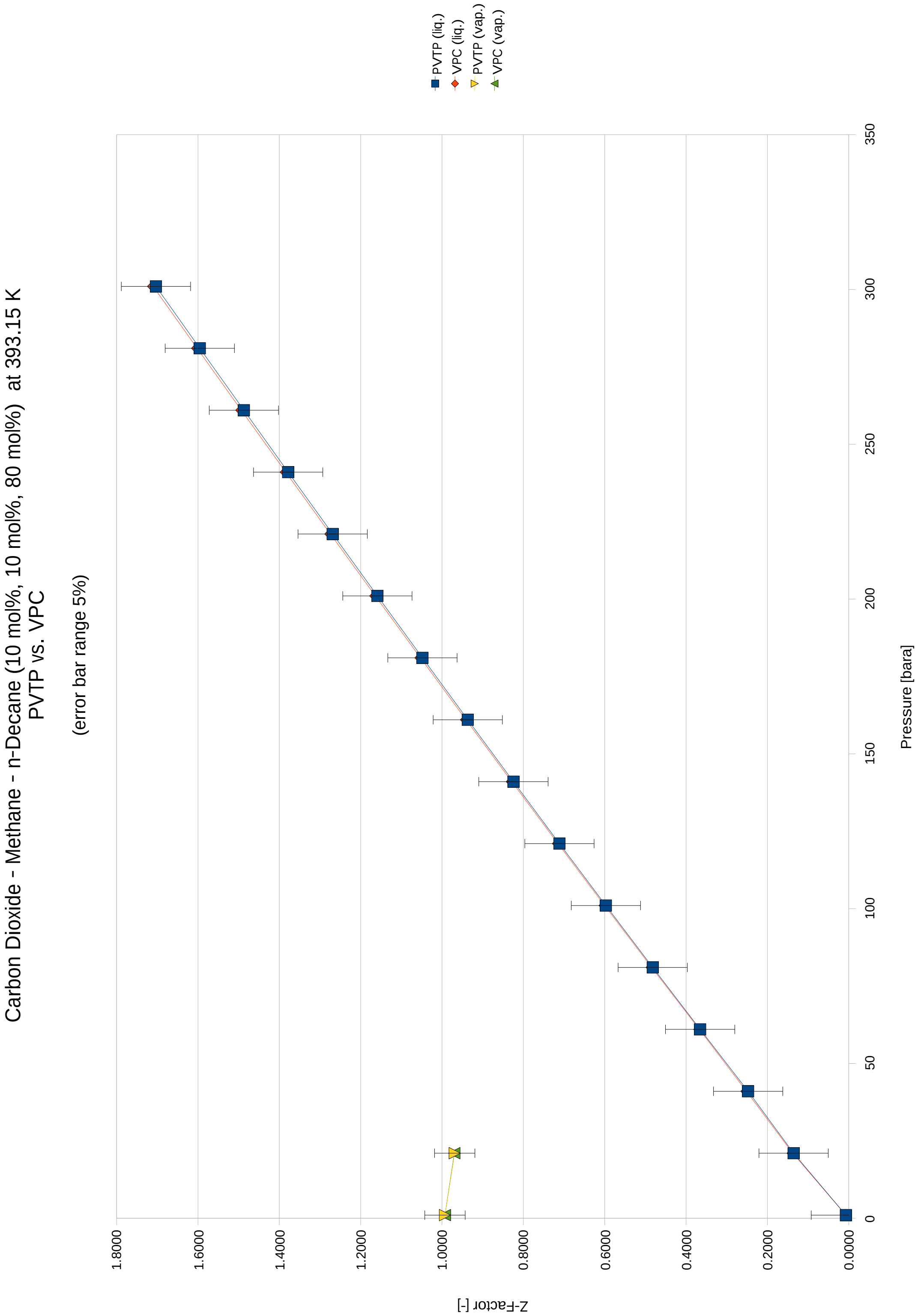


Figure 3.17.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 393.15 K

Table 3.29.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 393.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	PVTP	**VPC**	**Difference (base is PVTP) [%]**	**PVTP**	**VPC**	**Difference (base is PVTP) [%]**
1.01	0.0071	0.0071	0.45%	0.9927	0.9929	0.02%
21.01	0.1356	0.1377	1.55%	0.9687	0.9697	0.11%
41.01	0.2474	0.2515	1.63%			
61.01	0.3654	0.3673	0.53%			
81.01	0.4819	0.4844	0.51%			
101.01	0.5971	0.6001	0.50%			
121.01	0.7113	0.7147	0.48%			
141.01	0.8244	0.8283	0.47%			
161.01	0.9367	0.9410	0.46%			
181.01	1.0481	1.0528	0.45%			
201.01	1.1588	1.1639	0.44%			
221.01	1.2688	1.2743	0.43%			
241.01	1.3783	1.3841	0.43%			
261.01	1.4871	1.4934	0.42%			
281.01	1.5955	1.6021	0.41%			
301.01	1.7033	1.7103	0.41%			

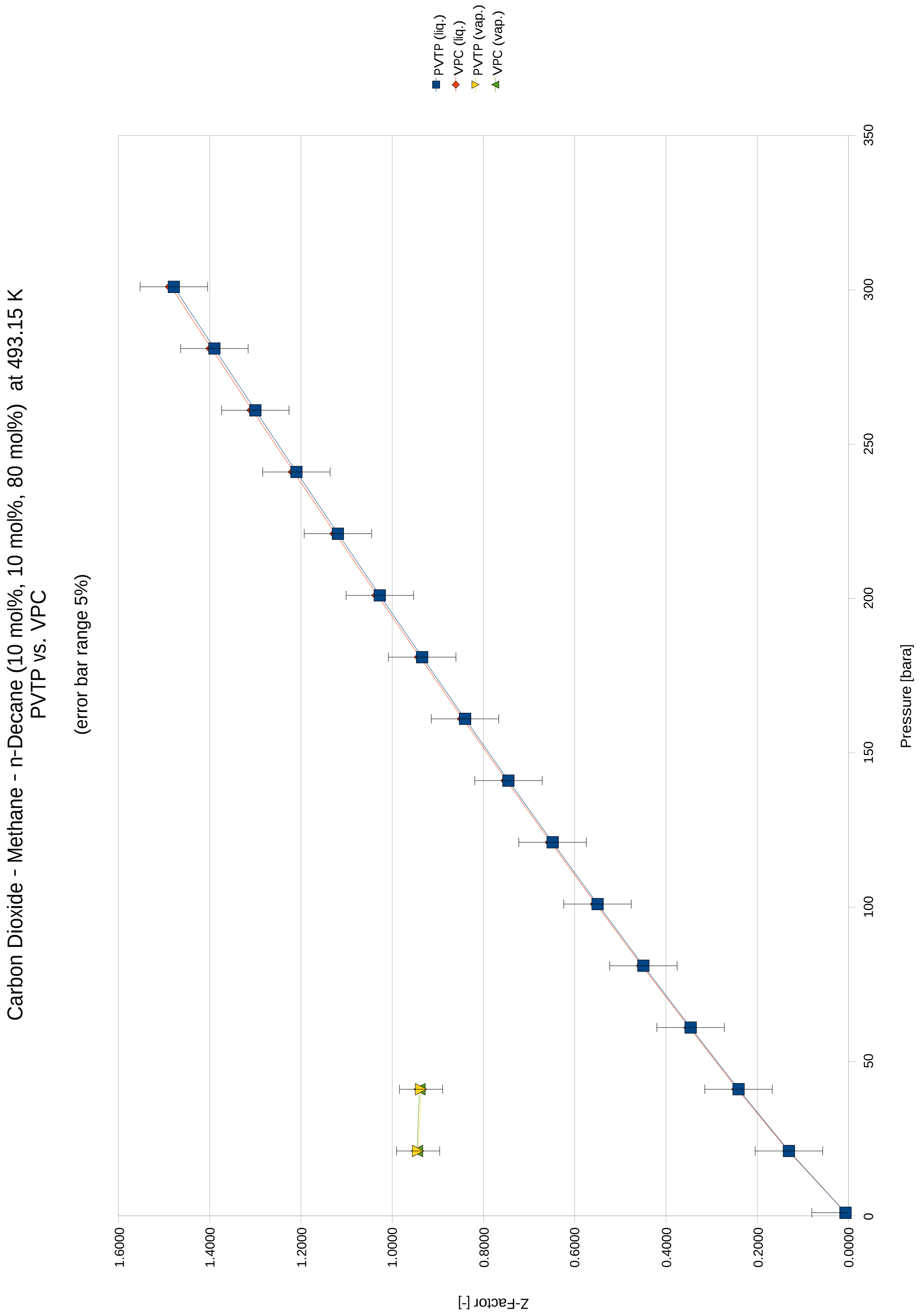


Figure 3.18.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 493.15 K

Table 3.30.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 493.15 K

Pressure [bar]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	PVTP	**VPC**	**Difference (base is PVTP) [%]**	**PVTP**	**VPC**	**Difference (base is PVTP) [%]**
1.01	0.0064	0.0065	1.37%			
21.01	0.1306	0.1318	0.88%	0.9432	0.9456	0.26%
41.01	0.2410	0.2438	1.15%	0.9368	0.9403	0.37%
61.01	0.3461	0.3487	0.76%			
81.01	0.4495	0.4526	0.69%			
101.01	0.5501	0.5536	0.64%			
121.01	0.6486	0.6524	0.60%			
141.01	0.7452	0.7495	0.57%			
161.01	0.8404	0.8450	0.54%			
181.01	0.9343	0.9392	0.52%			
201.01	1.0271	1.0323	0.50%			
221.01	1.1190	1.1244	0.48%			
241.01	1.2099	1.2156	0.47%			
261.01	1.3001	1.3061	0.46%			
281.01	1.3896	1.3959	0.45%			
301.01	1.4785	1.4850	0.44%			

Table 3.31.: Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 1.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
200	0.0086	0.0086	-0.10%	0.9923	0.9923	0.00%
220	0.0080	0.0080	-0.10%	0.9932	0.9933	0.00%
240	0.0077	0.0076	-0.25%	0.9929	0.9930	0.01%
260	0.0076	0.0076	-0.34%	0.9915	0.9916	0.01%
280	0.0078	0.0078	-0.38%	0.9908	0.9908	0.00%
300	0.0079	0.0079	-0.22%	0.9914	0.9913	0.00%
320	0.0078	0.0078	-0.16%	0.9922	0.9921	0.00%
340	0.0076	0.0076	-0.12%	0.9927	0.9926	0.00%
360	0.0074	0.0074	-0.06%	0.9924	0.9923	-0.01%
380	0.0072	0.0072	-0.12%	0.9908	0.9907	-0.01%
400	0.0070	0.0070	-0.10%	0.9866	0.9864	-0.02%
420				0.9866	0.9866	0.00%
440				0.9884	0.9884	0.00%
460				0.9899	0.9899	0.00%
480				0.9912	0.9912	0.00%
500				0.9923	0.9924	0.00%
520				0.9933	0.9933	0.00%
540				0.9941	0.9942	0.00%
560				0.9949	0.9949	0.00%
580				0.9770	0.9955	1.90%

3.3.2. Fixed Pressure

For the pressure the values 1.013 25 bar, 101.013 25 bar and 201.013 25 bar were selected and the temperature ranges from 200 K to 580 K.

3.3.2.1. Methane - n-Butane - n-Decane

Figure 3.19 on page 89 to Figure 3.21 on page 92 and Table 3.31 on page 88 to Table 3.33 on page 93.

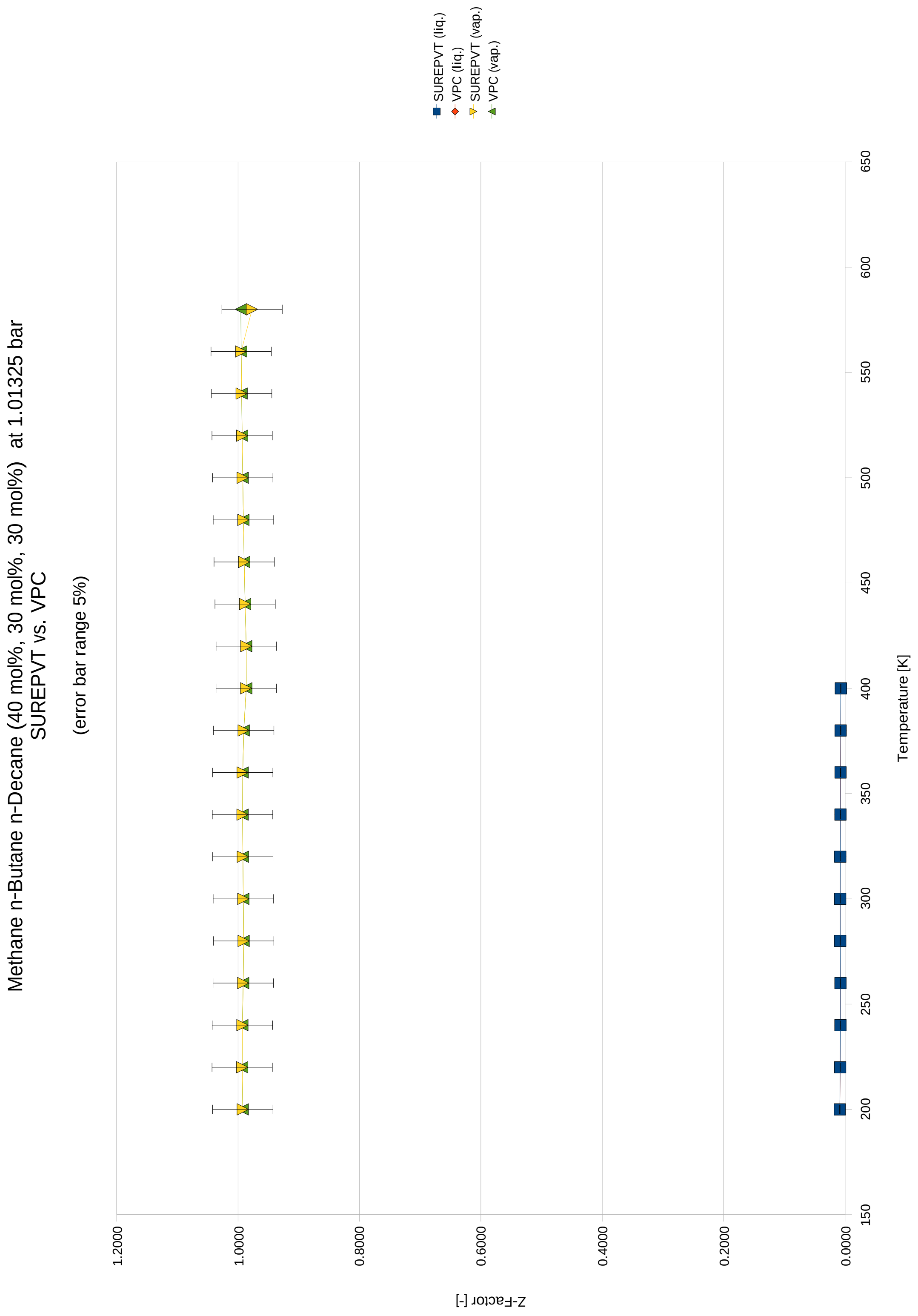


Figure 3.19.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 1.013 25 bar

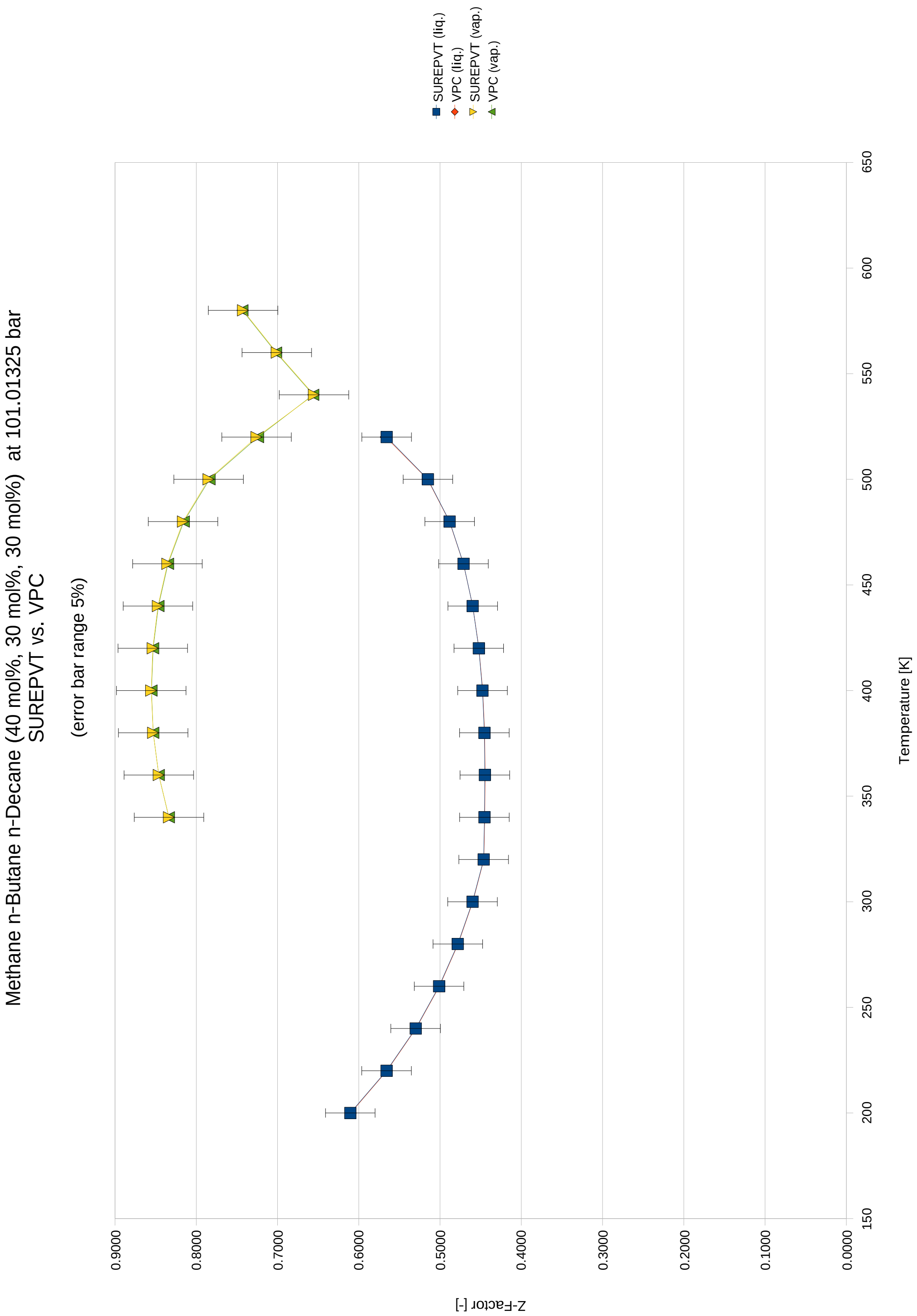


Figure 3.20.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 101.013 25 bar

Table 3.32.: Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 101.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
200	0.6104	0.6099	-0.10%			
220	0.5658	0.5653	-0.09%			
240	0.5300	0.5296	-0.09%			
260	0.5012	0.5008	-0.08%			
280	0.4781	0.4778	-0.08%			
300	0.4600	0.4597	-0.07%			
320	0.4463	0.4460	-0.06%			
340	0.4454	0.4449	-0.10%	0.8336	0.8337	0.02%
360	0.4448	0.4444	-0.09%	0.8461	0.8462	0.01%
380	0.4454	0.4451	-0.07%	0.8531	0.8530	-0.01%
400	0.4477	0.4475	-0.06%	0.8554	0.8552	-0.03%
420	0.4523	0.4521	-0.04%	0.8535	0.8531	-0.05%
440	0.4598	0.4597	-0.01%	0.8472	0.8466	-0.07%
460	0.4711	0.4712	0.01%	0.8355	0.8348	-0.09%
480	0.4882	0.4884	0.05%	0.8163	0.8154	-0.11%
500	0.5149	0.5153	0.09%	0.7849	0.7837	-0.15%
520	0.5657	0.5668	0.19%	0.7258	0.7240	-0.24%
540				0.6552	0.6560	0.14%
560				0.7009	0.7018	0.12%
580				0.7424	0.7432	0.11%

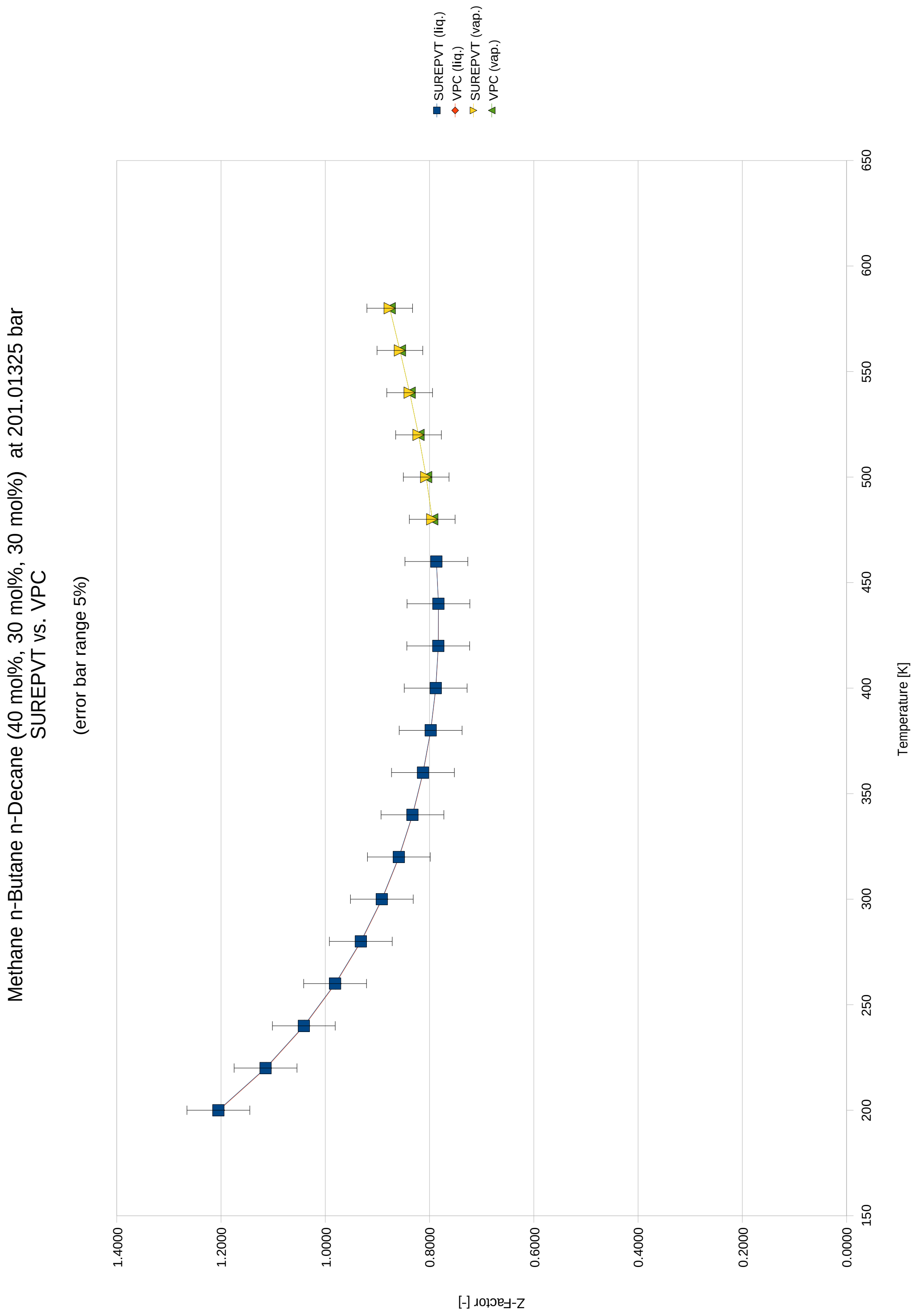


Figure 3.21.: Comparison of Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 201.013 25 bar

Table 3.33.: Methane - n-Butane - n-Decane (40 mol%, 30 mol%, 30 mol%) at 201.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	SUREPVT	**VPC**	**Difference (base is SUREPVT) [%]**	**SUREPVT**	**VPC**	**Difference (base is SUREPVT) [%]**
200	1.2051	1.2039	-0.10%			
220	1.1146	1.1135	-0.09%			
240	1.0411	1.0402	-0.09%			
260	0.9811	0.9802	-0.09%			
280	0.9318	0.9311	-0.08%			
300	0.8915	0.8908	-0.08%			
320	0.8588	0.8582	-0.07%			
340	0.8328	0.8322	-0.07%			
360	0.8126	0.8121	-0.06%			
380	0.7979	0.7975	-0.05%			
400	0.7882	0.7878	-0.04%			
420	0.7833	0.7830	-0.03%			
440	0.7829	0.7827	-0.02%			
460	0.7869	0.7868	-0.01%			
480				0.7949	0.7948	0.00%
500				0.8064	0.8064	0.00%
520				0.8210	0.8211	0.01%
540				0.8380	0.8382	0.02%
560				0.8566	0.8568	0.02%
580				0.8762	0.8764	0.03%

Table 3.34.: Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 1.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	PVTP	**VPC**	**Difference (base is PVTP) [%]**	**PVTP**	**VPC**	**Difference (PVTP) [%]**
200	0.0112	0.0117	3.73%	0.9908	0.9899	-0.09%
220	0.0106	0.0109	2.96%	0.9920	0.9918	-0.02%
240	0.0100	0.0102	1.91%	0.9933	0.9935	0.01%
260	0.0095	0.0096	1.26%	0.9945	0.9948	0.02%
280	0.0090	0.0090	0.90%	0.9955	0.9958	0.02%
300	0.0085	0.0086	0.71%	0.9963	0.9965	0.02%
320	0.0081	0.0082	0.59%	0.9968	0.9970	0.02%
340	0.0078	0.0078	0.53%	0.9969	0.9971	0.02%
360	0.0075	0.0075	0.48%	0.9965	0.9967	0.02%
380	0.0072	0.0073	0.46%	0.9949	0.9951	0.02%
400	0.0070	0.0071	0.44%	0.9909	0.9910	0.01%
420	0.0069	0.0069	0.44%	0.9813	0.9812	-0.02%
440	0.0061	0.0061	0.78%			
460	0.0061	0.0062	0.92%			
480	0.0063	0.0063	1.13%			
500	0.0066				0.0067	
520	0.0075				0.0078	
540	0.9804				0.9806	
560	0.9827				0.9828	
580	0.9847				0.9848	

3.3.2.2. Carbon dioxide - Methane - n-Decane

Figure 3.22 on page 95 to Figure 3.24 on page 98 and Table 3.34 on page 94 to Table 3.36 on page 99.

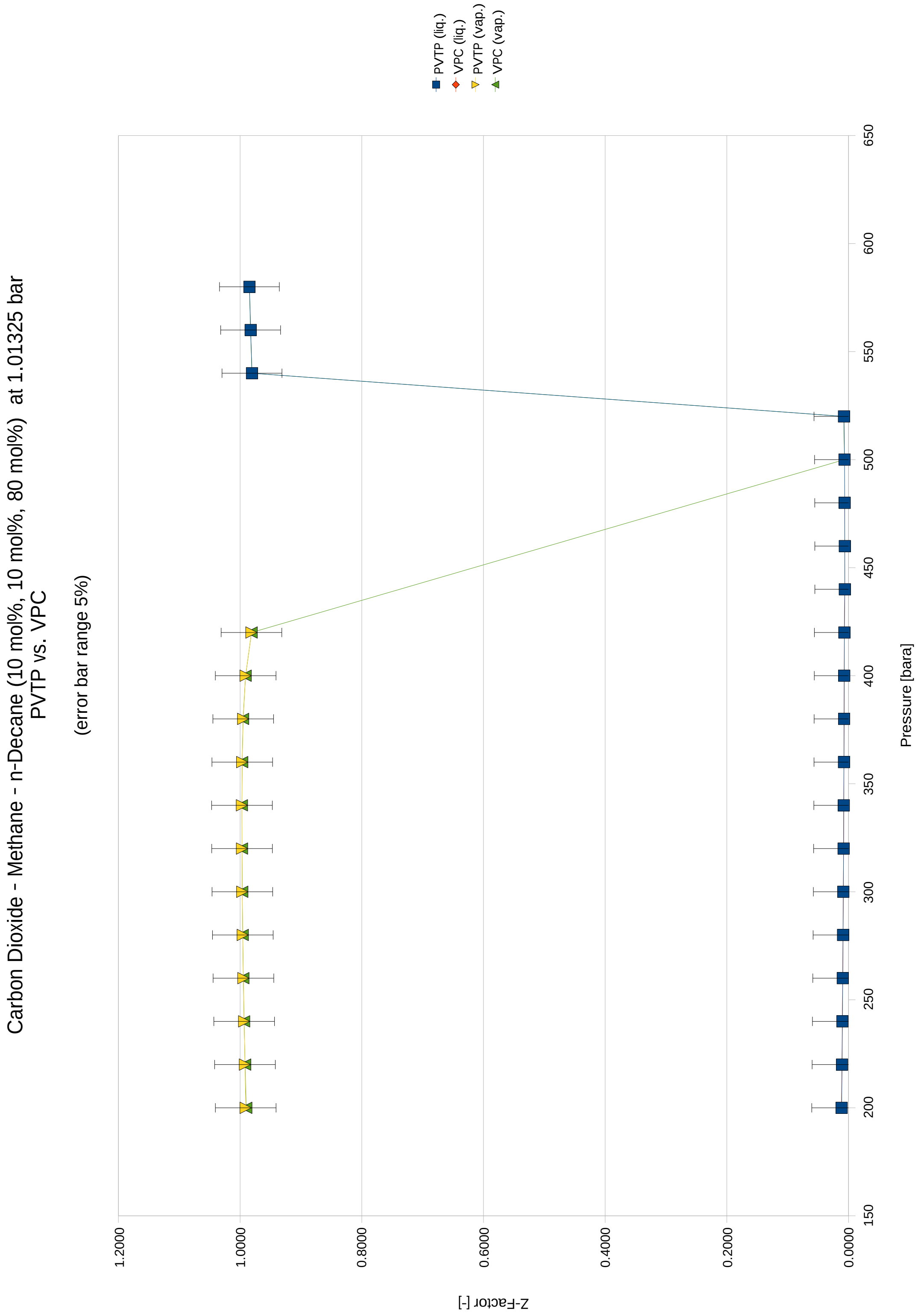


Figure 3.22.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 1.013 25 bar

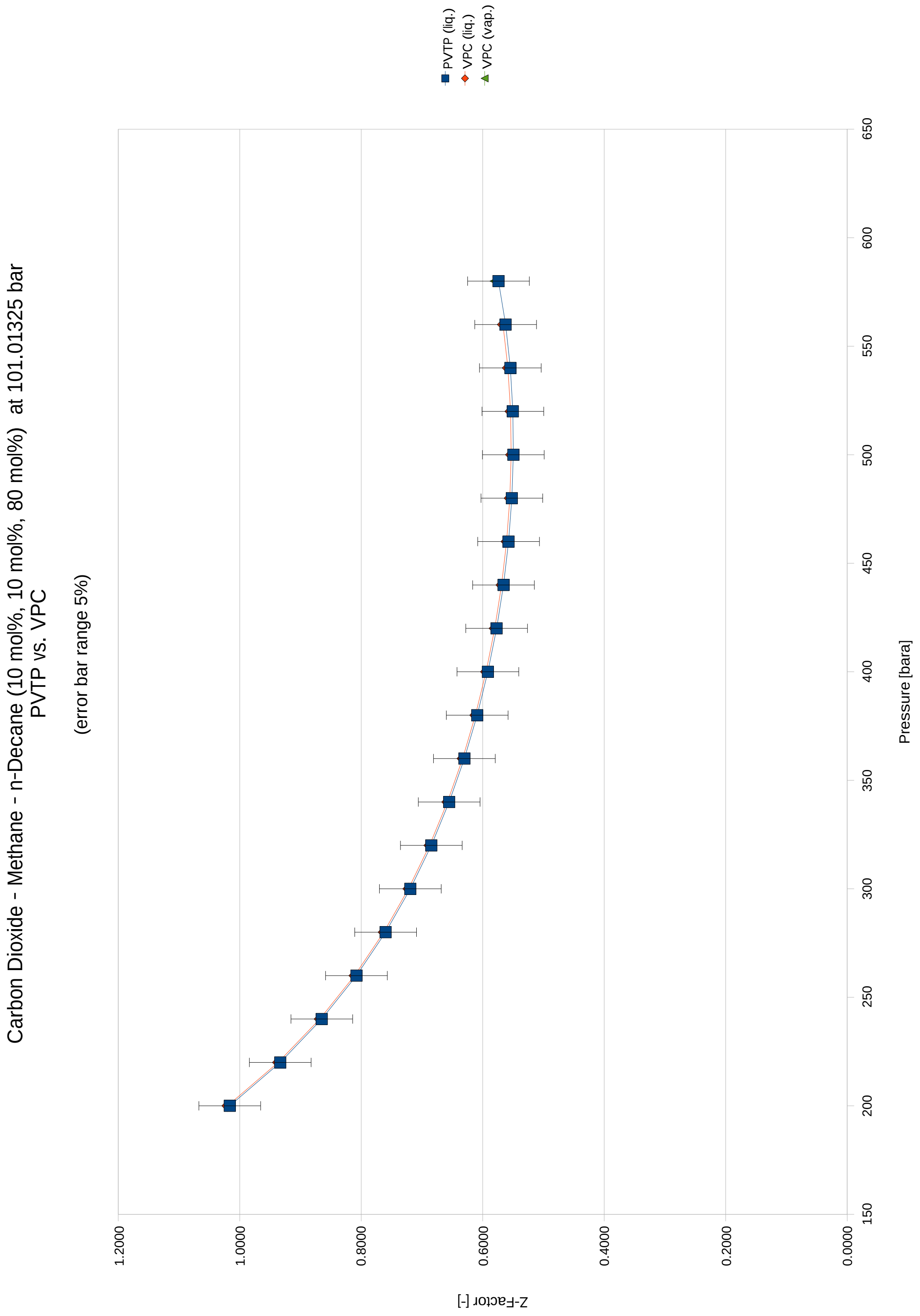


Figure 3.23.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 101.013 25 bar

Table 3.35.: Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 101.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	PVTP	**VPC**	**Difference (PVTP) [%]**	**PVTP**	**VPC**	**Difference (base is PVTP) [%]**
200	1.0164	1.0201	0.36%			
220	0.9333	0.9368	0.37%			
240	0.8649	0.8682	0.38%			
260	0.8079	0.8110	0.39%			
280	0.7599	0.7629	0.40%			
300	0.7192	0.7222	0.42%			
320	0.6846	0.6876	0.43%			
340	0.6552	0.6581	0.45%			
360	0.6302	0.6331	0.46%			
380	0.6091	0.6120	0.48%			
400	0.5915	0.5945	0.50%			
420	0.5771	0.5802	0.53%			
440	0.5658	0.5689	0.56%			
460	0.5574	0.5607	0.58%			
480	0.5520	0.5554	0.62%			
500	0.5496	0.5532	0.65%			
520	0.5504	0.5542	0.69%			
540	0.5545	0.5586	0.73%			
560	0.5623	0.5666	0.77%			
580	0.5740				0.5787	

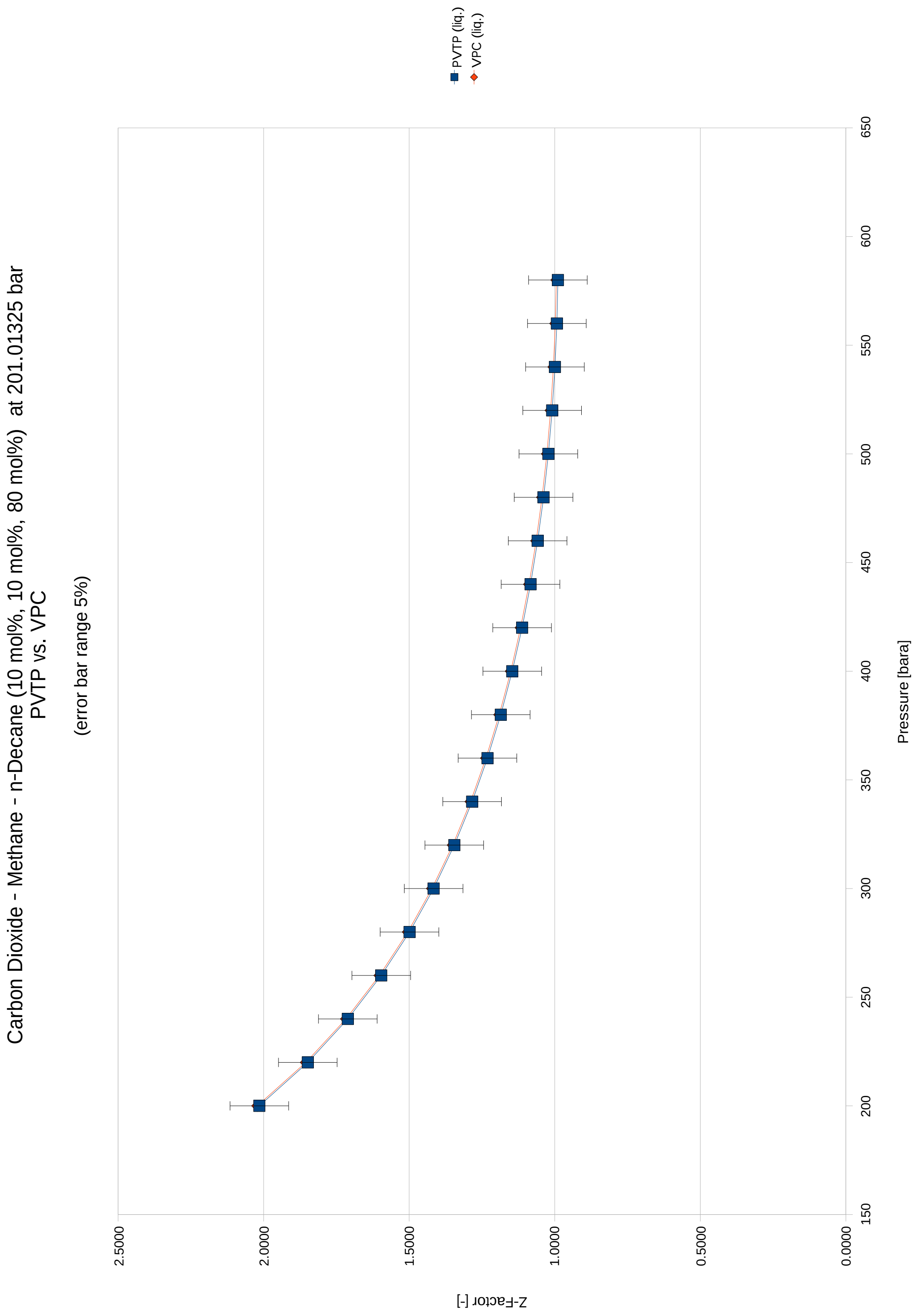


Figure 3.24.: Comparison of Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 201.013 25 bar

Table 3.36.: Carbon dioxide - Methane - n-Decane (10 mol%, 10 mol%, 80 mol%) at 201.013 25 bar

Temperature [K]	**Z-Factor [-]**					
	Liquid			**Vapor**		
	PVTP	**VPC**	**Difference (base is PVTP) [%]**	**PVTP**	**VPC**	**Difference (base is PVTP) [%]**
200	2.0147	2.0218	0.35%			
220	1.8482	1.8549	0.36%			
240	1.7109	1.7171	0.37%			
260	1.5960	1.6019	0.37%			
280	1.4988	1.5046	0.38%			
300	1.4160	1.4216	0.39%			
320	1.3450	1.3504	0.40%			
340	1.2839	1.2891	0.41%			
360	1.2310	1.2362	0.42%			
380	1.1854	1.1905	0.43%			
400	1.1460	1.1511	0.45%			
420	1.1121	1.1172	0.46%			
440	1.0832	1.0882	0.47%			
460	1.0587	1.0638	0.48%			
480	1.0384	1.0435	0.49%			
500	1.0219	1.0270	0.50%			
520	1.0089	1.0141	0.52%			
540	0.9992	1.0045	0.53%			
560	0.9927	0.9980	0.53%			
580	0.9891	0.9944	0.54%			

Appendix

A. Property Tables

A.1. Component Library

From [2].

A.1.1. Field Units

Table A.1.: Component Library in Field Units

Compound	**Formula**	**Molar Mass [lbm/lbm mol]**	**Critical Pressure [psia]**	**Critical Temperature [°F]**	**Acentric Factor [-]**
Methane	CH4	16.042	667.0	-116.66	0.0115
Ethane	C2H6	30.069	706.6	89.92	0.0994
Propane	C3H8	44.096	615.5	205.92	0.1529
Isobutane	C4H10	58.122	527.9	274.41	0.1865
n-Butane	C4H10	58.122	550.9	305.55	0.2003
Isopentane	C5H12	72.149	490.4	369.00	0.2284
n-Pentane	C5H12	72.149	488.8	385.80	0.2515
Neopentane	C5H12	72.149	463.5	321.00	0.1966
n-Hexane	C6H14	86.175	436.9	453.80	0.2993
2-Methylpentane	C6H14	86.175	436.6	435.80	0.2777
3-Methylpentane	C6H14	86.175	452.5	448.30	0.2726
Neohexane	C6H14	86.175	446.7	420.00	0.2331
2,3-Dimethylbutane	C6H14	86.175	454.0	440.20	0.2481
n-Heptane	C7H16	100.202	396.8	512.90	0.3483
2-Methylhexane	C7H16	100.202	396.0	494.50	0.3312
3-Methylhexane	C7H16	100.202	407.6	503.70	0.3231
3-Ethylpentane	C7H16	100.202	419.2	513.20	0.3111

(continue...)

Table A.1.: Component Library in Field Units

(continued)

Compound	**Formula**	**Molar Mass [lbm/lbm mol]**	**Critical Pressure [psia]**	**Critical Temperature [°F]**	**Acentric Factor [-]**
2.2-Dimethylpentane	C7H16	100.202	401.8	477.10	0.2870
24-Dimethylpentane	C7H16	100.202	397.4	475.80	0.3035
3.3-Dimethylpentane	C7H16	100.202	427.9	505.70	0.2687
Triptane	C7H16	100.202	427.9	496.30	0.2501
n-Octane	C8H18	114.229	360.7	564.20	0.3977
Diisobutyl	C8H18	114.229	361.1	530.30	0.3571
Isooctane	C8H18	114.229	372.7	519.40	0.3043
n-Nonane	C9H20	128.255	330.7	610.80	0.4421
n-Decane	C10H22	142.282	304.6	652.20	0.4875
Cyclopentane	C5H10	70.133	653.8	461.20	0.1950
Methylcyclopentane	C6H12	84.159	548.8	499.40	0.2267
Cyclohexane	C6H12	84.159	590.7	536.60	0.2105
Methylcyclohexane	C7H14	98.186	503.4	570.30	0.2352
Ethene(Ethylene)	C2H4	28.053	731.0	48.50	0.0865
Propene(Propylene)	C3H6	42.080	676.6	198.40	0.1407
1-Butene(Butylene)	C4H8	56.106	586.4	296.20	0.1923
cis-2-Butene	C4H8	56.106	615.4	324.40	0.2056
trans-2-Butene	C4H8	56.106	574.9	311.90	0.2035
Isobutene	C4H8	56.106	580.2	292.60	0.1995
1-Pentene	C5H10	70.133	509.5	376.90	0.2314
1,2-Butadiene	C4H6	54.090	655.6	354.30	0.1715
1.3-Butadiene	C4H6	54.090	620.3	305.60	0.1887
Isoprene	C5H8	68.117	581.6	402.90	0.2149
Acetylene	C2H2	26.037	890.4	95.30	0.1976
Benzene	C6H6	78.112	710.4	552.20	0.2092
Toluene	C7H8	92.138	595.5	605.60	0.2637
Ethylbenzene	C8H10	106.165	523.0	651.30	0.3026
o-Xylene	C8H10	106.165	541.6	674.90	0.3118

(continue...)

Table A.1.: Component Library in Field Units

(continued)

Compound	**Formula**	**Molar Mass [lbm/lbm mol]**	**Critical Pressure [psia]**	**Critical Temperature [°F]**	**Acentric Factor [-]**
m-Xylene	C8H10	106.165	512.9	651.00	0.3255
p-Xylene	C8H10	106.165	509.2	649.50	0.3211
Styrene	C8H8	104.149	587.8	703.00	0.2453
Isopropylbenzene	C9H12	120.192	465.4	676.30	0.3256
Methyl alcohol	CH4O	32.042	1174.0	463.10	0.5649
Ethyl alcohol	C2H6O	46.068	891.7	465.40	0.6446
Carbon monoxide	CO	28.010	506.7	-220.63	0.0510
Carbon dioxide	CO2	44.010	1070.0	87.76	0.2239
Hydrogen sulfide	H2S	34.082	1306.5	212.81	0.1010
Sulfur dioxide	SO2	64.065	1143.0	315.48	0.2570
Ammonia	NH3	17.0306	1644.0	270.10	0.2560
Hydrogen	H2	2.0159	190.7	-399.90	-0.2140
Oxygen	O2	31.9988	731.4	-181.43	0.0222
Nitrogen	N2	28.0135	492.5	-232.53	0.0372
Chlorine	Cl2	70.9054	1117.0	290.93	0.0722
Water	H2O	18.0153	3200.1	705.10	0.3443
Helium	He	4.003	33.0	-450.32	-0.3820
Hydrogen chloride	HCl	36.4606	1205.0	124.77	0.1269

A.1.2. SI Units

This is the field unit component library (A.1.1) converted to SI Units with conversion factors.

Table A.2.: Component Library in SI Units

Compound	**Formula**	**Molar Mass [kg/mol]**	**Critical Pressure [Pa]**	**Critical Temperature [K]**	**Acentric Factor [-]**
Methane	CH4	0.016042	4.598803E+06	190.56	0.0115

(continue...)

Table A.2.: Component Library in SI Units

(continued)

Compound	**Formula**	**Molar Mass [kg/mol]**	**Critical Pressure [Pa]**	**Critical Temperature [K]**	**Acentric Factor [-]**
Ethane	C2H6	0.030069	4.871835E+06	305.33	0.0994
Propane	C3H8	0.044096	4.243723E+06	369.77	0.1529
Isobutane	C4H10	0.058122	3.639742E+06	407.82	0.1865
n-Butane	C4H10	0.058122	3.798322E+06	425.12	0.2003
Isopentane	C5H12	0.072149	3.381189E+06	460.37	0.2284
n-Pentane	C5H12	0.072149	3.370157E+06	469.71	0.2515
Neopentane	C5H12	0.072149	3.195720E+06	433.71	0.1966
n-Hexane	C6H14	0.086175	3.012319E+06	507.48	0.2993
2-Methylpentane	C6H14	0.086175	3.010251E+06	497.48	0.2777
3-Methylpentane	C6H14	0.086175	3.119878E+06	504.43	0.2726
Neohexane	C6H14	0.086175	3.079888E+06	488.71	0.2331
2,3-Dimethylbutane	C6H14	0.086175	3.130220E+06	499.93	0.2481
n-Heptane	C7H16	0.100202	2.735840E+06	540.32	0.3483
2-Methylhexane	C7H16	0.100202	2.730324E+06	530.09	0.3312
3-Methylhexane	C7H16	0.100202	2.810303E+06	535.21	0.3231
3-Ethylpentane	C7H16	0.100202	2.890282E+06	540.48	0.3111
2.2-Dimethylpentane	C7H16	0.100202	2.770313E+06	520.43	0.2870
24-Dimethylpentane	C7H16	0.100202	2.739976E+06	519.71	0.3035
3.3-Dimethylpentane	C7H16	0.100202	2.950267E+06	536.32	0.2687
Triptane	C7H16	0.100202	2.950267E+06	531.09	0.2501
n-Octane	C8H18	0.114229	2.486939E+06	568.82	0.3977
Diisobutyl	C8H18	0.114229	2.489697E+06	549.98	0.3571
Isooctane	C8H18	0.114229	2.569676E+06	543.93	0.3043
n-Nonane	C9H20	0.128255	2.280096E+06	594.71	0.4421
n-Decane	C10H22	0.142282	2.100143E+06	617.71	0.4875
Cyclopentane	C5H10	0.070133	4.507792E+06	511.59	0.1950
Methylcyclopentane	C6H12	0.084159	3.783843E+06	532.82	0.2267
Cyclohexane	C6H12	0.084159	4.072733E+06	553.48	0.2105

(continue...)

Table A.2.: Component Library in SI Units

(continued)

Compound	**Formula**	**Molar Mass [kg/mol]**	**Critical Pressure [Pa]**	**Critical Temperature [K]**	**Acentric Factor [-]**
Methylcyclohexane	C7H14	0.098186	3.470821E+06	572.21	0.2352
Ethene(Ethylene)	C2H4	0.028053	5.040067E+06	282.32	0.0865
Propene(Propylene)	C3H6	0.042080	4.664993E+06	365.59	0.1407
1-Butene(Butylene)	C4H8	0.056106	4.043086E+06	419.93	0.1923
cis-2-Butene	C4H8	0.056106	4.243033E+06	435.59	0.2056
trans-2-Butene	C4H8	0.056106	3.963796E+06	428.65	0.2035
Isobutene	C4H8	0.056106	4.000338E+06	417.93	0.1995
1-Pentene	C5H10	0.070133	3.512879E+06	464.76	0.2314
1,2-Butadiene	C4H6	0.054090	4.520203E+06	452.21	0.1715
1.3-Butadiene	C4H6	0.054090	4.276818E+06	425.15	0.1887
Isoprene	C5H8	0.068117	4.009991E+06	479.21	0.2149
Acetylene	C2H2	0.026037	6.139092E+06	308.32	0.1976
Benzene	C6H6	0.078112	4.898035E+06	562.15	0.2092
Toluene	C7H8	0.092138	4.105828E+06	591.82	0.2637
Ethylbenzene	C8H10	0.106165	3.605958E+06	617.21	0.3026
o-Xylene	C8H10	0.106165	3.734200E+06	630.32	0.3118
m-Xylene	C8H10	0.106165	3.536321E+06	617.04	0.3255
p-Xylene	C8H10	0.106165	3.510810E+06	616.21	0.3211
Styrene	C8H8	0.104149	4.052738E+06	645.93	0.2453
Isopropylbenzene	C9H12	0.120192	3.208820E+06	631.09	0.3256
Methyl alcohol	CH4O	0.032042	8.094445E+06	512.65	0.5649
Ethyl alcohol	C2H6O	0.046068	6.148055E+06	513.93	0.6446
Carbon monoxide	CO	0.028010	3.493573E+06	132.80	0.0510
Carbon dioxide	CO2	0.044010	7.377390E+06	304.13	0.2239
Hydrogen sulfide	H2S	0.034082	9.008000E+06	373.60	0.1010
Sulfur dioxide	SO2	0.064065	7.880707E+06	430.64	0.2570
Ammonia	NH3	0.017031	1.133498E+07	405.43	0.2560
Hydrogen	H2	0.002016	1.314830E+06	33.21	-0.2140

(continue...)

Table A.2.: Component Library in SI Units

(continued)

Compound	**Formula**	**Molar Mass [kg/mol]**	**Critical Pressure [Pa]**	**Critical Temperature [K]**	**Acentric Factor [-]**
Oxygen	O2	0.031999	5.042825E+06	154.58	0.0222
Nitrogen	N2	0.028014	3.395668E+06	126.19	0.0372
Chlorine	Cl2	0.070905	7.701444E+06	417.00	0.0722
Water	H2O	0.018015	2.206391E+07	647.09	0.3443
Helium	He	0.004003	2.275270E+05	5.19	-0.3820
Hydrogen chloride	HCl	0.036461	8.308182E+06	324.69	0.1269

A.2. Binary Interaction Parameters

In VPC the BIP's for the Peng-Robinson EOS are implemented as suggested by [7].

Table A.3.: Binary Interaction Parameters for Peng-Robinson

	Nitrogen	**Carbon dioxide**	**Hydrogen sulfide**
Nitrogen	0	0	0
Carbon dioxide	0.000	0	0
Hydrogen sulfide	0.130	0.135	0
Methane	0.025	0.105	0.070
Ethane	0.010	0.130	0.085
Propane	0.090	0.125	0.080
Isobutane	0.095	0.120	0.075
n-Butane	0.095	0.115	0.075
Isopentane	0.100	0.115	0.070
n-Pentane	0.110	0.115	0.070
C_{7+}	0.110	0.115	0.055

B. Conversion Factors

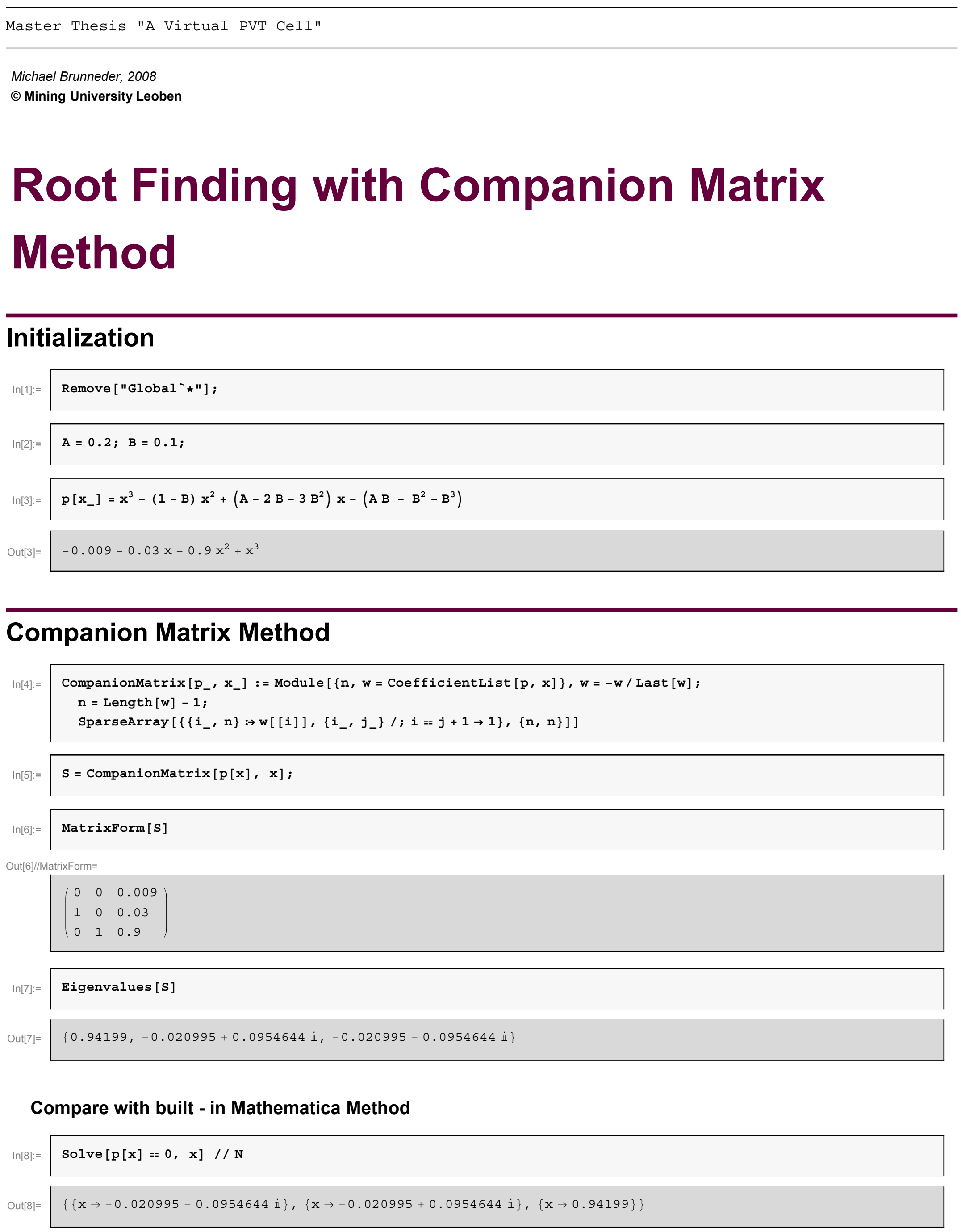
Table B.1.: Conversion Factors

From	**Operation**			**To**
°C	°C + 273.15		=	K
°F	(°F + 459.67) / 1.8		=	K
°R	°R / 1.8		=	K
ft	x	3.048×10^{-1}	=	m
atm	x	$1.013\,25 \times 10^{5}$	=	Pa
in	x	2.54×10^{-2}	=	m
lbm	x	$4.535\,924 \times 10^{-1}$	=	kg
lbm mol	x	$4.535\,923\,7 \times 10^{-3}$	=	mol
psi	x	$6.894\,757 \times 10^{3}$	=	Pa

C. Mathematica Files

The following files were created with the software Mathematica v6.0.0. Please be aware that, due to naming restrictions in Mathematica, there are minor differences in the nomenclature in some expressions to the one used in this thesis paper. The main purpose of these examples is to create a reliable prototype for later implementation in a programming language, therefore the powerful built-in Mathematica solution methods are not used on purpose.

C.1. Companion Matrix Method



Master Thesis "A Virtual PVT Cell"

Michael Brunneder, 2008

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Root Finding with Companion Matrix Method

Initialization

In[1]:=
```
Remove["Global`*"];
```

In[2]:=
```
A = 0.2; B = 0.1;
```

In[3]:=
```
p[x_] = x^3 - (1 - B) x^2 + (A - 2 B - 3 B^2) x - (A B - B^2 - B^3)
```

Out[3]=
```
-0.009 - 0.03 x - 0.9 x^2 + x^3
```

Companion Matrix Method

In[4]:=
```
CompanionMatrix[p_, x_] := Module[{n, w = CoefficientList[p, x]}, w = -w / Last[w];
  n = Length[w] - 1;
  SparseArray[{{i_, n} :→ w[[i]], {i_, j_} /; i == j + 1 → 1}, {n, n}]]
```

In[5]:=
```
S = CompanionMatrix[p[x], x];
```

In[6]:=
```
MatrixForm[S]
```

Out[6]//MatrixForm=

$$\begin{pmatrix} 0 & 0 & 0.009 \\ 1 & 0 & 0.03 \\ 0 & 1 & 0.9 \end{pmatrix}$$

In[7]:=
```
Eigenvalues[S]
```

Out[7]=
```
{0.94199, -0.020995 + 0.0954644 i, -0.020995 - 0.0954644 i}
```

Compare with built - in Mathematica Method

In[8]:=
```
Solve[p[x] == 0, x] // N
```

Out[8]=
```
{{x → -0.020995 - 0.0954644 i}, {x → -0.020995 + 0.0954644 i}, {x → 0.94199}}
```

C.2. Single Component Calculation

```
Master Thesis "A Virtual PVT Cell"
```

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VLE Calculation for Single Component

Notebook initialization

In[2]:=
```
Remove["Global`*"];
```

In[3]:=
```
<< Units`; (* laod the units package to use SI units *)
```

Peng-Robinson EOS

In[4]:=

$$\Omega_a = 0.45724;$$

In[5]:=

$$\texttt{ac[i\_] := }\Omega_a \frac{R^2\ \texttt{Tc[[i]]}^2}{\texttt{pc[[i]]}};$$

In[6]:=

$$\Omega_b = 0.07780;$$

In[7]:=

$$\texttt{b[i\_] := }\Omega_b \frac{R\ \texttt{Tc[[i]]}}{\texttt{pc[[i]]}};$$

In[8]:=

$$\begin{aligned}&\texttt{m[i\_] := If}\Big[\omega\texttt{[[i]]} \texttt{<=} 0.49,\ 0.37464 + 1.54226\ \omega\texttt{[[i]]} - 0.26992\ (\omega\texttt{[[i]]})^2,\\&\quad 0.3796 + 1.485\ \omega\texttt{[[i]]} - 0.1644\ \omega\texttt{[[i]]}^2 + 0.01667\ \omega\texttt{[[i]]}^3\Big];\end{aligned}$$

In[9]:=

$$\texttt{Tre[i\_] := }\frac{T}{\texttt{Tc[[i]]}}\texttt{; (* reduced temperature *)}$$

In[10]:=

$$\alpha\texttt{[i\_] := }\left(1 + \texttt{m[i]}\left(1 - \sqrt{\texttt{Tre[i]}}\right)\right)^2;$$

In[11]:=

$$\texttt{aTi[i\_] := ac[i] }\alpha\texttt{[i]};$$

In[12]:=

$$\texttt{aTij[i\_, j\_] := (1 - k[[i, j]])}\sqrt{\texttt{aTi[i] aTi[j]}};$$

In[13]:=

$$\begin{aligned}&\texttt{aTmix[f\_] := }\sum_{i=1}^{\texttt{Length[f]}}\sum_{j=1}^{\texttt{Length[f]}}\texttt{(f[[i]] f[[j]] aTij[i, j]) /. }\sqrt{\frac{\texttt{Pascal}^2}{\texttt{Meter}^4\ \texttt{Mole}^4}} \to \frac{\texttt{Pascal}}{\texttt{Meter}^2\ \texttt{Mole}^2}\\&\quad\texttt{(* Methematica cannot take roots of units so it has to be done manually *);}\end{aligned}$$

In[14]:=

$$\texttt{bmix[f\_] := }\sum_{j=1}^{\texttt{Length[f]}}\texttt{f[[j]] b[j];}$$

Setup Z - Factor Equation

```
In[15]:= A[f_] := aTmix[f] p/(R T)^2 /. Sqrt[Meter^12 Pascal^2/Mole^4] -> Meter^6 Pascal/Mole^2
           (* Methematica cannot take roots of units so it has to be done manually *);;
```

```
In[16]:= B[f_] := bmix[f] p/(R T);
```

```
In[17]:= Z[f_] := Z^3 - (1 - B[f]) Z^2 + (A[f] - 2 B[f] - 3 B[f]^2) Z - (A[f] B[f] - B[f]^2 - B[f]^3) == 0;
```

Setup Fugacity Expression

```
In[18]:= Af[f_, j_] := 1/aTmix[f] (2 Sqrt[aTi[j]] Sum[(f[[i]] Sqrt[aTi[i]] (1 - k[[i, j]])), {i, 1, Length[f]}]) /.
           1/Sqrt[Meter^12 Pascal^2/Mole^4] → 1/(Meter^6 Pascal/Mole^2);
```

```
In[19]:= Bf[f_, j_] := b[j]/bmix[f];
```

```
In[20]:= phi[f_, Z_, j_] :=
           Exp[-Log[Z - B[f]] + (Z - 1) Bf[f, j] - A[f]/(2 Sqrt[2] B[f]) (Af[f, j] - Bf[f, j]) Log[(Z + (Sqrt[2] + 1) B[f])/(Z - (Sqrt[2] - 1) B[f])]]
          (* fugacity coefficient *);
```

```
In[21]:= f[f_, phi_, j_] := f[[j]] * p * phi (* fugacity *);
```

Real Gas Law

```
In[22]:= Vm[Z_] := R T Z/p
```

```
In[23]:= RealGasLaw[Z_] := p V == n R T Z
```

Example 1: Single Component

```
In[24]:= (* from McCain "Properties of Petroleum Fluids", Example 15-1*)
```

Given

```
In[25]:= T = ConvertTemperature[190, Fahrenheit, Kelvin] Kelvin; (* input temperature *)
```

```
In[26]:= p = Convert[228.79 PoundForce/Inch^2, Pascal]; (* input pressure *)
```

```
In[27]:= components = {"i-C4"}; (* component names *)
```

```
In[28]:= z = {1}; (* input mole fractions in total mixture *)

In[29]:= len = Length[z]; (* number of components *)

In[30]:= Tc = {ConvertTemperature[734.13, Rankine, Kelvin] Kelvin}; (* critical temperatures *)

In[31]:= pc = {Convert[527.9 PoundForce/Inch^2, Pascal]}; (* critical pressure *)

In[32]:= R = 8.314472 (Meter^3 Pascal)/(Kelvin Mole); (* universal gas constant *)

In[33]:= ω = {0.1852}; (* acentric factor *)

In[34]:= k = {{0, 0}, {0, 0}}; (* binary interaction parameters *)

In[35]:= n = 1 Mole; (* number of mixture moles *)
```

Perform Calculations

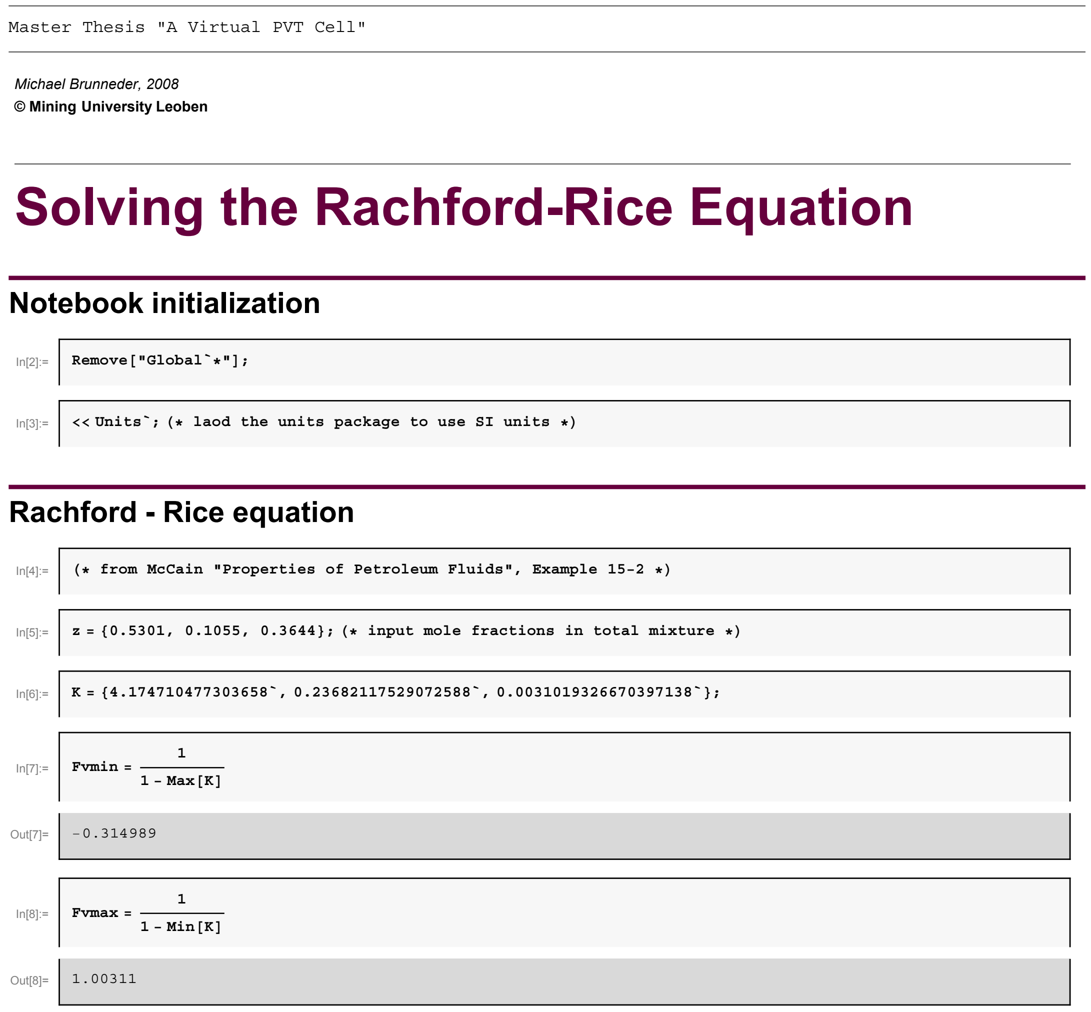
```
In[36]:= Tre[1]

Out[36]= 0.884952

In[37]:= b[1]

Out[37]= 0.0000724844 Meter^3/Mole

In[38]:= ac[1]

Out[38]= 1.44459 Meter^6 Pascal/Mole^2

In[39]:= α[1]

Out[39]= 1.07867

In[40]:= aTi[1]

Out[40]= 1.55824 Meter^6 Pascal/Mole^2

In[41]:= A[z]

Out[41]= 0.272948
```

```
In[42]:= B[z]

Out[42]= 0.0381018

In[43]:= ZFactors = Select[Z /. Solve[Z[z], Z], # ∈ Reals &]
          (* calculate Z-factors and take only real solutions *)

Out[43]= {0.0672587, 0.186786, 0.707854}

               T                    p
In[44]:= If[-------- ≥  1 && -------- ≥ 1, (* then *) phasestate = "supercritical",
            Tc[[1]]               pc[[1]]
           (* else *)
           If [Length[ZFactors] == 3, (* then *) Zliquid = Min[ZFactors];
            phiLiquid = phi[z, Zliquid, 1]; Zvapor = Max[ZFactors]; phiVapor = phi[z, Zvapor, 1];
            If [phiLiquid == phiVapor, phasestate = "two-phase",
             If[phiLiquid < phiVapor, phasestate = "liquid"; Z = Zliquid, phasestate = "vapor"; Z = Zvapor]],
            (* else *)
            If [Length[ZFactors] == 1, (* then *)Z = ZFactors[[1]];
                   Vm[Z]
             If [-------- ≤ 1.7, phasestate = "liquid", phasestate = "vapor"];, (* else *)]
                  bmix[z]
           ]
          ];
```

Compare Results

```
In[45]:= phasestate

Out[45]= liquid

                                                       PoundForce
In[46]:= liquidFugacity = Convert[f[z, phiLiquid, 1], ----------]
                                                         Inch^2

          176.772 PoundForce
Out[46]=  ------------------
               Inch^2

                                                     PoundForce
In[47]:= vaporFugacity = Convert[f[z, phiVapor, 1], ----------]
                                                       Inch^2

          176.79 PoundForce
Out[47]=  -----------------
              Inch^2
```

C.3. Rachford Rice



Master Thesis "A Virtual PVT Cell"

Michael Brunneder, 2008

Solving the Rachford-Rice Equation

Notebook initialization

In[2]:=
```
Remove["Global`*"];
```

In[3]:=
```
<< Units`; (* laod the units package to use SI units *)
```

Rachford - Rice equation

In[4]:=
```
(* from McCain "Properties of Petroleum Fluids", Example 15-2 *)
```

In[5]:=
```
z = {0.5301, 0.1055, 0.3644}; (* input mole fractions in total mixture *)
```

In[6]:=
```
K = {4.174710477303658`, 0.23682117529072588`, 0.0031019326670397138`};
```

In[7]:=
```
             1
Fvmin = ----------
        1 - Max[K]
```

Out[7]=
```
-0.314989
```

In[8]:=
```
             1
Fvmax = ----------
        1 - Min[K]
```

Out[8]=
```
1.00311
```

In[9]:=

$$\texttt{hFv[Fv\_] :=} \sum_{\texttt{i=1}}^{\texttt{Length[K]}} \frac{\texttt{z[[i]] (K[[i]] - 1)}}{\texttt{1 + Fv (K[[i]] - 1)}};$$

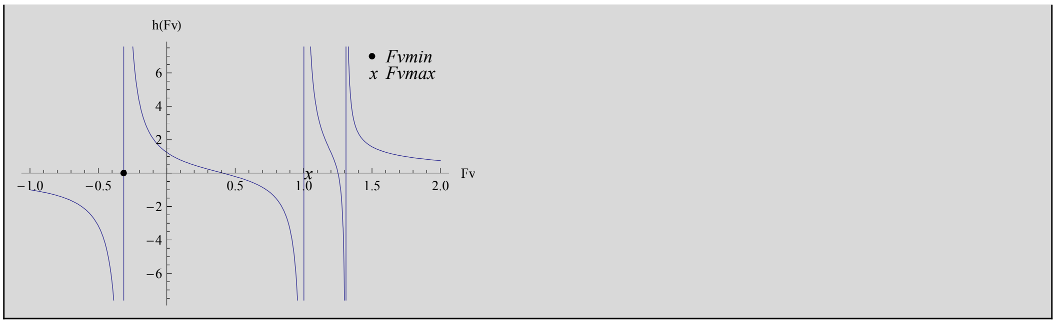
In[10]:=

$$\texttt{dhFv[Fv\_] := -} \sum_{\texttt{i=1}}^{\texttt{Length[K]}} \frac{\texttt{z[[i]] (K[[i]] - 1)}^2}{\texttt{(Fv (K[[i]] - 1) + 1)}^2};$$

```
In[11]:= f[x_] := hFv[x];
```

```
In[12]:= Plot[f[x], {x, -1, 2}, AxesLabel -> {"Fv", "h(Fv)"}, Epilog → {
            PointSize[.015],
            (* key *)
            {RGBColor[0, 0, 0], Point[{1.5, 7}]}, Text[Style["Fvmin", 12, Italic], {1.6, 7}, {-1, 0}],
            {RGBColor[0, 0, 0], Text[Style["x", 12, Italic], {1.48, 6}, {-1, 0}]},
            Text[Style["Fvmax", 12, Italic], {1.6, 6}, {-1, 0}],
            (* Fvmin *)
            RGBColor[0, 0, 0],
            Point[{Fvmin, 0}],
            (* Fvmax *)
            RGBColor[0, 0, 0],
            Text[Style["x", 12, Italic], {Fvmax, 0}, {-1, 0}]
           }]
         (* Rachford-Rice Function *)
```

Out[12]=



Solution with Newton - Raphson

```
In[13]:= f[x_] := hFv[x];
```

```
In[14]:= df[x_] := dhFv[x];
```

```
In[15]:= xn = 0;
```

```
In[16]:= xnew = 0.5;
```

In[17]:= `errorLimit = 1 * 10`$^{\texttt{-13}}$`;`

```
In[18]:= iterLimit = 100;
```

```
In[19]:= i = 1;
```

In[20]:=

```
While[Abs[xn - xnew] > errorLimit && i <= iterLimit,
  xn = xnew;
               f[xn]
  xnew = xn - ------;
               df[xn]
  Print["Iteration: ", i , " Fv=", xn];
  Print["absolute difference to last iteration: ", Abs[xn - xnew]];
  i++;
  ];
```

```
Iteration: 1 Fv=0.5

absolute difference to last iteration: 0.0850785

Iteration: 2 Fv=0.414922

absolute difference to last iteration: 0.00509237

Iteration: 3 Fv=0.409829

absolute difference to last iteration: 6.54428×10^-6

Iteration: 4 Fv=0.409823

absolute difference to last iteration: 9.79594×10^-12

Iteration: 5 Fv=0.409823

absolute difference to last iteration: 0.
```

Verify solution with built-in *Mathematica* method:

In[21]:=

```
FindRoot[hFv[Fv], {Fv, 0.5}]
```

Out[21]=

```
{Fv → 0.409823}
```

In[22]:=

```
Fv = xnew
```

Out[22]=

```
0.409823
```

Bibliography

[1] Emil J. Burcik. *Properties of Petroleum Reservoir Fluids.* International Human Resources Developement Corporation, 1979.

[2] GPSA. *Engineering Data Book*, volume I & II. Gas Processors Suppliers Association (GPSA), twelfth edition - fps edition, 2004.

[3] M.O. Friend D.G. Lemmon, E.W. McLinden. *"Thermophysical Properties of Fluid Systems" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69.* National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov edition, June 2005. retrieved on May 12, 2008.

[4] William D. McCain Jr. *The Properties of Petroleum Fluids.* Pennwell Books, second edition, 1990.

[5] D. B. Peng, D. Y. Robinson. A new-constant equation of state. *Ind. & Eng. Chem.*, 15, No. 1:59–64, 1976.

[6] Todd Rowland. Companion matrix. http://mathworld.wolfram.com/CompanionMatrix.html. From MathWorld–A Wolfram Web Resource, created by Eric W. Weisstein retrieved May 24,2008.

[7] Curtis H. Whitson and Michael R. Brulé. *Phase Behavior*, volume 20 of *SPE Monograph Series.* Society of Petroleum Engineers, 2000.

[8] G. M. Wilson. A modified redlich-kwong equation of state, aplication to general physical data calculations. paper 15c presented at the 1969 AIChE Natl. Meeting, Cleveland, Ohio.

Index