Logbook condensation cell experiments

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Published: 01/01/2013

Document Version
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

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LOGBOOK CONDENSATION CELL EXPERIMENTS

B.J.C. Ruijten

September 25, 2013
I Sensor calibration analysis 7

1 Absolute pressure sensor 8
  1.1 Calibration pressure transducer 8
  1.2 Calibration validation experiment 8
  1.3 Conclusion pressure transducer calibration 9

2 Gas chromatographer 10
  2.1 GC method one 10
  2.2 GC method two 11
  2.3 Conclusion GC calibrations 12

3 Thermocouples 14
  3.1 Icebath measurements 15
  3.2 Difference measurements GE Drück calibrator 16
    3.2.1 Experiment #1 16
    3.2.2 Experiment #2 18
    3.2.3 Conclusion difference measurements GE Drück calibrator 20
  3.3 Chiller bath measurements 20
    3.3.1 Experiment #1 20
    3.3.2 Thermocouple check 22
    3.3.3 Experiment #2 24
  3.4 Conclusions 26

II Equilibrium gas composition experiments 27

1 Introduction 28

2 Measurement setup 29

3 Measurement procedure 30
  3.1 Preparations 30
  3.2 Actual measurement procedure 30
  3.3 Closure of experiment 31

4 Measurement plan 32

5 Gas composition experiments 34
  5.1 Gas composition experiment number 1 34
    5.1.1 Data points 34
    5.1.2 Results 34
    5.1.3 Conclusion experiment 37
  5.2 Gas composition experiment number 2 37
5.5.3 Results .......................................................... 68
5.5.4 Conclusion experiment ................................. 70
5.6 Liquid composition experiment number 6 ......... 71
5.6.1 Data points .................................................. 71
5.6.2 Adjustment measurement procedure ............. 71
5.6.3 Results .......................................................... 71
5.6.4 Conclusion experiment ................................. 74
5.7 Liquid composition experiment number 7 .......... 74
5.7.1 Data points .................................................. 74
5.7.2 Results .......................................................... 74
5.7.3 Conclusion experiment ................................. 77
5.8 Liquid composition experiment number 8 .......... 77
5.8.1 Data points .................................................. 77
5.8.2 Adjustment measurement procedure ............. 77
5.8.3 Results .......................................................... 77
5.8.4 Conclusion experiment ................................. 81
5.9 Liquid composition experiment number 9 .......... 81
5.9.1 Data points .................................................. 81
5.9.2 Adjustments measurement setup ................. 81
5.9.3 Adjustment measurement procedure ............. 82
5.9.4 Results .......................................................... 82
5.9.5 Conclusion experiment ................................. 86
5.10 Liquid composition experiment number 10 ..... 86
5.10.1 Data points .................................................. 86
5.10.2 Results .......................................................... 86
5.10.3 Conclusion experiment ................................. 88
5.11 Liquid composition experiment number 11 ..... 89
5.11.1 Data points .................................................. 89
5.11.2 Adjustments measurement setup ................. 89
5.11.3 Adjustment measurement procedure ............. 89
5.11.4 Results .......................................................... 90
5.11.5 Conclusion experiment ................................. 92
5.12 Liquid composition experiment number 12 ..... 92
5.12.1 Data points .................................................. 92
5.12.2 Results .......................................................... 93
5.12.3 Conclusion experiment ................................. 95
5.13 Liquid composition experiment number 13 ..... 95
5.13.1 Data points .................................................. 95
5.13.2 Results .......................................................... 95
5.13.3 Conclusion experiment ................................. 99

6 Conclusion liquid composition experiments .......... 100

IV Fog formation experiments .............................. 102

1 Introduction .................................................... 103

2 Measurement set up ........................................... 104

3 Measurement procedure ................................... 106
3.1 Preparations .................................................. 106
3.2 Actual measurement procedure ....................... 107
3.3 Closure .......................................................... 107
4 Experiment approach

5 Initial fog formation experiments

5.1 Initial fog formation experiment number 1

5.1.1 Experiment approach .................................................. 109
5.1.2 Experiment results ..................................................... 109
5.1.3 Experiment conclusion .................................................. 111

5.2 Initial fog formation experiment number 2

5.2.1 Experiment approach ..................................................... 112
5.2.2 Experiment conclusion .................................................. 112

6 Background analysis experiments

6.1 Obscuration experiment number 1

6.1.1 Experiment approach ...................................................... 113
6.1.2 Experiment results ....................................................... 113
6.1.3 Conclusion experiment .................................................... 116

6.2 Obscuration experiment number 2

6.2.1 Experiment approach ...................................................... 116
6.2.2 Conclusion experiment .................................................... 117

6.3 Obscuration experiment number 3

6.3.1 Measurement procedure adjustments .................................. 117
6.3.2 Experiment approach ...................................................... 117
6.3.3 Experiment results ....................................................... 118
6.3.4 Conclusion experiment .................................................... 121

6.4 Obscuration experiment number 4

6.4.1 Experiment approach ...................................................... 122
6.4.2 Experiment results ....................................................... 122
6.4.3 Conclusion experiment .................................................... 122

6.5 Obscuration experiment number 5

6.5.1 Measurement setup adjustments ....................................... 124
6.5.2 Experiment approach ...................................................... 124
6.5.3 Experiment results ....................................................... 125
6.5.4 Conclusion experiment .................................................... 126

6.6 Obscuration experiment number 6

6.6.1 Experiment approach ...................................................... 126
6.6.2 Experiment results ....................................................... 127
6.6.3 Conclusion experiment .................................................... 128

6.7 Obscuration experiment number 7

6.7.1 Experiment approach ...................................................... 128
6.7.2 Experiment results ....................................................... 128
6.7.3 Conclusion experiment .................................................... 129

6.8 Summary background experiments ....................................... 130

7 Spraytec fog formation experiments

7.1 Spraytec fog formation experiment 1 .................................... 135
7.1.1 Experiment approach ...................................................... 135
7.1.2 Experiment results ....................................................... 135
7.1.3 Conclusion experiment .................................................... 138

7.2 Spraytec fog formation experiment 2 ................................... 140
7.2.1 Experiment approach ...................................................... 140
7.2.2 Experiment results ....................................................... 140
7.2.3 Conclusion experiment .................................................... 147

7.3 Spraytec fog formation experiment 3 ................................... 148
7.3.1 Experiment approach ...................................................... 148
## Overview of Experiments in Condensation Cell

<table>
<thead>
<tr>
<th>Date</th>
<th>Experiment type</th>
<th>Part Logbook</th>
<th>Section Logbook</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 January 2013</td>
<td>Gas chromatographer: Cal</td>
<td>I</td>
<td>2.1</td>
</tr>
<tr>
<td>17 January 2013</td>
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<td>II</td>
<td>5.1</td>
</tr>
<tr>
<td>21 January 2013</td>
<td>Gas eq composition: Temperature is constant</td>
<td>II</td>
<td>5.2</td>
</tr>
<tr>
<td>22 January 2013</td>
<td>Gas eq composition: Temperature is constant</td>
<td>II</td>
<td>5.3</td>
</tr>
<tr>
<td>23 January 2013</td>
<td>Gas eq composition: Temperature is constant</td>
<td>II</td>
<td>5.4</td>
</tr>
<tr>
<td>22 February 2013</td>
<td>Thermocouples: Ice bath</td>
<td>I</td>
<td>3.1</td>
</tr>
<tr>
<td>25 February 2013</td>
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<td>I</td>
<td>3.1</td>
</tr>
<tr>
<td>25 February 2013</td>
<td>Thermocouples: GE Druck calibrator</td>
<td>I</td>
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<tr>
<td>5 March 2013</td>
<td>Pressure transducer: GE Druck calibrator</td>
<td>I</td>
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<tr>
<td>8 March 2013</td>
<td>Gas eq composition: Temperature is constant</td>
<td>II</td>
<td>5.5</td>
</tr>
<tr>
<td>19 March 2013</td>
<td>Liquid eq composition: Temperature is constant</td>
<td>III</td>
<td>5.1</td>
</tr>
<tr>
<td>20 March 2013</td>
<td>Liquid eq composition: Temperature is constant</td>
<td>III</td>
<td>5.2</td>
</tr>
<tr>
<td>23 March 2013</td>
<td>Gas chromatographer: Calibration</td>
<td>I</td>
<td>2.2</td>
</tr>
<tr>
<td>25 March 2013</td>
<td>Thermocouples: GE Druck calibrator</td>
<td>I</td>
<td>3.2.2</td>
</tr>
<tr>
<td>26 March 2013</td>
<td>Thermocouples: Chiller bath</td>
<td>I</td>
<td>3.3</td>
</tr>
<tr>
<td>27 March 2013</td>
<td>Liquid eq composition: Temperature is constant</td>
<td>III</td>
<td>5.3</td>
</tr>
<tr>
<td>2 April 2013</td>
<td>Thermocouples: Chiller bath</td>
<td>I</td>
<td>3.3</td>
</tr>
<tr>
<td>4 April 2013</td>
<td>Thermocouples: Eurotherm calibrator</td>
<td>I</td>
<td>3.3.2</td>
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<tr>
<td>4 April 2013</td>
<td>Thermocouples: Chiller bath</td>
<td>I</td>
<td>3.3</td>
</tr>
<tr>
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<td>I</td>
<td>3.3.2</td>
</tr>
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<td>Thermocouples: Chiller bath</td>
<td>I</td>
<td>3.3</td>
</tr>
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<td>I</td>
<td>3.3</td>
</tr>
<tr>
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<td>III</td>
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<td>III</td>
<td>5.7</td>
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<td>III</td>
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<td>III</td>
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<td>III</td>
<td>5.10</td>
</tr>
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<td>3 May 2013</td>
<td>Liquid eq composition: Pressure is constant</td>
<td>III</td>
<td>5.11</td>
</tr>
<tr>
<td>6 May 2013</td>
<td>Liquid eq composition: Pressure is constant</td>
<td>III</td>
<td>5.12</td>
</tr>
<tr>
<td>7 May 2013</td>
<td>Liquid eq composition: Temperature is constant</td>
<td>III</td>
<td>5.13</td>
</tr>
<tr>
<td>21 May 2013</td>
<td>Initial fog formation</td>
<td>IV</td>
<td>5.1</td>
</tr>
<tr>
<td>22 May 2013</td>
<td>Initial fog formation</td>
<td>IV</td>
<td>5.2</td>
</tr>
<tr>
<td>27 May 2013</td>
<td>Background analysis</td>
<td>IV</td>
<td>6.1</td>
</tr>
<tr>
<td>28 May 2013</td>
<td>Background analysis</td>
<td>IV</td>
<td>6.2</td>
</tr>
<tr>
<td>30 May 2013</td>
<td>Background analysis</td>
<td>IV</td>
<td>6.3</td>
</tr>
<tr>
<td>3 June 2013</td>
<td>Background analysis</td>
<td>IV</td>
<td>6.4</td>
</tr>
<tr>
<td>4 June 2013</td>
<td>Background analysis</td>
<td>IV</td>
<td>6.5</td>
</tr>
<tr>
<td>10 June 2013</td>
<td>Background analysis</td>
<td>IV</td>
<td>6.6</td>
</tr>
<tr>
<td>11 June 2013</td>
<td>Background analysis</td>
<td>IV</td>
<td>6.7</td>
</tr>
<tr>
<td>17 June 2013</td>
<td>Spraytec fog formation</td>
<td>IV</td>
<td>7.1</td>
</tr>
<tr>
<td>19 June 2013</td>
<td>Spraytec fog formation</td>
<td>IV</td>
<td>7.2</td>
</tr>
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<td>Spraytec fog formation</td>
<td>IV</td>
<td>7.3</td>
</tr>
<tr>
<td>24 June 2013</td>
<td>Spraytec fog formation</td>
<td>IV</td>
<td>7.4</td>
</tr>
<tr>
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<td>Camera fog formation</td>
<td>IV</td>
<td>8.1</td>
</tr>
<tr>
<td>15 July 2013</td>
<td>Camera fog formation background</td>
<td>IV</td>
<td>8.2</td>
</tr>
<tr>
<td>19 August 2013</td>
<td>Spraytec fog formation by expansion</td>
<td>IV</td>
<td>9</td>
</tr>
</tbody>
</table>
Part I

Sensor calibration analysis
Chapter 1

Absolute pressure sensor

The pressure transducer in the measurement setup is a Swagelock standard industrial pressure transducer with a span of 0-100 bar, which is connected to a NI module 9203[9].

1.1 Calibration pressure transducer

A pressure calibration is done with a GE Drück calibrator DPI 620 which is mounted at the top of the condensation cell. Pressures starting at ambient pressure with steps of 7 bar are set in the condensation cell with pure N₂ gas. The signal of the GE Drück calibrator DPI 620 is taken as reference, which accuracy in pressure calibration is about 0.0025 % rdg[8, 7]. The non reference value is averaged over 20 samples which are averaged values over a 5 sec time span of the pressure transducer signal at manufacture settings. In Table 1.1 the calibration report is given. The difference between the model is calculated by subtracting the reference values from the measured values. The overall mean squared error of the calibration is 0.068 bar². The difference has the tendency to increase for higher pressures.

Table 1.1: Calibration report

<table>
<thead>
<tr>
<th>Calibration point</th>
<th>$P_{\text{meas}}$ [bar]</th>
<th>$P_{\text{ref}}$ [bar]</th>
<th>Difference [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>1.150</td>
<td>1.134</td>
<td>0.017</td>
</tr>
<tr>
<td>#2</td>
<td>8.153</td>
<td>8.084</td>
<td>0.070</td>
</tr>
<tr>
<td>#3</td>
<td>16.225</td>
<td>16.133</td>
<td>0.092</td>
</tr>
<tr>
<td>#4</td>
<td>23.113</td>
<td>23.337</td>
<td>-0.224</td>
</tr>
<tr>
<td>#5</td>
<td>30.313</td>
<td>30.557</td>
<td>-0.244</td>
</tr>
<tr>
<td>#6</td>
<td>38.448</td>
<td>38.962</td>
<td>-0.513</td>
</tr>
<tr>
<td>#7</td>
<td>47.030</td>
<td>47.334</td>
<td>-0.304</td>
</tr>
</tbody>
</table>

1.2 Calibration validation experiment

The calibration error is determined for two cases. In the first case, the pressure transducer is operating without calibration, so when it works at manufacture settings. In the second case, the pressure transducer is operating with calibration. In order to find the calibration error of the cases difference measurements are done.

A GE Drück calibrator DPI 620 is mounted at the condensation cell. Pure N₂ gas is fed to the condensation cell. Various pressures at the ambient temperature from 1 till 50 bar with steps of 7 bar are set in the cell. For each case the signal of the pressure transducer is compared to the
1. Absolute pressure sensor

The signal of the GE Drück calibrator, which difference is depicted at various pressures in Figure 1.1. The signal of the GE Drück calibrator is used as reference signal.

![Figure 1.1: Absolute difference between experiments and reference versus pressure](image)

Table 1.2: Error analyses difference measurements

<table>
<thead>
<tr>
<th>$\epsilon_m$ [bar]</th>
<th>$\sigma_{\epsilon_m}$ [bar]</th>
<th>$\epsilon_{mc}$ [bar]</th>
<th>$\sigma_{\epsilon_{mc}}$ [bar]</th>
<th>$MSE_m$ [bar$^2$]</th>
<th>$MSE_{mc}$ [bar$^2$]</th>
<th>Ratio $MSE$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.1961</td>
<td>0.2464</td>
<td>-0.0215</td>
<td>0.1446</td>
<td>0.0916</td>
<td>0.0184</td>
<td>4.9784</td>
</tr>
</tbody>
</table>

The mean error before calibration ($\epsilon_m$) is about 0.2 bar and the mean square error ($MSE_m$) is 0.1. After the calibration the mean error ($MSE_{mc}$) is 0.02 bar. The mean square error is improved by a factor five. The standard deviation of the first measurement ($\sigma_{\epsilon_m}$) is about 0.25 bar and the second measurement ($\sigma_{\epsilon_{mc}}$) 0.15 bar. The signal of the pressure transducer fluctuates periodically around the mean. During the difference measurements the pressure was increased to above 50 bar. When the 50 bar was reached the pressure relief safety went open in order to reduce the pressure in the cell. The pressure relief safety is manufactured at a pressure of 50 bar. So in the cell no pressure higher than 50 bar can be reached. Although without the pressure relief the condensation cell can withstand 70 bar [11].

1.3 Conclusion pressure transducer calibration

The pressure transducer is calibrated with a GE Drück calibrator DPI 620, which is denoted as reference signal. The pressure transducer signal itself is the non reference signal in the Labvies calibration wizard. The overall mean squared error of the calibration is 0.068 bar$^2$. After the calibration two difference measurements were done. One experiment with disabled calibration and one experiment with enabled calibration. The mean squared error is reduced with a factor five when the calibration is enabled. When the pressure is higher than 47 bar the calibration gives a discontinuity error, because in the calibration experiment 47 bar is the highest point. However this will not be a problem for future experiments, because a pressure higher than 45 bar is not desired in this research. Moreover the condensation cell is limited to a pressure of 50 bar.
Chapter 2

Gas chromatographer

The gas chromatographer is a Varian micro GC 4900[1] which is controlled with the software package Prostation. Calibrations have to be performed in order to get reliable results. The calibrations are used to produce a so-called method. A method is a quadratic fit through calibration points. Calibration points are provided by gas calibration bottles, which compositions are the reference values of the method. The method can consist of single point calibration or multi point calibration. By a multi point calibration an amount x of chromatographies are taken to create a distribution around that single point. A multi point calibration is more accurate due to the fact that the sensors behavior is much more included into the method. In the following sections two methods will be discussed. The first method is be used for equilibrium gas composition experiments. The second method is be used for equilibrium liquid composition experiments.

2.1 GC method one

A multi point calibration for three calibration gas cylinders is used to create this method. The three calibration gas cylinders have a predefined composition of respectively 25.0, 50.3 and 74.8 \% CO$_2$, which are used as reference values. Each gas cylinder is mounted to the entrance of the GC. Gas is fed to the GC in order to analyze the gas composition. The GC analyzes the amount of CO$_2$ and the amount of N$_2$ in the gas in terms of peak areas, which are depicted in chromatographies. The area of a peak corresponds to a certain composition. In this case two peaks will be measured and the areas under the peaks are linked to the reference values of the gas bottles.

In the first chromatographies the gas is contaminated with impurities in the system. Eventually the impurities are removed. A GC run of about 80 chromatographies is done for each calibration bottle. For each calibration bottle the last 5 chromatographies are used for creating a quadratic fit, which is processed by the program Prostation itself.

In Figure 2.1 the quadratic fit and the calibration points are shown. The five selected chromatographies have the same reference value but each measured peak area differs in the calibration points. A larger sample size around a calibration point gives a higher goodness of the fit.
2.2 GC method two

The method discussed in the previous subsection can not be used for liquid composition experiments, because it does not contain a reference point at high CO$_2$ concentrations. Therefore a multi point calibration for four calibration gas cylinders is used to create this new method. The four calibration gas cylinders have a predefined composition of respectively 25.0, 50.3, 74.8 and 99.99 % CO$_2$, which are used as the reference values. For each gas cylinder the composition is analyzed in terms of peak areas which is related to the mole concentration in the measured sample.

In the first chromatographies the gas is contaminated with impurities in the system. Eventually the impurities are removed. A GC run of about 80 chromatographies is done for each calibration bottle. For each calibration bottle the 5 chromatographies are used for creating a quadratic fit. The 5 chromatographies are selected by hand in order to include the fluctuations of the GC signal. In Figure 2.2 the quadratic fit and the calibration points are shown.
2.3 Conclusion GC calibrations

Two calibration procedures are done in order to create two methods. The first discussed method is used in gas composition experiments. This method can not be used during liquid composition experiments, because it does not contain a high CO$_2$ reference value. So a new method is created. In Table 2.1 the coefficients of the quadratic fits are given.

Table 2.1: Coefficients fits of methods GC with fit: $y = ax^2 + bx + c$

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Method 1</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-1.109481443322e-11</td>
<td>-4.66982323700651e-12</td>
</tr>
<tr>
<td>b</td>
<td>8.58907574210584e-05</td>
<td>7.76053163677979e-05</td>
</tr>
<tr>
<td>c</td>
<td>-1.89986556132579</td>
<td>-8.628221311467539e-02</td>
</tr>
</tbody>
</table>

For each method the error in the calibration fit is calculated. The residual sum of squares (RSS) is calculated with Equation 2.1, which is the sum of the squares of the residuals.

$$RSS = \sum_{i=1}^{n} (y_i - (ax_i^2 + bx_i + c))^2$$  \hspace{1cm} (2.1)

$$\sigma = \sqrt{\frac{RSS}{n-p}}$$  \hspace{1cm} (2.2)

With \( n \) the total amount of calibration points, \( y_i \) the CO$_2$ concentration reference value of point \( i \), \( x_i \) the area of point \( i \) and \( a, b, c \) the fit coefficients. The root mean squared error is calculated with Equation 2.2. The RSS is divided by total amount of calibration points minus the amount of model parameters (\( p \)). \( p \) is in this case 3, because the calibration fit is a second order fit. The root is taken to get the RMSE also known as the standard deviation. In Table 2.2 the calibration error of the methods are depicted.
Table 2.2: Calibration error of both methods

<table>
<thead>
<tr>
<th>Method</th>
<th>RMSE fit [% mole]</th>
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<tbody>
<tr>
<td>Method 1</td>
<td>0.2866</td>
</tr>
<tr>
<td>Method 2</td>
<td>0.5063</td>
</tr>
</tbody>
</table>

The calibration error of method 1 is much smaller than the calibration error of method 2, which is caused by the selection of calibration points. In method 1 the last 5 chromatographies are used. In method 2 5 chromatographies are taken that cover the fluctuations of the signal. Apparently in method 1 the selected chromatographies do not cover the full extent of the GCs fluctuations. The relative standard deviation of the GC is about 0.1-1% [5]. In these cases the calibration errors are in the range of the predefined GC relative standard deviation, so the errors in the calibrations are in accordance with the prescribed relative errors.
Chapter 3
Thermocouples

The six thermocouples in the measurement setup are T-type thermocouples, which are copper-
constanten thermocouples. The range of such a thermocouple for short duration is -250 to 400 °C
and for long duration the range is -185 to 300 °C. The tolerance of the thermocouples is 1 °C for a
range of -40 to 135 °C[3]. For lower temperatures the accuracy is not given. The measurements are
typically done at a temperature range between -55 and -40 °C, so it is assumed that the tolerance
of 1 °C also holds for this specific temperature range.

The thermocouples are connected to a NI 9211 module. The error of the module for a T-type
thermocouple is depicted in Figure 3.1[6]. The error comprises of gain errors, offset errors, noise
errors, isothermal errors, quantization errors, cold junction temperature errors, differential and
integral nonlinearity errors. The cold junction temperature compensation (CJC) of the thermo-
couples is not known. It is automatically been measured by an internal channel in the NI 9211
module. The maximum error in the cold junction temperature is 1.7 °C. The maximum error at
room temperature is given by the dashed line in Figure 1.2, because the auto zero function is not
used. The typical working temperature of the measurement is -50 °C, so the maximum error is
2.3 °C.

The thermocouples were not calibrated. The thermocouples were used at production settings. Ice
bath measurements are done in order to determine the relative difference between the thermo-
couples, which is discussed in subsection 3.1. The relative difference between thermocouples is
measured with a GE Drück calibrator and if possible calibration is performed.

3.1 Icebath measurements

The thermocouples are positioned in a bath filled with ice and water to get a temperature of 0°C. The thermocouples are tapped together to measure the same local temperature in the bath. The thermocouple signals are compared to each other by subtracting the signals from the reference signal. The thermocouple positioned in the lower part of the cell is the reference signal.

The initial results showed a temperature difference between thermocouples when thermocouples were in a different position. When a thermocouple was moved in the bath, the signal changed significantly. The ice bath had not a uniform temperature. The bottom and walls of the small bath were not 0°C due to heat transfer from the ambient to the bath. Moreover the thermocouples have different lengths, which results in different conduction and radiation properties. The thermocouples with a length of 10 cm with only the tip in the ice water give a higher temperature due to conduction and radiation of heat to the tip. So these initial results are not useful for the error analyses.

New ice bath measurements were done. This time the ice bath is put in another ice bath to get uniform bottom and wall temperatures. In order to get less temperature fluctuations the total setup is covered with insulation material. The thermocouples are tapped together and positioned in the ice bath. Again the signals are compared by subtracting the signals from the reference signal, which is the thermocouple positioned in the lower part of the cell. In Figure 3.2 the difference between the thermocouples is given for three ice bath measurements. In Figure 3.3 and in Figure 3.4 the difference between thermocouples along a number of samples for respectively measurement 2 and measurement 3 are given.

![Figure 3.2: Difference between thermocouples with thermocouple in the lower part of the cell as reference](image-url)
3. Thermocouples

3.2. Difference measurements GE Drück calibrator

The first ice bath temperature differences deviate from the other two measurements. The difference between the second and third ice bath measurements are rather small. Only the difference for the thermocouple at the chiller coolant outlet differ 0.15°C. In measurement 2 a lot of fluctuations in the signal occur. The signals cross each other, so the difference measurement is compromised due to a non uniform bath temperature and heat transfer in the thermocouples. The ice bath measurements are not reliable to determine the relative errors between the thermocouples.

3.2 Difference measurements GE Drück calibrator

In this subsection difference experiments with the GE Drück calibrator and calibration of the thermocouples are discussed.

3.2.1 Experiment #1

A GE Drück calibrator is attached to the NI 9211 module instead of the thermocouples. The GE Drück calibrator is used for simulating a thermocouple. The output signal is subtracted from the input signal to calculate the errors of the thermocouples. The GE Drück calibrator can simulate only one thermocouple at the same time. The set points for the GE Drück calibrator are listed in Table 3.1. The sample size for each set point is about 100 samples. The GE Drück calibrator CJC is set at automatic like the CJC in Labview.

<table>
<thead>
<tr>
<th>Setpoint number</th>
<th>Temperature set point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>-150</td>
</tr>
<tr>
<td>#2</td>
<td>-100</td>
</tr>
<tr>
<td>#3</td>
<td>-75</td>
</tr>
<tr>
<td>#4</td>
<td>-50</td>
</tr>
<tr>
<td>#5</td>
<td>-25</td>
</tr>
<tr>
<td>#6</td>
<td>0</td>
</tr>
<tr>
<td>#7</td>
<td>25</td>
</tr>
<tr>
<td>#8</td>
<td>50</td>
</tr>
<tr>
<td>#9</td>
<td>100</td>
</tr>
</tbody>
</table>

In Table 3.1: Set points for the GE Drück calibrator

In Figure 3.5 the difference of the measured value versus actual value before calibration is given. The error decreases for all sensors when there is an increase in temperature. The purge thermo-
3. Thermocouples  

3.2. Difference measurements GE Drück calibrator

![Graph of temperature deviation](image)

Figure 3.5: Difference of the measured value versus actual value before calibration

Couple deviates more than the other sensors. Between these sensors the error are similar. All sensors measured a lower temperature than the expected temperature.

In order to reduce the errors of the thermocouples the thermocouples are calibrated with the GE Drück calibrator. The set points of the GE Drück calibrator (Table 3.1) are the reference values. The non reference values are generated with a sample rate of 200 Hz and a sample size of 50.

After the calibrations the difference measurement was performed again to check if the accuracies of the thermocouples were improved. The set points of the GE Drück calibrator are given in Table 3.1. Except for set point number 3, because this set point is not in the range of future experiments. The difference measurement after calibration is depicted in Figure 3.6. The errors for the lower temperatures are positioned above the reference line indicating that the measured temperatures were higher than the expected temperatures. The error decreases with increasing temperature. For room temperature the error is close to zero.
3. Thermocouples 3.2. Difference measurements

GE Drück calibrator

![Graph showing difference measured value versus actual value after calibration]

Figure 3.6: Difference measured value versus actual value after calibration

Table 3.2: Error analyses difference measurements

<table>
<thead>
<tr>
<th>Thermocouple position</th>
<th>$c_m$ [°C]</th>
<th>$c_{mc}$ [°C]</th>
<th>$MSE_m$ [°C²]</th>
<th>$MSE_{mc}$ [°C²]</th>
<th>Ratio $MSE$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper part cell</td>
<td>-0.4277</td>
<td>0.2200</td>
<td>0.3018</td>
<td>0.1636</td>
<td>1.8454</td>
</tr>
<tr>
<td>Lower part cell</td>
<td>-0.3109</td>
<td>0.1332</td>
<td>0.1716</td>
<td>0.0788</td>
<td>2.1785</td>
</tr>
<tr>
<td>Inlet cell</td>
<td>-0.3366</td>
<td>0.0748</td>
<td>0.2255</td>
<td>0.0269</td>
<td>8.3885</td>
</tr>
<tr>
<td>Purge</td>
<td>-0.5857</td>
<td>0.1341</td>
<td>0.6697</td>
<td>0.0672</td>
<td>9.9713</td>
</tr>
<tr>
<td>Coolant in</td>
<td>-0.3557</td>
<td>0.0746</td>
<td>0.2641</td>
<td>0.0167</td>
<td>15.8365</td>
</tr>
<tr>
<td>Coolant out</td>
<td>-0.3853</td>
<td>0.0771</td>
<td>0.2637</td>
<td>0.0209</td>
<td>12.5982</td>
</tr>
</tbody>
</table>

In Table 3.2 the mean error, mean square error (MSE) and the ratio of the MSE of the difference measurements are given. The errors for all thermocouples were reduced. Regarding the MSE ratio, the errors of the thermocouples positioned at the coolant flow were reduced by factor of more than twelve. The MSE reduction for the thermocouples in the cell is about 2, which is a mediocre reduction in comparison with the other thermocouples, especially because the thermocouples in the condensation cell are the most important ones considering their use in the data processing.

3.2.2 Experiment #2

The difference measurements are repeated in order to check if the differences uphold when the measurements are repeated. A GE Drück calibrator is attached to the NI 9211 module instead of the thermocouples. The output signal is subtracted from the input signal to calculate the errors of the thermocouples. The sample size for each set point is about 100 samples. The GE Drück calibrator CJC is set at automatic like the CJC in Labview. This procedure is used for calibration disabled (Figure 3.7) and for calibration enabled (Figure 3.8).

The differences in Figure 3.7 are larger than the differences in Figure 3.8. The temperature offset is about 0.5 °C. The differences drop for increasing temperatures, but the result is that the differences are larger than in the previous experiments. The differences in Figure 3.8 are not consistent with the differences in Figure 3.6 in which the differences for all thermocouples were almost zero at high
3. Thermocouples

3.2. Difference measurements GE Drück calibrator

Figure 3.7: Check measurement: Difference measured value versus actual value with calibration disabled

Figure 3.8: Check measurement: Difference measured value versus actual value with calibration enabled

temperatures. In Figure 3.8 the differences of the thermocouples are not in accordance with each other. Moreover the upper part thermocouple error is positive, but the other thermocouples give negative errors. The tendency of the errors is that the errors decrease with increasing temperature.
3. Thermocouples

3.2.3 Conclusion difference measurements GE Drück calibrator

The check measurements are not consistent with the calibration difference measurements. Significant difference exists which is the consequence of wrong CJC compensations. In Figure 3.9 a schematic overview of the working principle between the GE Drück calibrator and the DAQ module 9211 is shown. A set temperature ($T_s$) is the input of the GE Drück calibrator. The CJC of the GE Drück calibrator is determined automatically and it is subtracted from the set temperature. Then the temperature is converted into millivolt which is defined by thermoelectric properties of the thermocouple. The millivolts are converted in the DAQ module 9211 to a temperature which still have to be corrected. Then the DAQ CJC is applied to the signal resulting in an output temperature.

![Figure 3.9: Schematic overview working principle GE Drück calibrator with DAQ module 9211](image)

Basically the difference measurements are measurements that measures the differences between the DAQ CJC and GE Drück calibrator CJC. The DAQ CJC differs constantly and it is dependent on the ambient temperature and the heat transfer in the module itself. If Figure 3.5 and Figure 3.7 are compared to each other the difference between the measurements is basically the difference in CJC values of the equipment. So the calibration performed with the calibrator can not be used due to the fact that the unknown DAQ CJC calibration value is not the same as the DAQ CJC value during future experiments. The results depicted in Figure 3.5 and Figure 3.7 show that the error decreases for increasing temperature, which is exactly what Figure 3.1 depicts. The DAQ error decreases for increasing temperature. The working principle of the DAQ is validated in this case.

3.3 Chiller bath measurements

The determination of relative errors is not succeeded by ice bath measurements and by calibration measurements with a calibrator. The relative differences between thermocouples have to be constant for the whole temperature domain, which is the consequence of the thermoelectric properties of the thermocouple. The ice bath is replaced with a liquid cooling bath of the 'small' chiller. The temperature of the cooling bath can be controlled with the control panel of the small chiller from $-30\, ^\circ C$ till $50\, ^\circ C$. The cooling liquid in the bath is glycol which gives a slightly different heat transfer when in contact with the thermocouples, but this effect is neglected. The thermocouples are taped on a small block of wood so that the thermocouples tips are positioned at the same height. The tips are positioned in the liquid bath, which is covered with insulation material to reduce heat transfer effect from the ambient.

3.3.1 Experiment #1

The relative errors are evaluated at two temperatures: ambient temperature and $-15\, ^\circ C$. At ambient temperature the thermocouples are positioned in a box, which is closed in order to reduce the convective heat transfer in the ambient air. The temperature of $-15\, ^\circ C$ is generated by the chiller bath in which the thermocouples are positioned with their tips in the cooling liquid. The cooling cycle of the chiller bath has a periodical tendency (Figure 3.10). The cooling cycle has an amplitude of $1\, ^\circ C$. The steep increase of the tendency is a consequence of that the chiller does not cool the bath until a certain offset of the set point is reached. Then the bath starts to cool.
the bath until its lower limit is reached and the cycle is repeated. When looking at the close up of Figure 3.10 the thermocouples signals will cross each other during the heating cycle part. The thermal responses of the thermocouples are different. Moveover the thermal response time of a 3 mm ungrounded thermocouple is about 0.525s [4]. The different lengths of the thermocouples also have influence on the thermal response due to the heat transfer in the thermocouples shaft. The main conclusion here is that due to the different thermal responses and slow responses it is not possible to perform accurate supersaturation measurements. In super saturation measurements the thermal response times have to be identical in order to compare. These response times have to be very fast due to the non equilibrium state in the cell.

\[ 0.525s \]

Figure 3.10: Temperature chiller bath according to six thermocouples

![Overall graph](image1)

![Close-up of graph](image2)

Figure 3.11: Difference thermocouples displayed on temperature set point

The differences between the thermocouples with the thermocouple in the lower part of the cell as
3. Thermocouples

3.3. Chiller bath measurements

The differences at ambient error are in a range of ±0.1 °C and they are much smaller than the difference at -15 °C. It seems like the relative differences increases at lower temperatures, but the theory states that the relative differences are constant. An extra measurement is done in order to gain more evidence. This time the relative errors are evaluated at 4 temperatures: ambient temperature, 0 °C, -15 °C and -30 °C. The measurement procedure is the same as described in the previous paragraph. The differences between the thermocouples with the thermocouple in the lower part of the cell as reference are displayed on its temperature set point in Figure 3.11. The results depicted in Figure 3.11 are also included in Figure 3.12.

![Figure 3.12: Difference thermocouples displayed on temperature set point](image)

The differences between the thermocouples at -15 °C are not in accordance with each other. For example, the purge thermocouple differs in one measurement 0.1 °C from the lower part thermocouple and in the second measurement 0.45 °C, which is theoretically not possible. The differences have to be the same at least at the same temperature. It was stated that the relative differences increase at lower temperatures, which is not confirmed in this measurement, because the quantity of the errors at -30 °C is in accordance with the quantity of the errors at -15 °C. The main conclusion is that the errors are not in accordance with previous experiments nor the theory. There must be problems in the thermocouple chain, which might be that the thermocouples are broke, the DAQ module is not working properly or the settings in Labview are wrong. Each component in the thermocouple chain has to be checked, starting with the thermocouples.

3.3.2 Thermocouple check

The thermocouples were connected one by one to a Eurotherm memocal 2000 calibrator in order to check if all thermocouples are working properly. The Eurotherm memocal 2000 calibrator has an accuracy of 0.045% in the range of -200°C to 0 °C for a T-type thermocouple [2]. The thermocouples were positioned in the small chiller bath covered with insulation material. The temperature of the bath was set at 0 °C, but in reality the periodically cooling and heating of the
bath was accomplished to maintain an average temperature of zero degrees. In Figure 3.10 the cooling cycle of the bath was given, which was periodically. For each thermocouple the millivolts were measured by the Eurotherm. Each thermocouple is measured during five cooling cycles, the upper and lower bounds are noted. So for every thermocouple ten samples (in mV) are measured and averaged for data processing. No CJC values are included in this experiment. This experiment is repeated three times. The remaining thermocouples are connected to the DAQ in order to give an indication when the maximum and minimum bath temperature will occur. Fluctuations of the bath are between $-0.4\, ^\circ C$ till $0.6\, ^\circ C$ degrees, these maximum and minimum values are not always reached. Thermocouple measuring order per experiment:

- **Experiment 1:**
  1. Thermocouple in upper part cell
  2. Thermocouple in lower part cell
  3. Thermocouple in inlet cell
  4. Thermocouple in purge system
  5. Thermocouple in outlet cooling liquid cell
  6. Thermocouple in inlet cooling liquid cell

- **Experiment 2:**
  1. Thermocouple in upper part cell
  2. Thermocouple in lower part cell
  3. Thermocouple in inlet cell
  4. Thermocouple in purge system
  5. Thermocouple in outlet cooling liquid cell
  6. Thermocouple in inlet cooling liquid cell

- **Experiment 3:**
  1. Thermocouple in outlet cooling liquid cell
  2. Thermocouple in upper part cell
  3. Thermocouple in inlet cooling liquid cell
  4. Thermocouple in lower part cell
  5. Thermocouple in purge system
  6. Thermocouple in inlet cell

- **Experiment 4:**
  1. Thermocouple in lower part cell
  2. Thermocouple in purge system
  3. Thermocouple in inlet cell
  4. Thermocouple in upper part cell
  5. Thermocouple in inlet cooling liquid cell
  6. Thermocouple in outlet cooling liquid cell

In Figure 3.13 the results are given. Experiment 2 was conducted at first in the morning when thermocouples had a half an hour residence time in the bath. But the millivolts decreased over time after each thermocouple which means that a higher temperature was measured in the early beginning of the experiment. Apparently some heat (convection, radiation) was still left in the
3. Thermocouples

3.3. Chiller bath measurements

thermocouples which disturbed the experiment. So this experiment cannot be used for the difference measurement. Experiment 1 differs from experiment 2 and therefore it is indeed useful, because the thermocouples were placed in the bath 3 hours before starting the experiment. The last two measurements in experiment 4 differ more than the average due to an unwanted temperature drop in the chiller bath, which disturbed this measurement. The experiments are consistent with each other if the 'bad' measurement points are not included. The maximum distance between the experiments is about 0.01mV which corresponds to a maximum temperature distance of about 0.2° C. This is in between the acceptable range, because the thermocouples are not measured at the same time. Moreover the cooling cycles are not always steady, which results in unwanted deviations in the results.

Figure 3.13: Difference between thermocouples with the lower part cell thermocouple as reference

3.3.3 Experiment #2

The thermocouples are working properly, so the next component to be checked is the DAQ assistant. The problem in the DAQ may be the result of local heat transfer near the connections between thermocouples and the module which results in deviation in mV. Moreover the CJC of the DAQ variates constantly, which also causes deviations. An insulation box is positioned over the DAQ module to reduce the local convective heat transfer. In order to explore these causes new difference experiments have to be done. These experiments are similar to the experiment described in Section 3.3.1. The thermocouples tips are positioned in the liquid bath covered with insulation material. The relative errors are evaluated only at 0° C. In total six measurements are performed. The DAQ CJC value is set at 'built in' feature for 3 measurements. For the other 3 measurements the DAQ CJC value is set at constant feature where the CJC values are respectively 0 °C, 24 °C and 25 °C. In Figure 3.14 the differences between thermocouples with thermocouple in lower part as reference are depicted.

The difference between the thermocouple in lower part of cell and the reference thermocouple is zero because it is chosen to be the reference thermocouple. The experiments with built in CJC are
3. Thermocouples

3.3. Chiller bath measurements

consistent with each other, which are in the acceptable range of 0.1 °C. Only the difference in the thermocouple in the coolant flow is not uniform. Regarding the experiments with constant CJC, the difference between the thermocouples is not uniform. The difference in the thermocouple in the coolant flow and in the thermocouple coolant flow out differ from the difference between the other thermocouples. These thermocouples are attached to another module 9211. One module 9211 contains 4 thermocouple connections. Each module has its own 'built in' CJC value. If the 'built in' CJC is enabled, the differences are consistent. If the constant CJC is enabled, the differences are not consistent for thermocouples positioned in the coolant flow. So the CJC value of the modules are not the same. Main conclusion of the experiments is that the differences between the thermocouples are consistent when an insulation box is placed over the DAQ module.

Finally a difference measurement at ambient temperature is performed in the chiller bath. The insulation box covers the DAQ and the CJC feature is set at built in. In Table 3.3 the differences between the thermocouples with thermocouple in lower part as reference are given. The relative errors are very small at these temperatures. The relative differences between the thermocouples are neglected.

<table>
<thead>
<tr>
<th>Position Thermocouple</th>
<th>Relative error [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermocouple in upper part cell</td>
<td>-0.0075</td>
</tr>
<tr>
<td>Thermocouple in lower part cell</td>
<td>0</td>
</tr>
<tr>
<td>Thermocouple in inlet cell</td>
<td>0.0474</td>
</tr>
<tr>
<td>Thermocouple in purge system</td>
<td>0.0605</td>
</tr>
<tr>
<td>Thermocouple in outlet cooling liquid cell</td>
<td>-0.0143</td>
</tr>
<tr>
<td>Thermocouple in inlet cooling liquid cell</td>
<td>-0.0436</td>
</tr>
</tbody>
</table>

Figure 3.14: Difference between thermocouples with the lower part cell thermocouple as reference
3. Thermocouples

3.4 Conclusions

Firstly, the relative differences between thermocouples were evaluated by at first ice bath measurements. The obtained data from the ice bath measurement were not useful for data processing due to non uniform bath temperatures. Heat transfer from the ambient caused severe temperature fluctuations in the bath.

In order to simulate a thermocouple a GE druck calibrator was used. A set temperature was entered in the calibrator which sent a signal to the DAQ module, where it was processed. The difference was the measurement error. To reduce the measurement error a calibration was done, but it turned out to be useless due to the fact the check experiment was not in accordance with the previous measurement. In fact these experiments proved that only the difference in CJC values of the DAQ module and GE druck calibrator was determined. Although it does indicate that the error drops when the temperature increases which is exactly what in Figure 3.1 was shown.

The relative differences can not be determined with the ice bath measurement, so the thermocouples were tapped to a wooden piece and were positioned in the small chiller bath at various temperatures. The results gave in fact scattering. None of the results were consistent with other data. Due to the thermoelectric properties of the thermocouples, the difference has to be constant for all temperatures, which was not the case. Moreover, it is not possible to perform accurate supersaturation measurements due to the different thermal responses and slow responses of the thermocouples. In super saturation measurements the thermal response times have to be identical for comparison and have to be very fast due to the non equilibrium state in the cell. All components in the thermocouple chain had to be checked.

The thermocouples were attached to a Eurotherm memocal 2000 calibrator and the tips were positioned in the chiller bath. Each thermocouple was attached four times to the calibrator. The experiments are consistent with each other. The maximum distance between the experiments is about 0.01 mV which corresponds to a maximum temperature distance of about 0.2 °C. This is in between the acceptable range, because the thermocouples are not measured at the same time. Moreover, the cooling cycles are not always steady, which results in unwanted deviations in the results.

Local heat transfer near the connections between thermocouples and the module results in deviations in mV. Moreover the CJC of the DAQ varies constantly, which also causes deviations. An insulation box is positioned over the DAQ module to reduce the local convective heat transfer. Again the thermocouples were tapped to a wooden piece and they were positioned in the small chiller bath at 0.2 °C in which the CJC was set at built in feature for 3 measurements. For the remaining measurements the CJC was set at a constant value. The differences between the thermocouples are consistent when an insulation box is placed over the DAQ module. When the CJC was set at a constant value, the temperatures in the coolant flow differed from the other temperatures, because these thermocouples were attached to a second module 9211.

Finally a difference measurement at ambient temperature with the insulation box was done. The differences were so small that they are neglected. The differences have the tendency to get higher for lower temperatures, which is caused by the DAQ. The absolute temperature error of the DAQ drops for increasing temperature (Figure 3.1). In order to get good temperature results the DAQ has to be running for at least a couple of hours to get good heat transfer in the modules. Moreover an insulation box is placed over the DAQ to reduce the local convective heat transfer near the connections. The 'built in' CJC has to be enabled to receive good results for all thermocouples, although this value is not known.
Part II

Equilibrium gas composition experiments
Chapter 1

Introduction

In this chapter equilibrium gas compositions experiments will be discussed. A predefined binary mixture of CO₂ and N₂ is used for this type of experiments in the condensation cell. At certain process conditions the mixture will condensate in the cell to its equilibrium state. When the condensation cell is in equilibrium state gas samples will be taken from the cell to analyze its composition. The experiments are used to validate the phase calculation modeling[10].

In Chapter 2 the basic lay out of the measurement setup is discussed in order to perform these experiments. The measurement procedure is discussed in Chapter 3. In Chapter 4 the measurement plan is discussed in which the experimental process conditions are determined. The results of the experiments are discussed in Chapter 5. For each experiment the experimental data points and the overall results are described. If necessary, adjustments to the measurement setup and measurement procedure are mentioned. Finally in Chapter 6 the conclusions of the equilibrium gas composition experiments are discussed.
Chapter 2

Measurement setup

A schematic representation of the measurement set up is given in Figure 2.1. In this figure only the most important components are described which are necessary for these experiments. A premixed gas cylinder is used for providing the gas for the condensation cell. The gas bottle is used for controlling the pressure in the cell. When the gas enters the cell it will condensate under specific process conditions. A gas fraction and liquid fraction will establish, which ratio is dependent on the process conditions. The outer shell of the condensation cell is filled with cooling liquid of the chiller. The chiller is used for controlling the temperature in the cell. In these experiments two T type thermocouples, positioned respectively in the lower part and in the upper part of the condensation cell, are used to measure the temperature. In the upper part of the cell a pressure transducer is positioned which measures the pressure in bars. A gas chromatographer (GC) is used to measure the composition of the gas. The sample line starts at the top of the condensation cell. A pressure relief system is built in the sample line. When the pressure exceeds 50 bar the pressure relief system will open. A valve is introduced to deflate the condensation cell after experiments. After the primary valve an expansion spiral is used to increase the heat transfer area in order to heat up the gas before entering the GC.

Figure 2.1: Measurement setup for gas composition measurements
Chapter 3

Measurement procedure

The measurement procedure is divided into three parts: preparations, actual measurements and the closure of the experiment.

3.1 Preparations

When starting a measurement, most valves around the condensation cell in the system have to be closed. Only the valves in the pressure reducers have to be open as well as the valve of the chillers cooling liquids. The windows have to be covered with the isolation caps for preventing unnecessary heat loss through the windows. The condensation cell is filled twice with a mixture of about 5 bar and the cell is deflated twice in order to remove impurities in the cell for the experiments.

The large chiller has to be connected to the power station and to the water supply station. The temperature of the large chiller is set at six degrees under the desired temperature in the cell. The impeller in the cell has to be started at least at position number 3 in order to increase the mass and heat transfer in the system. If necessary, the temperature and pressure can be adjusted by the gas bottle and the chiller. This can not be done during measurements, only before and after.

The gas chromatographer has to be put on first. The helium supply has to be set at a pressure of 5.5 bar. It is very important to send the real time clock and method to the GC, otherwise measurements are converted wrongly due to wrong methods and measurements results get overwritten. A small leakage flow of about 1.2 bar has to be established by tightening the pressure reducer screw of the GC.

3.2 Actual measurement procedure

When the condensation cell is in equilibrium, which can be perceived when the pressure and the temperature are steady, a measurement is started. Prostation and Labview have to be started at the same time. During the measurement, the results of the GC are monitored to determine when a measurement has to be stopped, that is when the chromatographies are steady for a certain period of time.

After completing a measurement of a data point, the pressure reducer screw has to be loosened until the leakage flow is equal to zero. The pressure is increased by setting the pressure reducer of the gas bottle at the desired pressure. The next measurement is started when the cell is in equilibrium. The above mentioned steps are repeated for all data points.
3.3 Closure of experiment

The large chiller has to be set at a temperature of 0°C in order to heat up the condensation cell. The gas bottle and the helium bottle have to be closed. The condensation cell is deflated by opening the valve positioned at the upper part of the cell (valve(1) in Figure 2.1). Due to expansion of the gas the temperature in the cell will drop. Temperature has to be higher than \(-55^\circ C\) otherwise solid CO\(_2\) will form. When the cell is empty the chillers have to be put off. If necessary, the premixed gas bottle has to be replaced, when the bottle pressure is too low for the next experiment.
Chapter 4

Measurement plan

According to the phase calculating modeling [10] the gas concentration has to be validated by two different experiments.

1. Temperature is constant and pressure is the adjusting variable.

2. Pressure is constant and temperature is the adjusting variable.

The gas concentration according to the phase calculating modeling is already validated for the experiment wherein the pressure is kept constant and the temperature is the adjusting variable[11]. In this chapter the phase calculation modeling is validated for gas concentration wherein the temperature is kept constant.

![Figure 4.1: Phase diagram of a CO2-N2 mixtures with constant temperature lines 223K, 233K, 243K according to phase calculation modeling [10]](image)

The limitations of the condensation cell are a pressure of 50 bar and a temperature of $-55^\circ\text{C}$. In Figure 4.1 the phase diagram for constant temperatures is given. The gas measurement range is very small due to the limitations of the condensation cell. The temperature of the gas experiments for constant temperature is set at $-50^\circ\text{C}$. When one temperature is validated, it can be assumed
4. Measurement plan

that the validation also holds for higher temperatures. In Table 4.1 the measurement points for the constant temperature experiments are given. 70-30 %CO$_2$-N$_2$ or 80-20 %CO$_2$-N$_2$ gas bottles are used, because at low pressures the phase calculation modeling have to be validated with high CO$_2$ content gas bottles.

Table 4.1: Measurement points for gas composition measurement

<table>
<thead>
<tr>
<th>Data point</th>
<th>T [°C]</th>
<th>p [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>-50</td>
<td>6</td>
</tr>
<tr>
<td>#2</td>
<td>-50</td>
<td>12</td>
</tr>
<tr>
<td>#3</td>
<td>-50</td>
<td>18</td>
</tr>
<tr>
<td>#4</td>
<td>-50</td>
<td>24</td>
</tr>
<tr>
<td>#5</td>
<td>-50</td>
<td>30</td>
</tr>
<tr>
<td>#6</td>
<td>-50</td>
<td>36</td>
</tr>
<tr>
<td>#7</td>
<td>-50</td>
<td>42</td>
</tr>
</tbody>
</table>

In the next chapter the experiments will be discussed. For each experiment the set data points used are discussed. If necessary, adjustments to the measurement setup and procedure are discussed. In every experiment the data points will be compared to the phase calculation modeling and the most important data will be given per experiment.
Chapter 5

Gas composition experiments

5.1 Gas composition experiment number 1

The results of gas experiment number 1 are described in this section.

5.1.1 Data points

The premixed gas bottle is a 69.9-30.1 \%CO₂-N₂ mixture with an accuracy of ±2\%. Gas samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of a total of seven measurement points. The temperature of all measurement points is about −50 °C in the upper part of the condensation cell. The pressures of the measurement points can be found in Table 4.1. The measurement setup for the experiment is described in Chapter 2. The measurement procedure for the experiment is described in Chapter 3.

5.1.2 Results

Data selection

During the data processing a selection of samples are analyzed. 15 samples are used which corresponds to an actual runtime of about 8 minutes. In Figure 5.1 the chromatographies of data point 1 are shown. The fluctuations in the signal have the tendency to increase into the time until an amplitude is reached of about 1\% around a steady mean. In the beginning some impurities can be present in the sample line, which distort the chromatographies. In order to avoid contaminated results, only the last 15 chromatographies are taken for data processing. The pressure signal of data point 1 is shown in Figure 5.2. The signal has a periodical behavior around a steady mean which is divided in a period of high fluctuations of 1.5 bar and a period of low fluctuations of 0.1 bar. Data points 2, 3 and 4 are processed in the same manner as data point 1.
5. Gas composition experiments

5.1. Gas composition experiment number 1

In Figure 5.3 the chromatographies of data point 5 are shown. The fluctuations in the signal have the tendency to get large into time until an amplitude is reached of about 1%. Impurities are present in the sample line in the first minutes of the measurements, which distorts the chromatographies. Moreover the mean concentration has the tendency to drop in time. This tendency is also observed in the pressure signal, which is shown in Figure 5.4. The signal has a periodical behavior around a decreasing mean which is divided in a period of high fluctuations of 1.5 bar and a period of low fluctuations of 0.1 bar. The pressure is set with the pressure reducer at 30 bar, but the pressure in the condensation cell is about 24 bar. The pressure in the gas bottle is too low to provide a pressure of 30 bar. The slow decrease of pressure is a result of operating at the gas bottles pressure. The condensation cell is not leakage free, so the pressure drops. When the pressure drops, the CO₂ concentration in the gas increases. When process conditions change in the condensation cell the cell is not in equilibrium state. However, due to the slow pressure decay this data point is included in the overall result. (Also in this case) The last 15 chromatographies are used for data processing. The gas bottle pressure is reached at data point 5, therefore it was not possible to measure the remaining data points.

Overall result

The selected chromatographies of the data points are processed and compared with the phase calculation modeling [10]. During the data processing the lower part cell temperature is used for
comparison instead of the upper part cell temperature, because the gas-liquid phase boundary is positioned in the lower part of the cell. Around the phase boundary, the liquid and gas are in equilibrium state.

The model line is positioned in the range of the standard deviation of data point 1. In the condensation cell no condensation occurred during the measurement of data point 1. This measurement is done to check if the concentrations in the cell are the same as provided by the gas bottle. The model line is calculated by using the average temperature of the experiment. However the temperature of the data points differ a lot (Table 5.2). Temperature was not regulated to maintain a steady temperature throughout the experiment. The difference in Table 5.1 is the models concentration at the data points process conditions minus the measured concentration. The differences of data points 2, 4 and 5 are large. However the standard deviations of the pressure and temperature is rather small, so the process conditions were steady during the measurements. Nevertheless, it could be that the process conditions were steady, but that the concentrations in the cell were not steady. In order to avoid these effects, the time between the data points has to be prolonged.

### Table 5.1: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>$\text{CO}_2, \text{meas} [%]$</th>
<th>$\text{CO}_2, \text{model} [%]$</th>
<th>Difference [%]</th>
<th>$\sigma_{\text{CO}_2, \text{meas}} [%]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>70.01</td>
<td>69.90</td>
<td>-0.11</td>
<td>0.83</td>
</tr>
<tr>
<td>#2</td>
<td>56.11</td>
<td>57.60</td>
<td>1.58</td>
<td>0.61</td>
</tr>
<tr>
<td>#3</td>
<td>38.61</td>
<td>39.47</td>
<td>0.86</td>
<td>0.43</td>
</tr>
<tr>
<td>#4</td>
<td>32.39</td>
<td>30.68</td>
<td>-1.71</td>
<td>0.67</td>
</tr>
<tr>
<td>#5</td>
<td>31.90</td>
<td>30.34</td>
<td>-1.56</td>
<td>0.14</td>
</tr>
</tbody>
</table>

During the measurement of data point 3 the processing conditions were also steady and the $\text{CO}_2$ gas concentration was not in accordance with the modeling. Hence the difference is larger than the concentrations standard deviation.
### 5.1.3 Conclusion experiment

In this experiment gas measurements at -50°C were done with a 69.9-30.1 %CO₂-N₂ mixture. This experiment consisted of 7 data points, however only 5 data points were performed. During the measurement of data point 5, the pressure decayed constantly which was a result of operating at gas bottle pressure. The pressure of the remaining data points could not be reached with the gas bottle. The lower part cell temperature was taken for comparison instead of the upper part cell temperature, because the gas-liquid phase boundary is positioned in the lower part of the cell. Around the phase boundary the liquid and gas is in equilibrium state.

Data point 1 was in accordance with the phase calculation modeling. However, this data point was to check if the measurement of the gas composition in the cell is the same as provided by the gas bottle. Data point 3 was not in accordance with the model. The temperature of the experiment was not steady. In the next experiments the temperatures of the data points have to be set in 1°C of each other, which can be achieved by regulating the temperature setpoint of the large chiller. In order to reach an equilibrium state in the cell, the time between the data points has to be prolonged, because the process conditions can be steady, but the concentrations in the cell do not have to be steady at the same time.

### 5.2 Gas composition experiment number 2

The results of gas experiment number 2 are described in this section.

#### 5.2.1 Data points

The premixed gas bottle is a 48.6-51.4 %CO₂-N₂ mixture with an accuracy of ±2%. Gas samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of a total of seven measurement points. The temperature of all measurement points is about -50°C in the lower part of the condensation cell. The pressures of the measurement points can be found in Table 4.1. The measurement setup for the experiment is described in Chapter 2. The measurement procedure for the experiment is described in Chapter 3.

#### 5.2.2 Results

Only five measurements were done, because during data point 5 the pressure decayed constantly which was the result of operating at gas bottle pressure. The pressure of the remaining data points could not be reached with the gas bottle. The lower part cell temperature of data point 3 was not logged during the measurement for an unknown reason. Only one value was logged, which will be used in the data processing. The temperature standard deviation is for this reason zero. The data points chromatographies have the same behavior as the data points chromatographies of gas experiment 1 which is described in Section 5.1.2. For all data points the last 15 chromatographies are taken for data processing.
5. Gas composition experiments  

5.2. Gas composition experiment number 2

![Fraction CO₂ in gas phase versus pressure at a temperature of −47.9°C](image)

Figure 5.6: Fraction CO₂ in gas phase versus pressure at a temperature of −47.9°C

In Figure 5.6 the fraction CO₂ in gas phase versus pressure at a temperature of −47.9°C is shown. The first two data points are positioned just above the model line not within the range of the data points standard deviations. The condensation cell probably contained some impurities of the previous measurement. So the condensation cell has to be flushed with much more care. More gas has to be used for removing the impurities. The difference in Table 5.3 is the models concentration at the data points process conditions minus the measured concentration. Data points 3 and 4 are in accordance with the phase calculation modeling. The difference is smaller than the standard deviations of the concentrations. Data point 5 is not consisted with the modeling, because during this measurement the pressure decayed over time and the difference is too large in comparison with the standard deviation.

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂,meas [%]</th>
<th>CO₂,model [%]</th>
<th>Difference [%]</th>
<th>σCO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>49.17</td>
<td>48.60</td>
<td>-0.57</td>
<td>0.83</td>
</tr>
<tr>
<td>#2</td>
<td>49.56</td>
<td>48.60</td>
<td>0.96</td>
<td>0.61</td>
</tr>
<tr>
<td>#3</td>
<td>40.68</td>
<td>41.10</td>
<td>0.43</td>
<td>0.43</td>
</tr>
<tr>
<td>#4</td>
<td>33.54</td>
<td>33.41</td>
<td>-0.13</td>
<td>0.67</td>
</tr>
<tr>
<td>#5</td>
<td>35.02</td>
<td>35.48</td>
<td>0.46</td>
<td>0.14</td>
</tr>
</tbody>
</table>

In Table 5.4 the temperatures, pressures, their standard deviations and the chiller temperature are given. The temperature were steady during the experiments except for data point 1. The set point temperature of the chiller was too low. In fact the condensation cell was not in equilibrium during the first measurement point. The temperature standard deviation is much higher than the other temperature standard deviations. The pre-cooling of the condensation cell has to be prolonged in order to gain a steady temperature. Moreover the temperature should be regulated when it does not reach the desired temperature.
5.2.3 Conclusion experiment

In this experiment gas measurements at -50 °C are done with a 48.6-51.4 %CO₂-N₂ mixture. This experiment consisted of 7 data points, however only 5 data points were performed. During the measurement of data point 5, the pressure decayed constantly which was a result of operating at gas bottle pressure. The pressure of the remaining data points could not be reached with the gas bottle. The first two measurements were check measurements. The results of these check measurements were positioned above the model line due to impurities in the condensation cell. The cell has to be flushed with more gas in order to remove the impurities from the cell. The lower part temperature of data point 3 is not logged for unknown reasons. Data point 4 is in accordance with the phase calculation modeling. The pre-cooling of the condensation cell has to be prolonged in order to gain a steady temperature in the cell.

5.3 Gas composition experiment number 3

The results of gas experiment number 3 are described in this section.

5.3.1 Data points

The premixed gas bottle is a 79.6-20.4 %CO₂-N₂ mixture with an accuracy of ±2%. Gas samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of a total of five measurement points. The temperature of all measurement points is about -50 °C in the lower part of the condensation cell. The pressures of the measurement points can be found in Table 4.1. The last data points at high pressure are skipped due to the fact that a very large liquid fraction in the cell will form at high pressures, which empties the gas bottle very fast. At the beginning of the experiment, the cell was flushed twice to remove impurities. The measurement setup for the experiment is described in Chapter 2. The measurement procedure for the experiment is described in Chapter 3.

5.3.2 Results

During the data processing a selection of samples are analyzed. The last 15 samples are used which corresponds to an actual runtime of about 8 minutes. The data points chromatographies have the same behavior as the data points chromatographies of gas experiment 1 which is described in Section 5.1.2.

In Figure 5.7 the fraction CO₂ in the gas phase versus pressure at a temperature of -49.6 °C is shown. The first data point is a check measurement. The measured composition is exactly the same as the gas bottle composition. The difference in Table 5.5 is the models concentration at the data points process conditions minus the measured concentration. Data point 2 and 3 deviate around 1.3% from the phase calculation modeling, but the standard deviations are a factor 2 smaller. Data points 4 and 5 are in accordance with the modeling. Its standard deviations are smaller than the differences.
5. Gas composition experiments  

5.3. Gas composition experiment number 3

Figure 5.7: Fraction CO₂ in gas phase versus pressure at a temperature of −49.6°C

Table 5.5: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂,meas [%]</th>
<th>CO₂,model [%]</th>
<th>Difference [%]</th>
<th>σCO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>79.56</td>
<td>79.60</td>
<td>0.04</td>
<td>0.61</td>
</tr>
<tr>
<td>#2</td>
<td>75.07</td>
<td>76.35</td>
<td>1.28</td>
<td>0.54</td>
</tr>
<tr>
<td>#3</td>
<td>53.32</td>
<td>54.68</td>
<td>1.36</td>
<td>0.63</td>
</tr>
<tr>
<td>#4</td>
<td>43.63</td>
<td>44.11</td>
<td>0.48</td>
<td>0.53</td>
</tr>
<tr>
<td>#5</td>
<td>37.86</td>
<td>37.38</td>
<td>-0.48</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 5.6: Temperature, pressure and standard deviations of data points

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>4.26</td>
<td>0.51</td>
<td>-47.26</td>
<td>0.03</td>
<td>-56.5</td>
</tr>
<tr>
<td>#2</td>
<td>10.34</td>
<td>0.48</td>
<td>-46.69</td>
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<td>-52.0</td>
</tr>
<tr>
<td>#3</td>
<td>15.74</td>
<td>0.48</td>
<td>-45.96</td>
<td>0.10</td>
<td>-52.0</td>
</tr>
<tr>
<td>#4</td>
<td>21.05</td>
<td>0.52</td>
<td>-45.41</td>
<td>0.02</td>
<td>-51.5</td>
</tr>
<tr>
<td>#5</td>
<td>25.24</td>
<td>0.52</td>
<td>-46.22</td>
<td>0.14</td>
<td>-51.5</td>
</tr>
</tbody>
</table>

In Table 5.6 the temperatures, pressures, their standard deviations and the chiller temperature are given. The temperatures were steady during the experiments, but the distance between the data points temperatures is too large. It has to be in the range of 1 °C. The temperature in the lower part of the condensation cell has to be regulated more strictly. The temperature standard deviation of data point 5 is quite high due to large fluctuations. The pressure signal has a periodical behavior which is described in Section 5.1.2.
5.3.3 Conclusion experiment

In this experiment gas measurements at $-50^\circ\text{C}$ are done with a 79.6-20.4\% CO$_2$-N$_2$ mixture. This experiment consisted of 5 data points. The composition in the cell was identical to the gas bottle composition. Data points 2 and 3 are not consistent with the modeling due to large deviations. Probably the condensation cell was not yet in its equilibrium state. More time is needed to get an equilibrium state in the cell. Data points 4 and 5 are in accordance with the modeling, because the difference is smaller than the standard deviations. However the temperature deviations of data point 5 is rather large, indicating that the temperature was not steady.

The overall experiment temperature is much more steady in comparison with previous experiments. Between the measurements the temperature is regulated with the large chiller. The time between these measurements is prolonged in order to get an equilibrium state in the cell. However, the time should be prolonged even more to get more accurate results in the future experiments.

5.4 Gas composition experiment number 4

The results of gas experiment number 4 are described in this section.

5.4.1 Data points

The premixed gas bottle is a 49.9-50.1\% CO$_2$-N$_2$ mixture with an accuracy of ±2\%. Gas samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of a total of seven measurement points. The temperature of all measurement points is about $-50^\circ\text{C}$ in the lower part of the condensation cell. The pressures of the measurement points can be found in Table 4.1. The measurement setup for the experiment is described in Chapter 2. The measurement procedure for the experiment is described in Chapter 3.

5.4.2 Results

Only five measurements were done, because during data point 5 the pressure decayed constantly which was a result of operating at the gas bottle pressure. The pressure of the remaining data points could not be reached with the gas bottle. The data points chromatographies have the same behavior as the data points chromatographies of gas experiment 1 which is described in Section 5.1.2. For all data points the last 15 chromatographies are used for data processing.

In Figure 5.8 the fraction CO$_2$ in gas phase versus pressure at a temperature of $-47.2^\circ\text{C}$ is shown. The first two data points are check measurements. The measured composition is exactly the same as the gas bottle composition. The difference in Table 5.7 is the models concentration at the data points process conditions minus the measured concentration. For data point 3 the difference is larger than the standard deviation. But when the systematic sensor errors are included, the data point is consistent with the phase calculating modeling. Data point 4 and 5 are in accordance with the phase calculating modeling. The differences are smaller than the standard deviations. Moreover the standard deviations of the process conditions are also small.

In Table 5.8 the temperatures, pressures, their standard deviations and the chiller temperature are given. The temperatures were steady during the experiments. The maximum distance between the data points temperature is in the range of 1\(^\circ\text{C}\), which is desired. The temperature standard deviations are small, so the temperatures are very steady during the measurements. The pressure signal has a periodical behavior which is described in Section 5.1.2.
5. Gas composition experiments

5.4. Gas composition experiment number 4

Figure 5.8: Fraction CO$_2$ in gas phase versus pressure at a temperature of $-47.2^\circ$C

Table 5.7: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO$_{2,meas}$ [%]</th>
<th>CO$_{2,model}$ [%]</th>
<th>Difference [%]</th>
<th>$\sigma_{CO_{2,meas}}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>50.07</td>
<td>49.90</td>
<td>-0.17</td>
<td>0.64</td>
</tr>
<tr>
<td>#2</td>
<td>50.17</td>
<td>49.90</td>
<td>-0.27</td>
<td>0.73</td>
</tr>
<tr>
<td>#3</td>
<td>41.19</td>
<td>41.64</td>
<td>0.45</td>
<td>0.26</td>
</tr>
<tr>
<td>#4</td>
<td>36.22</td>
<td>36.46</td>
<td>0.24</td>
<td>0.58</td>
</tr>
<tr>
<td>#5</td>
<td>35.08</td>
<td>34.97</td>
<td>-0.11</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 5.8: Temperature, pressure and standard deviations of data points

<table>
<thead>
<tr>
<th>Data point</th>
<th>$p_{avg}$ [bar]</th>
<th>$\sigma_p$ [bar]</th>
<th>$T_{avg}$ [$^\circ$C]</th>
<th>$\sigma_T$ [$^\circ$C]</th>
<th>$T_{chiller}$ [$^\circ$C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>7.62</td>
<td>0.51</td>
<td>-47.58</td>
<td>0.06</td>
<td>-56.0</td>
</tr>
<tr>
<td>#2</td>
<td>15.55</td>
<td>0.54</td>
<td>-46.91</td>
<td>0.06</td>
<td>-54.0</td>
</tr>
<tr>
<td>#3</td>
<td>20.37</td>
<td>0.51</td>
<td>-47.12</td>
<td>0.04</td>
<td>-53.0</td>
</tr>
<tr>
<td>#4</td>
<td>25.55</td>
<td>0.57</td>
<td>-46.69</td>
<td>0.03</td>
<td>-53.0</td>
</tr>
<tr>
<td>#5</td>
<td>25.97</td>
<td>0.50</td>
<td>-47.54</td>
<td>0.03</td>
<td>-52.7</td>
</tr>
</tbody>
</table>

5.4.3 Conclusion experiment

In this experiment gas measurements at $-50^\circ$C are done with a 49.9-50.1 %CO$_2$-N$_2$ mixture. This experiment consisted of 7 data points, however only 5 data points were performed. During the measurement of data point 5 the pressure decayed constantly which was a result of operating at gas bottle pressure. The pressure of the remaining data points could not be reached with the gas bottle. The first two measurements were check measurements. The results of these check measurements confirmed that the cell composition was identical to the gas bottle composition. Data point 4 and 5 are in accordance with the phase calculating modeling, because the differences
are smaller than the standard deviations. For data point 3 the difference is larger than the standard deviation, but when the systematic sensor errors are included the data point is consistent with the phase calculating modeling. The phase calculation modeling is validated for low pressures at constant temperatures. However high pressures are not yet measured, so in the next experiment compositions at high pressures have to be measured.

5.5 Gas composition experiment number 5

The results of gas experiment number 5 are described in this section.

5.5.1 Data points

The premixed gas bottle is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. Gas samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of a total of six measurement points. The temperature of all measurement points is about –50°C in the lower part of the condensation cell. The pressures of the measurement points are high pressures, because the modeling is only validated for low pressures. The pressures are 10, 20, 30, 38, 42 and 46 bar. The measurement setup for the experiment is described in Chapter 2. The measurement procedure for the experiment is described in Chapter 3.

5.5.2 Results

During the data processing a selection of samples were taken to be analyzed. The last 15 samples are analyzed which corresponds to an actual runtime of about 8 minutes. The data points chromatographies have the same behavior as the data points chromatographies of gas experiment 1 which is described in Section 5.1.2.

![Figure 5.9: Fraction CO₂ in gas phase versus pressure at a temperature of –51.3°C](image)

Figure 5.9: Fraction CO₂ in gas phase versus pressure at a temperature of –51.3°C
In Figure 5.9 the fraction CO₂ in the gas phase versus pressure at a temperature of −49.6 °C is shown. The first data point is a check measurement. The measured composition is exactly the same as the gas bottle composition. The difference in Table 5.9 is the models concentration at the data points process conditions minus the measured concentration. All data points are positioned slightly below the phase calculation modeling line, but the differences are smaller than the standard deviations. Except for data point 4 where the difference is larger. However, when systematic sensor errors are included, data point 4 is in accordance with the phase calculation modeling.

Table 5.9: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂,meas [%]</th>
<th>CO₂,model [%]</th>
<th>Difference [%]</th>
<th>σ_CO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>50.09</td>
<td>49.60</td>
<td>-0.49</td>
<td>0.58</td>
</tr>
<tr>
<td>#2</td>
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<td>33.98</td>
<td>0.45</td>
<td>0.55</td>
</tr>
<tr>
<td>#3</td>
<td>26.13</td>
<td>26.86</td>
<td>0.43</td>
<td>0.47</td>
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<tr>
<td>#4</td>
<td>23.01</td>
<td>23.43</td>
<td>0.41</td>
<td>0.34</td>
</tr>
<tr>
<td>#5</td>
<td>22.15</td>
<td>22.42</td>
<td>0.27</td>
<td>0.42</td>
</tr>
<tr>
<td>#6</td>
<td>21.15</td>
<td>21.33</td>
<td>0.18</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 5.10: Temperature, pressure and standard deviations of data points

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>10.62</td>
<td>0.40</td>
<td>-54.48</td>
<td>0.29</td>
<td>-63.0</td>
</tr>
<tr>
<td>#2</td>
<td>22.11</td>
<td>0.48</td>
<td>-51.65</td>
<td>0.02</td>
<td>-57.5</td>
</tr>
<tr>
<td>#3</td>
<td>32.28</td>
<td>0.49</td>
<td>-51.10</td>
<td>0.04</td>
<td>-58.5</td>
</tr>
<tr>
<td>#4</td>
<td>39.18</td>
<td>0.45</td>
<td>-51.32</td>
<td>0.06</td>
<td>-58.8</td>
</tr>
<tr>
<td>#5</td>
<td>42.72</td>
<td>0.49</td>
<td>-51.24</td>
<td>0.02</td>
<td>-58.5</td>
</tr>
<tr>
<td>#6</td>
<td>47.73</td>
<td>0.46</td>
<td>-51.09</td>
<td>0.02</td>
<td>-58.5</td>
</tr>
</tbody>
</table>

In Table 5.10 the temperatures, pressures, their standard deviations and the chiller temperature are given. The temperatures were steady during the experiments. The maximum distance between the data points temperature at which condensation occurred is in the range of 1 °C, which is desired. The temperature standard deviations are small, so the temperatures are very steady during the measurements. Only the temperature in data point 1 has large fluctuations. The pressure signal has a periodical behavior which is described in Section 5.1.2.

5.5.3 Conclusion experiment

In this experiment gas measurements at −50 °C are done with a 49.6-50.4 %CO₂-N₂ mixture. This experiment consisted of 6 data points. The composition in the cell was identical to the gas bottle composition. All data points are in accordance with the phase calculation modeling. Only for data point 4 the difference is larger than the standard deviation, but when the systematic sensor errors are included, the data point is consistent with the phase calculating modeling. The phase calculation modeling is validated for high pressures at constant temperature in this experiment. In the previous experiments the phase calculation modeling was validated for low pressures at constant temperature as well. So the phase calculation modeling is validated for the gas concentrations.
Chapter 6

Conclusion gas composition experiments

In this chapter equilibrium gas composition experiments were discussed. A predefined binary mixture of CO₂ and N₂ was used for gas composition experiments in the condensation cell. At predefined process conditions the mixture condensates in the cell to its equilibrium state. When the condensation cell was in equilibrium state, gas samples were taken from the cell to analyze its composition. The results were compared to the phase calculation modeling [10]. The gas composition experiments are divided into two parts. The first part is gas composition measurements at constant temperature in which the pressure is the variable. The second part is the opposite of the first part, which is liquid composition measurement at constant pressure in which the temperature is the variable. The gas concentration according to the phase calculating modeling is already validated for the experiment wherein the pressure is kept constant and the temperature is the adjusting variable[11].

The initial measurements were not consistent with the modeling. The overall temperature fluctuations were too high. All measurement temperatures have to be in the range of 1°C. The cell temperature has to be regulated with the large chiller. Furthermore the time between the measurements was too short in the initial experiments. The condensation cell was not completely in equilibrium. The process conditions were steady, but the concentration in the cell was not in equilibrium. During the start up of the experiment the pre cooling time had to be prolonged. More heat had to be added to the condensation cell to get the temperature more steady. During three experiments the pressure of the gas bottle was lower than the desired pressure. The pressure decayed constantly which was a result of operating at gas bottle pressure. The pressure of the remaining data points could not be reached with the gas bottle. When the pressure decays the cell is not in equilibrium, but the slow decay makes it possible to include these measurements in the data processing. Data selection was not necessary, because every data points chromatographies have the tendency to large fluctuations of 1% around a steady value. For each data point the last 15 chromatographies were taken for data processing.

Initial experiments were not in accordance with the phase calculations due to the above mentioned reasons. In experiment number 3 and 4 the phase calculation modeling is validated for low pressure at constant temperature. In experiment number 5 the phase calculation modeling is validated for high pressure at constant temperature. So the phase calculation modeling is validated for gas equilibrium composition measurements.
Part III

Equilibrium liquid composition experiments
Chapter 1

Introduction

In this part of the logbook equilibrium liquid composition experiments will be discussed. A predefined binary mixture of CO$_2$ and N$_2$ will be used for this type of experiments in the condensation cell. When the condensation cell is in equilibrium state, liquid samples will be taken from the cell to analyze its composition. The experiments will be used to validate the phase calculation modeling [10].

In Chapter 5.3 the basic lay out of the measurement setup will be discussed in order to perform these experiments. The measurement procedure will be discussed in Chapter 5.3. In Chapter 4 the measurement plan will be discussed in which the experimental process conditions are determined. The results of the experiments are discussed in Chapter 5. For each experiment the experimental data points and the overall results will be described. If necessary, adjustments to the measurement setup and measurement procedure will be mentioned. Finally in Chapter 6 the conclusions of the equilibrium gas composition experiments will be discussed.
Chapter 2

Measurement setup

Samples have to be taken from the bottom of the cell instead of the top of the cell. Therefore the measurement setup has to be changed. In Figure 2.1 a schematic representation of the measurement setup is given, which only depicts the most important components necessary in these experiments.

A premixed gas cylinder is used for providing the gas for the condensation cell. The gas bottle is used for controlling the pressure in the cell. When the gas enters the cell it will condensate under specific process conditions. A gas fraction and liquid fraction will establish, which ratio is dependent on the process conditions. The outer shell of the condensation cell is filled with cooling liquid of the chiller. The chiller is used for controlling the temperature in the cell. In these experiments a T type thermocouple positioned in the lower part of the condensation cell is used to measure the temperature. In the upper part of the cell a pressure transducer is positioned which measures the pressure in bars. A gas chromatograph (GC) is used to measure the composition of the liquid.

In Figure 2.1 the pipe to the GC is denoted as the sample line. The sample line starts at the bottom of the condensation cell. A pressure relief system is built in the sample line. When the
2. Measurement setup

pressure exceeds 50 bar the pressure relief system will open. A valve is introduced to close the sample line when the condensation cell is in non equilibrium state. After the primary valve an expansion spiral is used to increase the heat transfer area in order to shift the sample from liquid to the gas phase.
Chapter 3

Measurement procedure

The measurement procedure is divided into three parts: preparations, actual measurements and the closure of the experiment.

3.1 Preparations

When starting a measurement, most valves around the condensation cell in the system have to be closed. Only the valves in the pressure reducers have to be open as well as the valve of the chillers cooling liquids. The windows have to be covered with the isolation caps for preventing unnecessary heat loss through the windows. The condensation cell is filled twice with a mixture of about 5 bar and the cell is deflated twice in order to remove impurities in the cell for the experiments.

The large chiller has to be connected to the power station and to the water supply station. The temperature of the large chiller is set at six degrees under the desired temperature in the cell. The impeller in the cell has to be started at least at position number 3 in order to increase the mass and heat transfer in the system. If necessary, the temperature and pressure can be adjusted by the gas bottle and the chiller. This can not be done during measurements, only before and after.

The gas chromatographer has to be put on first. The helium supply has to be set at a pressure of 5.5 bar. It is very important to send the real time clock and method to the GC, otherwise measurements are converted wrongly due to wrong methods and measurements results get overwritten. A small leakage flow of about 1.2 bar has to be established by tightening the pressure reducer screw of the GC.

3.2 Actual measurement procedure

When the condensation cell is in equilibrium, which can be perceived when the pressure and the temperature are steady, a measurement is started. Prostation and Labview have to be started at the same time. During the measurement, the results of the GC are monitored to determine when a measurement has to be stopped, that is when the chromatographies are steady for a certain period of time.

After completing a measurement of a data point, the pressure reducer screw has to be loosened until the leakage flow is equal to zero. The pressure is increased by setting the pressure reducer of the gas bottle at the desired pressure. The next measurement is started when the cell is in equilibrium. The above mentioned steps are repeated for all data points.
3.3 Closure of experiment

The large chiller has to be set at a temperature of 0°C in order to heat up the condensation cell. The gas bottle and the helium bottle have to be closed. The condensation cell is deflated by opening the valve positioned at the upper part of the cell (valve(1) in Figure 2.1). Due to expansion of the gas the temperature in the cell will drop. Temperature has to be higher than −55°C otherwise solid CO₂ will form. When the cell is empty the chillers have to be put off. If necessary, the premixed gas bottle has to be replaced, when the bottle pressure is too low for the next experiment.
Chapter 4

Measurement plan

The measurement plan of the liquid composition experiments consists of two parts.

1. Temperature is constant and pressure is the adjusting variable.
2. Pressure is constant and temperature is the adjusting variable.

Figure 4.1: Phase diagram of a CO₂-N₂ mixtures with constant temperature lines 223K, 233K, 243K according to phase calculation modeling[10]

The limitations of the condensation cell are a pressure of 50 bar and a temperature of −55°C. In Figure 4.1 the phase diagram for constant temperatures is given. The liquid measurement range is very small due to the limitations of the condensation cell. The temperature of the liquid experiments for constant temperature is set at −50°C. An experiment at higher temperatures makes no sense, because the liquid boundaries are very close to each other. When one temperature is validated, it can be assumed that the validation also holds for higher temperatures. In Table 4.1 the measurement points for the constant temperature experiments are given with the suggested gas bottle. For a low pressure a 70-30 % CO₂-N₂ gas bottle is used due to the fact that at low pressures no condensation occurs for lower CO₂ composition gas bottles (Figure 4.2).

Figure 4.2: Phase diagram of a CO₂-N₂ mixtures with constant pressure lines 30 bar and 40 bar according to phase calculation modeling[10]
4. Measurement plan

Table 4.1: Measurement points for liquid composition measurement with constant temperatures

<table>
<thead>
<tr>
<th>Data point</th>
<th>T [°C]</th>
<th>p [bar]</th>
<th>CO₂-N₂ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>-50</td>
<td>15</td>
<td>70-30</td>
</tr>
<tr>
<td>#2</td>
<td>-50</td>
<td>20</td>
<td>70-30</td>
</tr>
<tr>
<td>#3</td>
<td>-50</td>
<td>25</td>
<td>50-50</td>
</tr>
<tr>
<td>#4</td>
<td>-50</td>
<td>30</td>
<td>50-50</td>
</tr>
<tr>
<td>#5</td>
<td>-50</td>
<td>35</td>
<td>50-50</td>
</tr>
<tr>
<td>#6</td>
<td>-50</td>
<td>40</td>
<td>50-50</td>
</tr>
<tr>
<td>#7</td>
<td>-50</td>
<td>45</td>
<td>50-50</td>
</tr>
</tbody>
</table>

In Figure 4.2 the phase diagram for constant pressures is given. The liquid composition is strongly dependent on the pressure. At a pressure of 40 bar the liquid composition is about 2% lower than the liquid composition at 30 bar. For the liquid compositions in which the pressure is kept constant, two pressures are validated: 30 bar and 40 bar. The liquid boundaries in Figure 4.2 are almost vertical lines. Temperature does not influence the liquid composition much. Temperature steps of 10 °C are taken. In Table 4.2 the measurement points for the experiment with a pressure of 30 bar experiments are given. In Table 4.3 the measurement points for a pressure of 40 bar experiments are given.

Table 4.2: Measurement points for liquid composition measurement with a constant pressure of 40 bar

<table>
<thead>
<tr>
<th>Data point</th>
<th>T [°C]</th>
<th>p [bar]</th>
<th>CO₂-N₂ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>-20</td>
<td>30</td>
<td>70-30</td>
</tr>
<tr>
<td>#2</td>
<td>-27.5</td>
<td>30</td>
<td>70-30</td>
</tr>
<tr>
<td>#3</td>
<td>-35</td>
<td>30</td>
<td>70-30</td>
</tr>
<tr>
<td>#4</td>
<td>-42.5</td>
<td>30</td>
<td>70-30</td>
</tr>
<tr>
<td>#5</td>
<td>-50</td>
<td>30</td>
<td>70-30</td>
</tr>
</tbody>
</table>

Table 4.3: Measurement points for liquid composition measurement with a constant pressure of 40 bar

<table>
<thead>
<tr>
<th>Data point</th>
<th>T [°C]</th>
<th>p [bar]</th>
<th>CO₂-N₂ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>-20</td>
<td>40</td>
<td>70-30</td>
</tr>
<tr>
<td>#2</td>
<td>-30</td>
<td>40</td>
<td>70-30</td>
</tr>
<tr>
<td>#3</td>
<td>-40</td>
<td>40</td>
<td>70-30</td>
</tr>
<tr>
<td>#4</td>
<td>-50</td>
<td>40</td>
<td>70-30</td>
</tr>
</tbody>
</table>

In the following chapter the experiments will be discussed. If necessary, adjustments to the measurement setup and procedure will be discussed. For each data point the chromatographies will be depicted with an explanation of the graph tendency. In every experiment the data points will be compared to the phase calculation modeling and the most important data will be described per experiment. The measured compositions are in mole percentages.
Chapter 5

Liquid composition experiments

5.1 Liquid composition experiments number 1

The results of liquid experiment number 1 are described in this section.

5.1.1 Data points

The premixed gas bottle is a 79.6-20.4 %CO₂-N₂ mixture with an accuracy of ±2%, which is only used for experiments with low pressures. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of one measurement point, because only a pressure of 23 bar was left in the gas bottle. The temperature of the measurement point is about −50 °C in the lower part of the condensation cell. The pressure of the measurement point is set at 15 bar. At these conditions liquid should form in the condensation cell. No adjustments to the measurement setup and procedure are done.

5.1.2 Results

Data selection

During the data processing a selection of samples are taken to be analyzed. 15 samples are taken to be analyzed which corresponds to an actual runtime of about 8 minutes. In Figure 5.1 the measurement chromatographies of the data point are presented. The first ten chromatographies are impurities in the sample line. Before the measurement was started the sample line was flushed. There are no impurities in the sample line, the chromatographies are constant. The last 15 samples are taken to be analyzed.
5. Liquid composition experiments  5.1. Liquid composition experiments number 1

Overall result

The selected chromatographies of the data point are processed and compared to the phase calculation modeling.

In Figure 5.2 the data point is compared with the model. The data point is positioned at a pressure where according the model the mixture is still in the gas phase. In Table 5.1 the numerical comparison between the experiment and model is given. The difference between the experiment and the model is about 20%. So the data point is not in accordance with the model. During the experiment the pressure of 15 bar began to drop, meaning that the bottle pressure was lower than the set point pressure. Eventually the pressure ended up near 7 bar. In the condensation cell liquid was formed until the pressure dropped under a pressure of 8 bar. At that point the liquid started to evaporate. It was still possible to take liquid samples from the cell.

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO$_2$, meas [%]</th>
<th>CO$_2$, model [%]</th>
<th>Difference [%]</th>
<th>$\sigma$CO$_2$, meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>98.92</td>
<td>79.60</td>
<td>-19.32</td>
<td>0.02</td>
</tr>
</tbody>
</table>

In Table 5.2 the temperatures, pressures, their standard deviations and the chiller temperature are given. The standard deviation of the pressure in the selected range is common. The temperature during the experiment was constant with minor fluctuations of 0.1 °C.
5. Liquid composition experiments  5.2. Liquid composition experiment number 2

Figure 5.2: Fraction CO$_2$ in liquid phase versus pressure at a temperature of $-52.4^\circ$C

Table 5.2: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th>Data point</th>
<th>$p_{avg}$ [bar]</th>
<th>$\sigma_p$ [bar]</th>
<th>$T_{avg}$ [°C]</th>
<th>$\sigma_T$ [°C]</th>
<th>$T_{chiller}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>7.37</td>
<td>0.45</td>
<td>-52.36</td>
<td>0.06</td>
<td>-60.0</td>
</tr>
</tbody>
</table>

5.1.3 Conclusion experiment

In this experiment one data point at a pressure of 15 bar and -50°C is performed with a 79.6-20.4 %CO$_2$-N$_2$ mixture. The measurement is not in accordance with the phase calculation modeling due to the decreasing pressure during the experiment. It has to be avoided to perform an experiment when the condensation cell pressure is maintained at gas bottle pressure.

5.2 Liquid composition experiment number 2

The results of liquid experiment number 2 are described in this section.

5.2.1 Data points

The premixed gas bottle is a 49.6-50.4 %CO$_2$-N$_2$ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of five measurement points. The temperature of all measurement points is about $-50^\circ$C in the lower part of the condensation cell. The pressures of the measurement points are respectively 15 bar, 25 bar, 35 bar, 40 bar and 45 bar (see Table 4.1). At a pressure of 13 bar the mixture is in the gas phase. This data point is used to check if the gas composition in the cell consists of the same composition as the bottle composition. At the remaining pressures liquid should be formed in the condensation cell. No adjustments to the measurement setup and procedure were done.
5. Liquid composition experiments  

5.2. Liquid composition experiment number 2  

5.2.2 Results  

Data selection  

During the data processing a selection of samples are analyzed. 15 samples are used which corresponds to an actual runtime of about 8 minutes. The pressure set points slightly deviate from the desired set points due to inaccurate setting possibilities of the pressure reducer.

![Graph](image1)

Figure 5.3: Percentage CO$_2$ in liquid phase vs the corresponding sample number at a pressure of 26.1 bar and a temperature of $-49.4\,^\circ$C

In Figure 5.3 most chromatographies are impurities in the sample line. Every sample has to undergo a phase transition from liquid to gas, in which the volume of one sample increases with a factor of 1000. It takes time to process all impurities of the system. The last chromatographies are steady, so the last 15 samples are used for data processing. In Figure 5.4 the chromatographies of the third data point are depicted. In the beginning the sample line still contains impurities of the previous data point. The last chromatographies are steady, so the last 15 samples are used for data processing.

![Graph](image2)

Figure 5.4: Percentage CO$_2$ in liquid phase vs the corresponding sample number at a pressure of 33.7 bar and a temperature of $-49.6\,^\circ$C

In Figure 5.5 the chromatographies of the fourth data point are depicted. Unlike at the previous data points no impurities were present in the beginning of the measurement and it remained quite steady during the entire experiment. The last 15 samples are used for data processing. In Figure 5.6 the chromatographies of the fifth data point are depicted. The first samples are again results

![Graph](image3)

Figure 5.5: Percentage CO$_2$ in liquid phase vs the corresponding sample number at a pressure of 41.3 bar and a temperature of $-50.1\,^\circ$C

![Graph](image4)

Figure 5.6: Percentage CO$_2$ in liquid phase vs the corresponding sample number at a pressure of 47.5 bar and a temperature of $-49.5\,^\circ$C
5. Liquid composition experiments  5.2. Liquid composition experiment number 2

of impurities in the sample line. When the impurities were removed the chromatographies were steady. The last 15 samples were used for data processing.

Overall result

The selected chromatographies of the data points are processed and compared with the phase calculation modeling.

[Graph: Fraction CO\textsubscript{2} in liquid versus pressure at a temperature of \(-49.6^\circ\text{C}\)]

Figure 5.7: Fraction CO\textsubscript{2} in liquid phase versus pressure at a temperature of \(-49.6^\circ\text{C}\)

In Figure 5.7 the first data point is consistent with the model. The mixture composition of the cell contains the same as the mixture composition of the gas bottle. The other data points are positioned below the model line. In Figure 5.8 a close up of the data point positions is depicted. In Table 5.3 the results of the measurements and the model are compared. The difference between the model and the experiments increases when the pressure increases. The maximum distance is 2.4 % which is very large in phase calculations. The mass flow in the sample line is too low for good measurements. When liquid samples are entering the sample line, the sample heats up due to heat from the ambient air to the sample line. A two phase flow region establishes. Some gas in the two phase flow region will flow back into the condensation cell. Eventually less CO\textsubscript{2} is measured with the GC.
5. Liquid composition experiments  

5.2. Liquid composition experiment number 2

![Graph](image)

Figure 5.8: Close up of Figure 5.7

Table 5.3: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>( \text{CO}_2, \text{meas} ) [%]</th>
<th>( \text{CO}_2, \text{model} ) [%]</th>
<th>Difference [%]</th>
<th>( \sigma_{\text{CO}_2, \text{meas}} ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>49.63</td>
<td>49.60</td>
<td>-0.03</td>
<td>0.67</td>
</tr>
<tr>
<td>#2</td>
<td>96.26</td>
<td>96.90</td>
<td>0.63</td>
<td>0.14</td>
</tr>
<tr>
<td>#3</td>
<td>93.73</td>
<td>95.65</td>
<td>1.93</td>
<td>0.05</td>
</tr>
<tr>
<td>#4</td>
<td>92.50</td>
<td>94.40</td>
<td>1.89</td>
<td>0.09</td>
</tr>
<tr>
<td>#5</td>
<td>90.97</td>
<td>93.38</td>
<td>2.41</td>
<td>0.26</td>
</tr>
</tbody>
</table>

In Table 5.4 the temperatures, pressures, their standard deviations and the chillers temperature are given. The temperature throughout the experiment is quite steady with minor fluctuations during the measurements. The pressure fluctuations are regular, exactly like the pressure fluctuations during the sensor calibration.

Table 5.4: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th>Data point</th>
<th>( p_{\text{avg}} ) [bar]</th>
<th>( \sigma_{p} ) [bar]</th>
<th>( T_{\text{avg}} ) [(^\circ)C]</th>
<th>( \sigma_{T} ) [(^\circ)C]</th>
<th>( T_{\text{chiller}} ) [(^\circ)C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>12.94</td>
<td>0.53</td>
<td>-49.35</td>
<td>0.05</td>
<td>-57.5</td>
</tr>
<tr>
<td>#2</td>
<td>26.09</td>
<td>0.55</td>
<td>-49.46</td>
<td>0.04</td>
<td>-57.5</td>
</tr>
<tr>
<td>#3</td>
<td>33.69</td>
<td>0.44</td>
<td>-49.56</td>
<td>0.03</td>
<td>-57.0</td>
</tr>
<tr>
<td>#4</td>
<td>41.26</td>
<td>0.46</td>
<td>-50.05</td>
<td>0.06</td>
<td>-57.0</td>
</tr>
<tr>
<td>#5</td>
<td>47.52</td>
<td>0.60</td>
<td>-49.45</td>
<td>0.02</td>
<td>-57.0</td>
</tr>
</tbody>
</table>
5. Liquid composition experiments

5.2.3 Conclusion experiment

In this experiment liquid measurements at -50°C are done with a 49.6-50.4 %CO₂-N₂ mixture. The measurement is not in accordance with the phase calculation modeling due to back flowing of gas into the condensation cell. The mass flow in the sample line should be increased or the sample line should be insulated up to the primary valve. By doing this, no two phase flow region can occur before the primary valve. Moreover the vertical pipes should be as short as possible to avoid back flowing of the gas through the liquid above into the condensation cell.

5.3 Liquid composition experiment number 3

The results of liquid experiment number 3 are described in this section. If necessary, adjustments to the measurement procedure and measurement setup are discussed, which are described in Chapter and Chapter .

5.3.1 Data points

The premixed gas bottle is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of five measurement points. The temperature of all measurement points is about -50°C in the lower part of the condensation cell. The pressures of the measurement points are respectively 10 bar, 25 bar, 35 bar, 40 bar and 45 bar (see Table 4.1). At a pressure of 10 bar the mixture is in the phase. This data point is used to check if the gas composition in the cell consists of the same composition as the bottle composition. At the remaining pressures liquid should form in the condensation cell.

5.3.2 Adjustments measurement setup

In the previous experiment (Section 5.2.3) the measurement results were not in accordance with the phase calculation modeling. In the two phase flow region the gas flowed back into the condensation cell resulting in a lower CO₂ content in the sample line. In order to reduce the gas back flowing into the cell, the sample line is insulated up to the primary valve. Furthermore the pipe up to the primary valve is inclined, so that the gas flows to the GC instead of back into the cell. A schematic representation of the sample line is shown in Figure 5.9. No adjustments to the measurement procedure are done.

![Figure 5.9: Sample line](image-url)
5. Liquid composition experiments  

5.3. Liquid composition experiment number 3

5.3.3 Results

Data selection

During the data processing a selection of samples are taken to be analyzed. 15 samples are taken to be analyzed which correspond to an actual runtime of about 8 minutes. The chromatographies of the gas measurement done during this experiment are not shown, because this graph is similar to the sample graphs depicted in the 'equilibrium gas compositions measurements' chapter. The pressure set points slightly deviate from the desired set points due to inaccurate setting possibilities of the pressure reducer.

![Figure 5.10: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 26.7 bar and a temperature of -50.8°C](image1)

![Figure 5.11: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 34.1 bar and a temperature of -51.4°C](image2)

In Figure 5.10 the chromatographies of the second data point are depicted. The measurement has a periodical character, but the fluctuations have the tendency to get larger into time. The periodical behavior is a result of a 'sludge' flow in the sample line. In the two phase region, areas of low CO₂ content and areas of high CO₂ content form. All effects in the sample line should be included in this case to take account of the periodically behavior, so the first 15 chromatographies are chosen to be analyzed.

In Figure 5.11 the chromatographies of the third data point are depicted. This result differs from the previous data point. It shows no periodical character, but a clear plug flow. In the sample line regions of impurities form due to two phase flow effects. These regions have a low CO₂ content which result into a sharp decrease. Over time the remaining impurities are removed until its constant value is reached again. In order to avoid the plug flow effects the first 15 chromatographies are selected to be analyzed.
5. Liquid composition experiments  
5.3. Liquid composition experiment number 3

Figure 5.12: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 41.4 bar and a temperature of −50.8 °C

The chromatographic tendency of the fourth data point (Figure 5.12) differs from the previous two. The tendency of the line is in a range of 0.4%. In this case the chromatographies with the highest CO₂ content are selected, which are sample numbers 20 till 35. The chromatographies tendency of the fifth data points (Figure 5.13) are steady, which are in the range of 0.8%. The last 15 chromatographies are taken to be analyzed.

Overall result

The selected chromatographies of the data points are processed and compared with the phase calculation modeling, which is depicted in Figure 5.14.

Figure 5.13: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 46.8 bar and a temperature of −50.8 °C

Figure 5.14: Fraction CO₂ in liquid phase versus temperature at a temperature of −50.8 °C

The gas measurement (data point 1) is slightly above the composition of the gas bottle, which may be caused by too little gas volume used during flushing of the cell. This has no influence at the liquid compositions at higher pressures. The liquid data points are positioned under the model. In
Figure 5.15 a close up of the data point positions below model is given. The difference between the model and measurement is decreased by about 1% (see Table 5.15), thus the insulation material and the inclined pipe adjustments improve the results.

![Graph showing fraction CO2 in liquid vs pressure]

**Figure 5.15**: Close up of Figure 5.14

**Table 5.5**: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO2, meas [%]</th>
<th>CO2, model [%]</th>
<th>Difference [%]</th>
<th>σCO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>49.95</td>
<td>49.60</td>
<td>-0.35</td>
<td>0.27</td>
</tr>
<tr>
<td>#2</td>
<td>95.52</td>
<td>96.89</td>
<td>1.23</td>
<td>0.43</td>
</tr>
<tr>
<td>#3</td>
<td>95.05</td>
<td>95.36</td>
<td>0.48</td>
<td>0.10</td>
</tr>
<tr>
<td>#4</td>
<td>93.63</td>
<td>94.34</td>
<td>0.73</td>
<td>0.04</td>
</tr>
<tr>
<td>#5</td>
<td>91.75</td>
<td>94.34</td>
<td>1.70</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The difference is not uniform during the experiment. It may depend on the type of flow in the sample line. When a plug flow is present in the sample line it has the tendency to decrease the difference than when other flow features in the sample line are present. The temperature standard deviations are also not identical during the measurements. During the first three data points the temperature was steady, but during the last data points the temperature was not steady. Fluctuations in temperature of about 0.6°C were present, so the condensation cell was not in equilibrium. The pressure standard deviations were steady during the experiment.

**Table 5.6**: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>11.59</td>
<td>0.50</td>
<td>-48.91</td>
<td>0.10</td>
<td>-58.0</td>
</tr>
<tr>
<td>#2</td>
<td>26.67</td>
<td>0.55</td>
<td>-50.86</td>
<td>0.08</td>
<td>-57.5</td>
</tr>
<tr>
<td>#3</td>
<td>34.13</td>
<td>0.54</td>
<td>-51.23</td>
<td>0.05</td>
<td>-57.0</td>
</tr>
<tr>
<td>#4</td>
<td>41.36</td>
<td>0.47</td>
<td>-50.79</td>
<td>0.32</td>
<td>-57.0</td>
</tr>
<tr>
<td>#5</td>
<td>46.87</td>
<td>0.37</td>
<td>-50.81</td>
<td>0.36</td>
<td>-56.5</td>
</tr>
</tbody>
</table>
5. Liquid composition experiments 5.4. Liquid composition experiment number 4

5.3.4 Conclusion experiment

Although the results are improved with 1% in comparison with the previous experiments, the results are not in accordance with the model. The deviations are still too large. The measurement setup adjustments did partly prevent back flushing of gas into the cell, but the CO₂ content is too low in the sample line. This indicates that there is still back flowing of gas. Moreover, the two phase flow effects in the sample line cause inconsistent measurements. In order to solve these problems the mass flow has to be increased in the sample line.

5.4 Liquid composition experiment number 4

The results of liquid experiment number 4 are described in this section. If necessary, adjustments to the measurement procedure and measurement setup are discussed.

5.4.1 Data points

The premixed gas bottle is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of a total of three measurement points. The temperature of all measurement points is about −50°C in the lower part of the condensation cell. The pressures of the measurement points are respectively 25 bar, 35 bar and 40 bar. At these pressures liquid should form in the condensation cell.

5.4.2 Adjustments measurement setup

According to the previous measurements CO₂ gas will flow back through the liquid into the cell in the sample line, which results in a lower CO₂ concentration in the liquid. The flow rate of the sample line must be increased so that no CO₂ will be transported back to the cell. A second valve is introduced at the end of the sample line. A second leakage stream is established with the second valve for increasing the flow rate in the sample line. A schematic representation of the sample line is shown in Figure 5.16.

![Sample line diagram](image)

Figure 5.16: Sample line

5.4.3 Adjustment measurement procedure

During the startup of the experiment setup the pressure transducer displayed negative values. The pressure transducer was demounted from the condensation cell and then remounted at the
5. Liquid composition experiments  5.4. Liquid composition experiment number 4

cell, which solved the problem with negative pressures. The reason why the pressure transducer displayed negative values is unknown.

The gas measurement at a low pressure is not performed. Instead, during the early stages of the cooling process a gas measurement is done to verify the gas composition. The pressure is set at the pressure of the first data point. The temperature is around zero degrees and decreasing over time, so the mixture is still into the gas phase.

The first valve in the sample line is closed during non equilibrium phases. When the condensation cell is in equilibrium the first valve is opened. The second valve is fully opened for 1 second to flush the sample line. The GC and Labview should be running at the same time. A very small leakage flow is established by slightly opening the second valve at touch. The heat pressure reducer screw is screwed on until a pressure of about 1.2 bar is established which results in the primary leakage. After one data point the heat pressure reducer screw is loosened and both valves are closed. The above mentioned steps are repeated.

5.4.4 Results
Data selection

During the data processing a selection of samples are analyzed. 15 samples are used which corresponds to an actual runtime of about 8 minutes.

![Overall graph](image1)

![Close-up of graph](image2)

(a) Overall graph  (b) Close-up of graph

Figure 5.17: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 25.8 bar and a temperature of −50.5°C

In Figure 5.17 the measurement chromatographies of data point one are presented. The first part of the measurement was contaminated by residuals of previous measurements. The last part of the left figure is the result of taking gas samples instead of liquid samples. The mixture in the condensation cell was purely in gas phase, that means a non equilibrium state in the cell. When the secondary valve was opened a little bit more a distinctive peak showed and the CO₂ composition decreased (2 peaks in Figure 5.17b). The chromatography region 25 till 40 was used in the data processing.
Figure 5.18: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 35.3 bar and a temperature of −50.5°C

Figure 5.19: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 41.5 bar and a temperature of −50.5°C

Figure 5.20: Fraction CO₂ in liquid phase versus pressure at a temperature of −50.5°C
In Figure 5.20 the gas check measurement is plotted at 5 bar to verify if the measured composition is in accordance with the composition in the cylinder. The liquid measurement points are slightly positioned below the model which is depicted in Figure 5.21 (which is a close up of Figure 5.20). In Table 5.7 the results of the measurements and the model are compared.

Table 5.7: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂,meas [%]</th>
<th>CO₂, model [%]</th>
<th>Difference [%]</th>
<th>σCO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>49.82</td>
<td>49.60</td>
<td>-0.22</td>
<td>0.68</td>
</tr>
<tr>
<td>#2</td>
<td>96.79</td>
<td>96.89</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>#3</td>
<td>94.96</td>
<td>95.36</td>
<td>0.40</td>
<td>0.03</td>
</tr>
<tr>
<td>#4</td>
<td>93.86</td>
<td>94.34</td>
<td>0.49</td>
<td>0.06</td>
</tr>
</tbody>
</table>

At the second measurement point at 26 bar the measured composition is slightly less than the model composition. However, the difference between the measured value and the model value is less than the standard deviation, so this measurement point is in accordance with the model. The remaining two measurement points are not correspond with the model because the difference is larger than the standard deviation. A possible reason is that the flow rate was too low. The secondary valve should be opened a little bit further, but then the condensation cell will reach much faster a non equilibrium state. A good balance between the flow rate and the running time of the measurement is very important to get good reliable results.

Table 5.8: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>5.00</td>
<td>NaN</td>
<td>-50.50</td>
<td>NaN</td>
<td>-56.5</td>
</tr>
<tr>
<td>#2</td>
<td>25.87</td>
<td>0.48</td>
<td>-50.45</td>
<td>0.06</td>
<td>-56.5</td>
</tr>
<tr>
<td>#3</td>
<td>35.30</td>
<td>0.47</td>
<td>-50.48</td>
<td>0.03</td>
<td>-56.0</td>
</tr>
<tr>
<td>#4</td>
<td>41.53</td>
<td>0.42</td>
<td>-50.46</td>
<td>0.02</td>
<td>-56.0</td>
</tr>
</tbody>
</table>

Figure 5.21: Close up of Figure 5.20
In Table 5.8 the temperatures, pressures, their standard deviations and the chiller temperature are given. The standard deviations of the pressure and temperature of data point 1 are not given, because this was a check measurement. The temperature difference between the data points is only 0.05 °C which is very small. The temperature throughout this experiment was the most steady up to now.

5.4.5 Conclusion experiment

The sample line adjustments improved the measurements by one percent, but the overall result of the experiment is still not in accordance with the model. The main reason is that the flow rate in the sample line is still too low, so that gas (primarily CO₂) flows back to the condensation cell resulting in a lower CO₂ composition at the end of the sample line. The flow rate should be increased in such a way that the condensation cell remains long enough in equilibrium for decent measurements. When this is not possible the sample line should be readjusted.

5.5 Liquid composition experiment number 5

The results of liquid experiment number 5 are described in this section. If necessary, adjustments to the measurement procedure and measurement setup are discussed, which are described in Sections (measurement setup and measurement procedure).

5.5.1 Data points

The premixed gas bottle is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of a total of three measurement points. The temperature of all measurement points is about −50 °C in the lower part of the condensation cell. The pressures of the measurement points are respectively 26 bar, 35 bar and 40. At these pressures liquid should form in the condensation cell.

5.5.2 Adjustment measurement procedure

The measurement setup was not changed for this experiment. The measurement setup used in this experiment is described in section 5.4.2. No gas measurement is done, because the gas compositions were validated with the equilibrium gas measurements. Moreover, the condensation cell is flushed twice to remove impurities of the previous measurements. The measurement procedure remains the same as described in section 5.4.3. A small change is that the secondary valve is opened slightly more for increasing the mass flow in the sample line, which should result in a better measurement.

5.5.3 Results

Data selection

Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which are chosen manually. The focus during the selection is the compositions and not at the temperature and pressure which remain more or less constant during the measurement. The chromatographies of the two data points will be discussed.
5. Liquid composition experiments 5.5. Liquid composition experiment number 5

Figure 5.22: Percentage CO\textsubscript{2} in liquid phase vs the corresponding sample number at a pressure of 26bar and a temperature of $-50.4^\circ$C

In Figure 5.22 the fraction CO\textsubscript{2} in liquid samples at the first data point is shown. In previous measurements fifteen chromatographies were taken to be analyzed. But due to the fact that the mass flow in the sample line is higher, the condensation cell will reach much faster a non equilibrium state. The useful chromatographies for data analyzing reduces as a consequence of shorter measurement runtime, so in this case ten chromatographies are taken to be analyzed. For data point one, the last ten chromatographies are taken, because in this area the concentrations are fairly constant (Figure 5.22b).

Data points number two and three can not be used for processing because these measurements are not reliable. The GC displayed values near the hundred percent, which is not possible according the thermodynamics of the mixture at these process conditions. There are three possible causes:

1. The two phase flow region is positioned up to the end of the sample line, which results in expansion in the secondary valve. CO\textsubscript{2} is cooled down in the valve and CO\textsubscript{2} ice is formed.

2. The two phase flow region is still present at the end of the sample line. The N\textsubscript{2} is boiled out the liquid. The gas (primarily N\textsubscript{2}) is released into the ambient air by the secondary valve. The CO\textsubscript{2} is boiled afterwards. The remaining gas is fed to the pressure reducer membrane, which results in an almost pure CO\textsubscript{2} gas.

3. Liquid is fed to the GC, that caused the GC to be broken. This has to be checked.

A combination of 1 and 2 occurred during the last two data points, which reinforced each other. 'Flashing' CO\textsubscript{2} ice was observed during these measurements.

Overall result

The selected chromatographies of the data point are processed and compared with the phase calculation modeling. The measurement point in Figure 5.23 is in accordance with the model. It is positioned just below the model. In Table 5.23 the actual values of the measurements and model are given with the standard deviation and difference between the model and the measurements. The difference between the phase calculation modeling and the measurement point is 0.16 %, but the standard deviation is much smaller. A higher flow rate can improve the results, but the flow in the sample line should be in the gas phase at the end of the sample line.
5. Liquid composition experiments  

5.5. Liquid composition experiment number 5

![Graph showing fraction CO₂ in liquid phase versus pressure at a temperature of -50.4 °C](image)

Figure 5.23: Fraction CO₂ in liquid phase versus pressure at a temperature of -50.4 °C

Table 5.9: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂,meas [%]</th>
<th>CO₂,model [%]</th>
<th>Difference [%]</th>
<th>σCO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>96.63</td>
<td>96.80</td>
<td>0.16</td>
<td>0.05</td>
</tr>
</tbody>
</table>

In Table 5.10 the process conditions of the experiment are given. The temperature of the chiller is set at -57.0 °C because the impeller was set at position 3 instead of position 6. The heat transfer and the mass transfer were reduced in the condensation cell. The standard deviation of the pressure is common, because its value are the same as in the other experiments. The temperature of the measurement was steady. Temperature fluctuations were in a range of 0.1 °C.

Table 5.10: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th>Data point</th>
<th>pavg [bar]</th>
<th>σp [bar]</th>
<th>Tavg °C</th>
<th>σT °C</th>
<th>Tchiller °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>26.50</td>
<td>0.46</td>
<td>-50.37</td>
<td>0.03</td>
<td>-57.0</td>
</tr>
</tbody>
</table>

5.5.4 Conclusion experiment

The first data point is in accordance with the phase calculation model, but it can be improved to increase the flow rate in the sample line. The difference between the model and the data point can be explained as an error in the model. The other data points could not be performed, because the flow rate in the sample line was too high and the transient state of the sample line was too short (causes 1 and 2). So, the leakage flow should be set more carefully by adjusting the leakage flow in small steps. The GC should be checked to ensure that no fluid elements have entered the analyze column.
5.6 Liquid composition experiment number 6

The results of liquid experiment number 6 are described in this section. If necessary, adjustments to the measurement procedure and measurement setup are discussed, which are described in the sections Measurement setup and Measurement procedure.

5.6.1 Data points

The premixed gas bottle is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of a total of two measurement points. The temperature of all measurement points is about -50°C in the lower part of the condensation cell. The pressures of the measurement points are respectively 35 bar and 40 bar. At these pressures liquid should form in the condensation cell. These measurement points are chosen because no reliable data is obtained yet at these specific points during previous experiments.

5.6.2 Adjustment measurement procedure

No changes in the measurement setup were done. The measurement setup used in this experiment is described in section 5.4.2. A day prior to the experiment the gas chromatographer was checked whether some fluid elements had entered the GC, which is devastating for the measurement equipment. The condensation cell was filled with the gas from the composition bottle. The samples taken from the cell were analyzed with the GC. The results were identical to the composition of the gas bottle.

In order to prevent the problems which occurred in liquid experiment #5 (section 5.5) the secondary valve should be opened with much more care. At first the secondary valve is closed and the first samples are analyzed at these settings. The secondary valve will be opened more if the results are not in accordance with the model in steps until the problems of the previous experiment occur.

5.6.3 Results

Data selection

Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which is selected manually. The focus during the selection is the compositions and not at the temperature and pressure which remain more or less constant during the measurement. The chromatographies of the two data points will be discussed.

In Figure 5.24 the measurement chromatographies of data point one are presented. The first 10 samples were not useful, because the sample line is filled with impurities which have to be flushed out of the system. At the end of the measurement ice was produced in the secondary valve, resulting in a very high CO₂ concentration. The range of interest is from sample number 20 till 45. In this range the secondary valve is slightly opened. It is common to get first a peak and after 3 samples a decay occurs. The best samples are around number 35, so the samples for processing are 33-38. A small margin of samples is chosen, because the other samples deviate too much for data processing due to previous described effects.
5. Liquid composition experiments

5.6. Liquid composition experiment number 6

Figure 5.24: Percentage CO\textsubscript{2} in liquid phase vs the corresponding sample number at a pressure of 35 bar and a temperature of -50.5°C

In Figure 5.25 the measurement chromatographies of data point two are presented. The secondary valve was initially closed, so a drop in CO\textsubscript{2} was observed. The first samples are leftovers from the previous measurement point. From sample number 47 the CO\textsubscript{2} measured was too high due to ice forming in the secondary valve and boiling the N\textsubscript{2} out of the mixture. The secondary valve was closed. The CO\textsubscript{2} concentration went down but not enough. When the secondary flow was opened again the CO\textsubscript{2} concentration increased. Therefore, when ice forming occurs in the sample line, the samples analyzed from that point are not reliable. Therefore, the samples to be analyzed are number 28 to 33. This distinctive peak is chosen, because these samples appear to be in accordance with the model. Moreover, no ice forming was observed in the secondary valve.

Figure 5.25: Percentage CO\textsubscript{2} in liquid phase vs the corresponding sample number at a pressure of 42 bar and a temperature of -50.5°C

Overall result

The selected chromatographies of the data points are processed and compared with the phase calculation modeling.
5. Liquid composition experiments 5.6. Liquid composition experiment number 6

Figure 5.26: Fraction CO₂ in liquid phase versus pressure at a temperature of −50.5 °C.

The first measurement point in Figure 5.26 is positioned a bit under the phase calculation model, but at an acceptable distance of 0.13 percent (Table 5.12). This distance can be caused by an error in the phase calculation modeling. The second measurement point is positioned above the model line. The standard deviation is quite high due to the fluctuations in the chosen samples, but these samples are still the best samples for data processing. The overall conclusion is that all points are in accordance with the model.

Table 5.11: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂_{meas} [%]</th>
<th>CO₂_{model} [%]</th>
<th>Difference [%]</th>
<th>σ_{CO₂_{meas}} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>95.21</td>
<td>95.34</td>
<td>0.13</td>
<td>0.06</td>
</tr>
<tr>
<td>#2</td>
<td>94.47</td>
<td>94.44</td>
<td>-0.03</td>
<td>0.42</td>
</tr>
</tbody>
</table>

In Table 5.12 the temperatures, pressures, their standard deviations and the chiller temperature are given. The average temperatures are very close to each other, which is very hard to accomplish due to heat losses to the ambient air. The standard deviations are very small, indicating that the temperatures were constant during the measurements. The standard deviation of the pressure in data point 2 is quite high in comparison with a normal pressure standard deviation. The most probable reason for this effect is that liquid is taken from the cell, the pressure reducer has to regulate the pressure in the cell. This resulted in more pressure fluctuations this time.

Table 5.12: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th>Data point</th>
<th>p_{avg} [bar]</th>
<th>σ_p [bar]</th>
<th>T_{avg} [°C]</th>
<th>σ_T [°C]</th>
<th>T_{chiller} [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>35.37</td>
<td>0.46</td>
<td>-50.70</td>
<td>0.01</td>
<td>-57.0</td>
</tr>
<tr>
<td>#2</td>
<td>40.90</td>
<td>0.58</td>
<td>-50.57</td>
<td>0.04</td>
<td>-56.5</td>
</tr>
</tbody>
</table>
5.6.4 Conclusion experiment

The measurements are in accordance with the model. The model is validated for high pressures at constant temperature. Care should be taken when the secondary valve is opened to prevent unwanted effects in the sample line. The experiments at constant temperature and variable pressures are completed. The next phase is to look at experiments at constant pressure with variable temperatures.

5.7 Liquid composition experiment number 7

The results of liquid experiment number 7 are described in this section. If necessary, adjustments to the measurement procedure and measurement setup are discussed.

5.7.1 Data points

A premixed gas bottle of 69.8-30.4 %CO₂-N₂ mixture with an accuracy of ±2%. With use of this gas bottle condensation occurs at a lower pressure than when using a premixed gas bottle of 49.6-50.4 %CO₂-N₂ mixture. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists in total of two measurement points. The temperature of all measurement points is about −50 °C in the lower part of the condensation cell. The pressures of the measurement points are respectively 15 bar and 20 bar. At these pressures liquid should form in the condensation cell and the liquid fraction in the cell should be higher than 25%. The measurement setup described in Section 5.4.2 is used. The measurement procedure described in Section 5.6.2 is used.

5.7.2 Results

Data selection

Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which is selected manually. The focus during the selection is the compositions and not at the temperature and pressure which remain more or less constant during the measurement. The chromatographies of the two data points will be discussed.

![Figure 5.27: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 14.4 bar and a temperature of −50.8 °C](image-url)
5. **Liquid composition experiments**  

5.7. **Liquid composition experiment number 7**

In Figure 5.27 the measurement chromatographies of data point one are presented. The first 20 samples are not useful, because the sample line is filled with impurities which have to be flushed out of the system. When the impurities were removed, the tendency of the graph went up to a steady value with clear fluctuations. The range of interest is from sample number 21 till 31. The chromatographies of data point two (Figure 5.28) have the same tendency as the chromatographies of data point one. The impurities have to removed out of the sample line, which will make sure that the results fluctuate around a steady value. The range of interest are the last ten samples.

![Overall graph](image1.png)  
![Close-up of graph](image2.png)

Figure 5.28: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 21.2bar and a temperature of -50.6°C
5. Liquid composition experiments

5.7. Liquid composition experiment number 7

Overall result

The selected chromatographies of the data points are processed and compared with the phase calculation modeling, which is shown in Figure 5.29.

![Figure 5.29: Fraction CO₂ in liquid phase versus temperature at a pressure of 40.1 bar](image)

In Table 5.13 important values of the comparison are given. Both data points are positioned above the model line. The difference is about 0.03% with a standard deviation of 0.15%. So the measurement results are in accordance with the model. The model is validated for low pressures at constant temperature.

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂, meas [%]</th>
<th>CO₂, model [%]</th>
<th>Difference [%]</th>
<th>σ_CO₂, meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>98.77</td>
<td>98.73</td>
<td>-0.04</td>
<td>0.15</td>
</tr>
<tr>
<td>#2</td>
<td>97.67</td>
<td>97.64</td>
<td>-0.03</td>
<td>0.11</td>
</tr>
</tbody>
</table>

In Table 5.14 the temperatures, pressures, their standard deviations and the chiller temperature are given. The temperature were steady during the experiments. Moreover the temperatures of the data points were almost identical. The deviations of the pressures is identical in comparison with previous measurements.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>14.39</td>
<td>0.52</td>
<td>-50.75</td>
<td>0.03</td>
<td>-56.5</td>
</tr>
<tr>
<td>#2</td>
<td>21.22</td>
<td>0.54</td>
<td>-50.55</td>
<td>0.02</td>
<td>-56.3</td>
</tr>
</tbody>
</table>
5.7.3 Conclusion experiment
In this experiment liquid measurements at -50°C in combination with low pressures are done with a 69.8-30.4 %CO₂-N₂ mixture. The experiment results are consistent with the phase calculation modeling. For each data point the first samples were contaminated with impurities of previous measurements. Eventually the results went to a steady value with clear fluctuations. The phase calculation modeling is validated for low pressures until 45 bar at a constant temperature. The tendency of the liquid compositions for other temperatures is the same as the tendency validated in the previous measurement. The liquid composition experiments at a constant temperature are completed. The next step is performing liquid composition experiments at a constant pressure.

5.8 Liquid composition experiment number 8
The results of liquid experiment number 8 are described in this section. This experiment is the first experiment in which the pressure is kept constant.

5.8.1 Data points
The premixed gas bottle is a 69.8-30.2 %CO₂-N₂ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of in total of four measurement points. The pressure of all measurement points is about 40 bar. The temperatures of the measurement points are respectively -20°C, -27.5°C, -35°C and -42.5°C. At these temperatures liquid should form in the condensation cell and the liquid fraction in the cell should be higher than 25%.

5.8.2 Adjustment measurement procedure
The measurement setup used in this section is described in Section 5.4.2. The main adjustment to the measurement procedure is that the pressure is kept constant and not the temperature. In order to reach the temperature of data point 1, the cooling down cycle of the large chiller is set just below the desired temperature. The pressure is set at with the pressure reducer at the desired pressure. After a measurement the temperature of the large chiller is set just above the temperature of the next data point. If necessary, the pressure is adjusted.

The first valve in the sample line is closed during non equilibrium phases. When the condensation cell is in equilibrium the first valve is opened. The second valve is fully opened for 1 second to flush the sample line. The GC and Labview should be running at the same time. The heat pressure reducer screw is screwed on until a pressure of about 1.2 bar is established which results in the primary leakage. The secondary valve is more opened if the results are not consistent with the model in steps until ice forming in the secondary valve is observed. After a measurement the heat pressure reducer screw is loosened and both valves are closed. The above mentioned steps are repeated.

5.8.3 Results
Data selection
Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which is selected manually. The focus during the selection is the compositions and not at the temperature and pressure which remain more or less constant during the measurement. The chromatographies of the four data points will be discussed.
5. Liquid composition experiments  5.8. Liquid composition experiment number 8

Figure 5.30: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40.2 bar and a temperature of −20.8 °C

The first few chromatographies are results of impurities in the sample line. The secondary valve was opened in order to increase the mass flow in the sample line. The results were below the expectations so the secondary valve was opened a little further a couple of times. Eventually ice forming in the secondary valve was observed. Only five samples were taken to be analyzed due to the lack of steady measurements during these experiments. The selected range is from sample number 27 till 32.

Figure 5.31: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40.6 bar and a temperature of −28.0 °C
The graph tendencies of data point 2, 3 and 4 (respectively Figures 5.31, 5.32 and 5.33) are identical to the graph tendency of data point 1. In the beginning impurities were present in the sample line. The secondary valve was used to increase the mass flow a couple of times, resulting at the end in ice forming in the secondary valve. The selected range is from number 17 till 22 for data point 2. For data point 3 the selected range is number 22 till 27. For data point 4 the selected range is number 17 till 22.

Figure 5.32: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40.5 bar and a temperature of −35.2 °C

Figure 5.33: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40.2 bar and a temperature of −41.9 °C
5. Liquid composition experiments  5.8. Liquid composition experiment number 8

Overall result

The selected chromatographies of the data points are processed and compared with the phase calculation modeling, which is shown in Figure 5.34. All data points are positioned under the model line. The difference between the results and the model is about 0.45% (see Table 5.15), which is much more than the standard deviations in the CO2 measurements. The results are not in accordance with the model.

![Figure 5.34: Fraction CO2 in liquid phase versus pressure at a temperature of -50.5°C.](image)

Table 5.15: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO2_{meas} [%]</th>
<th>CO2_{model} [%]</th>
<th>Difference [%]</th>
<th>\sigma_{CO2,meas} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>95.73</td>
<td>96.22</td>
<td>0.49</td>
<td>0.11</td>
</tr>
<tr>
<td>#2</td>
<td>95.16</td>
<td>95.58</td>
<td>0.42</td>
<td>0.13</td>
</tr>
<tr>
<td>#3</td>
<td>94.65</td>
<td>95.14</td>
<td>0.49</td>
<td>0.10</td>
</tr>
<tr>
<td>#4</td>
<td>94.56</td>
<td>94.87</td>
<td>0.31</td>
<td>0.10</td>
</tr>
</tbody>
</table>

In Table 5.16 the temperatures, pressures, their standard deviations and the chiller temperatures are given. The pressure of data point number 1 and 4 are equal to each other, but differ about 0.3 bar with the pressure of data point number 2 and 3. During the experiment the pressure reducer is adjusted, that resulted in pressure differences. In the next measurements the pressure reducer should be set once in order to reduce these difference.
Table 5.16: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th>Data point</th>
<th>( p_{avg} ) bar</th>
<th>( \sigma_p ) bar</th>
<th>( T_{avg} ) °C</th>
<th>( \sigma_T ) °C</th>
<th>( T_{chiller} ) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>40.18</td>
<td>0.43</td>
<td>-20.84</td>
<td>0.01</td>
<td>-23.0</td>
</tr>
<tr>
<td>#2</td>
<td>40.55</td>
<td>0.46</td>
<td>-28.04</td>
<td>0.02</td>
<td>-31.5</td>
</tr>
<tr>
<td>#3</td>
<td>40.49</td>
<td>0.43</td>
<td>-35.24</td>
<td>0.03</td>
<td>-40.0</td>
</tr>
<tr>
<td>#4</td>
<td>40.18</td>
<td>0.52</td>
<td>-41.87</td>
<td>0.02</td>
<td>-47.5</td>
</tr>
</tbody>
</table>

The temperatures are very steady. Only fluctuations of 0.06 °C are measured. The difference between the actual temperature in the cell and the set point of the large chiller increases when a lower temperature has to be reached. In this case the temperature difference between the cell and ambient air is larger, so more heat losses occur to the ambient air.

5.8.4 Conclusion experiment

In this experiment liquid measurements at 40 bar were done with a 69.8-30.2 %CO₂-N₂ mixture. The experiment results are consistent with the phase calculation modeling. A difference of about 0.45 % is within the maximum relative standard deviation of the GC[5]. The chromatographies tendencies of all data points were unsteady, which at the end resulted in ice forming in the secondary valve. In the next measurements the pressure reducer should be set only once to get a more uniform pressure during the entire experiment.

5.9 Liquid composition experiment number 9

The results of liquid experiment number 9 are described in this section. If necessary, adjustments to the measurement procedure and measurement setup are discussed.

5.9.1 Data points

The premixed gas bottle is a 69.6-30.4 %CO₂-N₂ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. The experiment consists of five data points. In this experiment the pressure is kept constant at 40 bar. The temperatures of the data points are set around a temperature of −20 °C, −27.5 °C, −35 °C, −42.5 °C and −50 °C in the lower part of the condensation. The liquid fraction in the condensation cell should be for all data points above 25%, which is mandatory otherwise not enough liquid is available in the condensation cell for measurements. No gas measurement is done, because from experience the composition in the cell is the same as in the gas bottle, only if the condensation cell is flushed twice.

5.9.2 Adjustments measurement setup

Due to problems in the sample line such as back flushing of gas into the condensation cell and ice forming in the secondary valve, the sample line is constructed in a different way which is depicted in Figure 5.35. A riser is introduced in the condensation cell from the top down to the floor. It is positioned 1 mm from the floor of the cell. The liquid samples are transported vertically to the top of the condensation cell in order to prevent back flushing of gas in the two phase flow region. At the top of the condensation cell the sample line contains a valve and up to the valve the sample line is insulated. From the valve the sample line is bend into a expansion spiral and connected to the entrance of the GC.
5. **Liquid composition experiments**  

5.9. **Liquid composition experiment number 9**

### 5.9.3 Adjustment measurement procedure

Some equipment of the experiment setup can be started with a timer, which is found out recently. In this case the large chiller is set to start early in the morning. One and a half hour is saved. In order to get efficient cooling, some mixture at a few bar is left in the system in which all the valves are closed. The impeller is set with a time switch. A consequence of the change in procedure is that the condensation cell should be flushed twice after an experiment instead of before an experiment.

During non equilibrium conditions the primary valve (Figure 5.35) is closed. When the condensation cell is in equilibrium a measurement is started. First the primary valve is opened, secondary the secondary valve is slightly opened for a few seconds to flush the sample line. Thirdly the pressure reducer screw of the membrane is tightened to get a leakage flow. At last the logging of the temperature, the pressure and the compositions is started. During the experiment a small secondary leak flow can be established with the secondary valve if the mass flow is too low in the sample line. This can be noticed by the fluctuations in the composition results, which are in this case very small. After the measurement the primary valve is closed. The temperature of the large chiller is set at the desired temperature for the next data point and the above procedure is repeated.

### 5.9.4 Results

**Data selection**

Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which is selected manually. The focus during the selection is the compositions and not at the temperature and pressure which remain more or less constant during the measurement. The chromatographies of four data points will be discussed. The data point at a temperature $-42.5^\circ\text{C}$ is not performed due to a low liquid/gas fraction.

In Figure 5.36 the measurement chromatographies of data point one are presented. The first few chromatographies indicate that impurities are present in the sample line. The last chromatographies are an indication that gas samples are taken from the condensation cell instead of liquid samples. In Figure 5.36b the distinctive peak around sample number 34 is a result of rapidly flushing the remaining liquid samples to the GC before gas samples are taken. 8 consecutive
5. Liquid composition experiments

5.9. Liquid composition experiment number 9

Figure 5.36: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40 bar and a temperature of −21°C

samples are taken to be processed. Sample numbers 15 till 23 are taken with their corresponding temperature and pressure points, because the measurement is the most consistent in that time period.

In Figure 5.37 the measurement chromatographies of data point two are presented. The first pair and last pair of the samples are results of impurities in the sample line. The sample numbers 6 till 13 are selected with their corresponding temperature and pressure points, because these samples are the most consistent.

Figure 5.37: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40 bar and a temperature of −27°C

In Figure 5.38 the measurement chromatographies of data point three are presented. The first pair and last pair of the samples are results of impurities in the sample line. The samples numbers 11 till 18 with their corresponding temperature and pressure points are selected, because these samples are the most consistent and the highest. It was noticed during the measurement that the fraction of CO₂ was 2% lower than the expected value, so the mass flow was increased in the sample line by slightly opening the secondary valve depicted in Figure 5.35. This resulted in a small peak around sample number 25. This is not the desired result, but the mass flow in the sample line could not increase more, because otherwise ice forming in the secondary valve would occur.
5.9. Liquid composition experiment number 9

Figure 5.38: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40bar and a temperature of −35 °C

Figure 5.39: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40bar and a temperature of −50 °C

In Figure 5.39 the measurement chromatographies of data point four are presented. From sample number 30, gas samples were taken instead of liquid samples, because no liquid was present anymore. Again, the first two samples, which were analyzed, were impurities from the previous measurement. Like the previous data point the CO₂ composition in the liquid samples were too low in comparison with the expected value. Thus secondary valve was used to increase the mass flow but this resulted not in better results. The range sample numbers used in the data processing is number 20 till 27.

At the end of the last data point a leakage was found around the primary valve. Both mountings have shown leakages, which resulted in flashing in the mountings, so gas escapes which consists primarily of CO₂. The overall result is that the samples have a lower CO₂ content than predicted.

Overall result

The selected chromatographies of the data points are processed and compared with the phase calculation modeling.

The measurement data points are positioned below the phase calculation modeling (see Figure 5.40). In Table 5.17 the actual values of the measurements and model are given together with the standard deviation and difference between the model and the measurements. The difference
increases at decreasing temperatures, so the leakage flows increase with decreasing temperatures due to thermal shrinkage of the sample line. The differences between the model and the measurements is about 1 to 1.5%. The standard deviations of the measurements are much smaller than the difference, so the measurements are not in accordance with the model.

Table 5.17: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂, meas [%]</th>
<th>CO₂, model [%]</th>
<th>Difference [%]</th>
<th>σCO₂, meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>95.20</td>
<td>96.07</td>
<td>0.87</td>
<td>0.13</td>
</tr>
<tr>
<td>#2</td>
<td>94.68</td>
<td>95.66</td>
<td>0.98</td>
<td>0.05</td>
</tr>
<tr>
<td>#3</td>
<td>93.94</td>
<td>95.28</td>
<td>1.33</td>
<td>0.13</td>
</tr>
<tr>
<td>#4</td>
<td>93.22</td>
<td>94.72</td>
<td>1.49</td>
<td>0.45</td>
</tr>
</tbody>
</table>

In Table 5.18 the temperatures, pressures, their standard deviations and the chiller temperature are given. The pressures of the data points are in a range of 1.2 bar of each other. This is fairly high for phase calculations. Due to leakages and taking samples from the condensation cell, the pressure reducer has to control the pressure in the system, which is not optimal. Throughout the experiment the pressure reducer is adjusted to maintain a pressure of 40 bar, but the membrane in the pressure reducer is vulnerable to hysteresis. So the pressure changes over time to an equilibrium position of the membrane.

Table 5.18: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>40.58</td>
<td>0.37</td>
<td>-21.70</td>
<td>0.01</td>
<td>-24.5</td>
</tr>
<tr>
<td>#2</td>
<td>40.41</td>
<td>0.46</td>
<td>-27.22</td>
<td>0.04</td>
<td>-31.0</td>
</tr>
<tr>
<td>#3</td>
<td>39.89</td>
<td>0.50</td>
<td>-34.65</td>
<td>0.03</td>
<td>-40.0</td>
</tr>
<tr>
<td>#4</td>
<td>39.39</td>
<td>0.46</td>
<td>-49.65</td>
<td>0.04</td>
<td>-56.0</td>
</tr>
</tbody>
</table>

Due to the heat in the condensation cell and the heat of the ambient air, the difference between the desired cell temperature and the chiller temperature is dependent on the desired cell temperature.
The highest difference (about 6 °C) is reached when the desired cell temperature is very low. The temperature measurements remain constant in the acceptable range of 0.1 °C.

### 5.9.5 Conclusion experiment

The data points are not in accordance with the phase calculation modeling due to a leakage around the primary valve. The sample line should be checked. If necessary it should be reconstructed. The pressure reducer has to be set once in the beginning of the experiment. No adjustments to the setting of the pressure reducer should be done, because the pressure will not coincide with the pressure of the previous data point. The chromatographies are independent of the mass flow in the sample line. Throughout the experiment it was noted that back flushing did not occur anymore, so it was decided that the data point with temperature −42.5 °C should be skipped. Another reason why was due to a low content of liquid in the cell.

### 5.10 Liquid composition experiment number 10

The results of liquid experiment number 10 are described in this section.

#### 5.10.1 Data points

The premixed gas bottle is a 69.8-30.4 %CO₂-N₂ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of in total of three measurement points. The pressure of all measurement points is about 30 bar. The temperatures of the measurement points are respectively −30 °C, −40 °C and −50.0 °C. At these temperatures liquid should form in the condensation cell and the liquid fraction in the cell should be higher than 25%. In Section 5.9.2 and in Section 5.9.3 the adjustments to the measurement setup and to the measurement procedure are described for this experiment. The leakages around the primary valve are fixed by checking every mounting in the sample line.

#### 5.10.2 Results

Data selection

Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which are selected manually. The focus during the selection is the compositions and not the temperature and pressure which remain more or less constant during the measurement. The chromatographies of the three data points will be discussed.

In Figure 5.41 the measurement chromatographies of data point one are presented. The first few chromatographies indicate that impurities are present in the sample line. After 25 samples the measurement has the tendency to go to a steady value. The last ten chromatographies are selected to be analyzed.
5. **Liquid composition experiments**  5.10. **Liquid composition experiment number 10**

![Graphs](image)

(a) Overall graph  
(b) Close-up of graph

Figure 5.41: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 30.5bar and a temperature of −30.4 °C

Figure 5.42: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 30.5bar and a temperature of −40.2 °C

In Figure 5.42 and in Figure 5.43 the first few samples contain impurities. Eventually the CO₂ content in the sample has the tendency to go the a steady value. Sample numbers 14 till 24 are selected for data point 2. Sample numbers 22 till 32 are selected for data point 3. During the last measurement minor leakages were found near the extension piece positioned behind the primary valve.

**Overall result**

The selected chromatographies of the data points are processed and compared with the phase calculation modeling.

The measurement data points are positioned below the phase calculation modeling (see Figure 5.44). In Table 5.19 the actual values of the measurements and model are given with the standard deviation and difference between the model and the measurements. The difference between the model and the measurements increases for decreasing temperature according to this experiment. The standard deviation of the CO₂ measured is dependent on the region selected in the previous subsection. The standard deviation of data point 3 is very small in comparison with the standard deviation of data point 2.
5. Liquid composition experiments  5.10. Liquid composition experiment number 10

![Figure 5.44: Fraction CO₂ in liquid phase versus temperature at a pressure of 30.4bar.](image)

Table 5.19: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂,meas [%]</th>
<th>CO₂,model [%]</th>
<th>Difference [%]</th>
<th>σCO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>96.80</td>
<td>97.17</td>
<td>0.37</td>
<td>0.08</td>
</tr>
<tr>
<td>#2</td>
<td>96.12</td>
<td>96.57</td>
<td>0.46</td>
<td>0.18</td>
</tr>
<tr>
<td>#3</td>
<td>95.66</td>
<td>96.24</td>
<td>0.58</td>
<td>0.03</td>
</tr>
</tbody>
</table>

In Table 5.20 the temperatures, pressures, their standard deviations and the chiller temperature are given. The pressure at data point 3 is less than at the other data points, although the fluctuations of the pressure are identical to the fluctuations in previous experiments. The temperatures were steady during the measurements.

Table 5.20: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>30.49</td>
<td>0.45</td>
<td>-30.36</td>
<td>0.03</td>
<td>-34.0</td>
</tr>
<tr>
<td>#2</td>
<td>30.51</td>
<td>0.56</td>
<td>-40.18</td>
<td>0.04</td>
<td>-45.0</td>
</tr>
<tr>
<td>#3</td>
<td>30.03</td>
<td>0.54</td>
<td>-49.91</td>
<td>0.06</td>
<td>-56.0</td>
</tr>
</tbody>
</table>

5.10.3 Conclusion experiment

In this experiment liquid measurements at 30 bar were done with a 69.8-30.2 %CO₂-N₂ mixture. The experiment results are not consistent with the phase calculation modeling, because of leakages behind the primary valve. The escaped gas, which primarily consists of CO₂, probably effected the measurement results. The measurement setup has to be changed in order to prevent leakages. The extension pipe should be replaced and if necessary the primary valve has to removed.
5. Liquid composition experiments  5.11. Liquid composition experiment number 11

5.11 Liquid composition experiment number 11

The results of liquid experiment number 11 are described in this section.

5.11.1 Data points

The premixed gas bottle is a 69.8-30.4 % CO₂-N₂ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of in total of four measurement points. The pressure of all measurement points is about 40 bar. The temperatures of the measurement points are respectively -20°C, -30°C, -40°C and -50.0°C. These measurement points differ from the measurement points described in Table 4.1. The step size is enlarged from 7.5 to 10. At these temperatures liquid should form in the condensation cell and the liquid fraction in the cell should be higher than 25%.

5.11.2 Adjustments measurement setup

Leakages were found close to the primary valve in the pipe in the previous experiment. Therefore the sample line presented in Figure 5.35 must be reconstructed. The primary valve is removed of the sample line and the extension pipe is replaced. In Figure 5.45 the reconstructed sample line is schematically presented. A riser is introduced in the condensation cell from the top down to the floor. It is positioned 1mm from the floor of the cell. The liquid samples are transported vertically to the top of the condensation cell in order to prevent back flushing of gas in the two phase flow region. At the top of the condensation cell the sample line is bend into a expansion spiral and connected to the entrance of the GC.

![Sample line diagram](image)

Figure 5.45: Sample line

5.11.3 Adjustment measurement procedure

Some equipment of the experiment setup can be started with a timer, which is found out recently. In this case the large chiller is set to start early in the morning. One and a half hour is saved. In order to get efficient cooling, some mixture at a few bar is left in the system in which all the valves are closed. The impeller is set with a time switch. A consequence of the change in procedure is that the condensation cell should be flushed twice after an experiment instead of before an experiment.

When the condensation cell is in equilibrium a measurement is started. The secondary valve is slightly opened for a few seconds to flush the sample line. The pressure reducer screw of the
membrane is tightened to get a leakage flow. Finally the logging of the temperatures, the pressures and the compositions is started. During the experiment a small secondary leak flow is established with the secondary valve if the mass flow is too low in the sample line. This can be noticed by the fluctuations in the composition results, which are in this case very small. After the measurement the pressure reducer screw is loosened. The temperature of the large chiller is set at the desired temperature for the next data point and the above procedure is repeated.

5.11.4 Results

Data selection

Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which is selected manually. The focus during the selection is the compositions and not the temperature and pressure which remain more or less constant during the measurement. The chromatographies of the four data points will be discussed.

![Figure 5.46: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 41.3 bar and a temperature of -21.7 °C](image)

![Figure 5.47: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 40.9 bar and a temperature of -30.6 °C](image)

In Figure 5.46 and in Figure 5.47 the chromatographies of each sample are given for respectively data point 1 and data point 2. The tendency of the curve shows in the beginning some fluctuations due to impurities in the sample line. At the end the curve reaches a constant value. For data point 3 and data point 4 the tendency of the curves is the same as the tendency of the curves of data point 1 and 2. In Figure 5.48 and in Figure 5.49 the chromatographies of each sample are given for respectively data point 3 and data point 4. For each data point the last fifteen chromatographies are taken for data processing.
5. Liquid composition experiments  5.11. Liquid composition experiment number 11

Figure 5.48: Percentage CO\textsubscript{2} in liquid phase vs the corresponding sample number at a pressure of 40.4bar and a temperature of $-39.9^\circ$C

Overall result

The selected chromatographies of the data points are processed and compared with the phase calculation modeling.

Figure 5.49: Percentage CO\textsubscript{2} in liquid phase vs the corresponding sample number at a pressure of 40.2bar and a temperature of $-49.5^\circ$C

The measurement data points are positioned below the phase calculation modeling (see Figure 5.50). In Table 5.21 the actual values of the measurements and model are given with the standard deviation and difference between the model and the measurements. The average difference is 0.85%. The difference between the model and the first data point is the smallest. However the standard deviation of data point 1 is slightly larger than the other data points standard deviations.

Figure 5.50: Fraction CO\textsubscript{2} in liquid phase versus temperature at a pressure of 40.7bar.
Table 5.21: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO$_2$, meas [%]</th>
<th>CO$_2$, model [%]</th>
<th>Difference [%]</th>
<th>$\sigma_{CO_2, meas}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>95.22</td>
<td>95.94</td>
<td>0.72</td>
<td>0.12</td>
</tr>
<tr>
<td>#2</td>
<td>94.48</td>
<td>95.35</td>
<td>0.87</td>
<td>0.03</td>
</tr>
<tr>
<td>#3</td>
<td>94.01</td>
<td>94.93</td>
<td>0.91</td>
<td>0.08</td>
</tr>
<tr>
<td>#4</td>
<td>93.73</td>
<td>94.58</td>
<td>0.85</td>
<td>0.04</td>
</tr>
</tbody>
</table>

In Table 5.22 the temperatures, pressures, their standard deviations and the chiller temperature are given. The standard deviations of the pressures are the same in comparison with other experiments. The temperatures were steady during the measurements. Due to the heat in the condensation cell and the heat of the ambient air, the difference between the desired cell temperature and the chiller temperature is dependent on the desired cell temperature. The highest difference (about 6°C) is reached when the desired cell temperature is very low.

Table 5.22: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th>Data point</th>
<th>$p_{avg}$ [bar]</th>
<th>$\sigma_p$ [bar]</th>
<th>$T_{avg}$ [°C]</th>
<th>$\sigma_T$ [°C]</th>
<th>$T_{chiller}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>41.28</td>
<td>0.50</td>
<td>-21.72</td>
<td>0.04</td>
<td>-24.5</td>
</tr>
<tr>
<td>#2</td>
<td>40.87</td>
<td>0.57</td>
<td>-30.62</td>
<td>0.03</td>
<td>-35.5</td>
</tr>
<tr>
<td>#3</td>
<td>40.37</td>
<td>0.48</td>
<td>-39.93</td>
<td>0.04</td>
<td>-45.0</td>
</tr>
<tr>
<td>#4</td>
<td>40.24</td>
<td>0.49</td>
<td>-49.50</td>
<td>0.04</td>
<td>-56.0</td>
</tr>
</tbody>
</table>

5.11.5 Conclusion experiment

In this experiment liquid measurements at 40 bar were done with a 69.8-30.2 %CO$_2$-N$_2$ mixture. The experiment results are consistent with the phase calculation modeling. The averaged differences are in the range of the maximum relative standard deviation of the GC[5]. Moreover the results are much more steady when looking at the chromatographies of the samples. The fluctuations in the chromatographies decreased significant due to the adjustment of the measurement setup. No leakages are present in the system anymore.

5.12 Liquid composition experiment number 12

The results of liquid experiment number 12 are described in this section.

5.12.1 Data points

The premixed gas bottle is a 69.8-30.4 %CO$_2$-N$_2$ mixture with an accuracy of ±2%. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of in total of three measurement points. The pressure of all measurement points is about 30 bar. The temperatures of the measurement points are respectively −30°C, −40°C and −50.0°C. At these temperatures liquid should form in the condensation cell. The liquid fraction in the cell should be higher than 25%. In Section 5.11.2 and in Section 5.11.3 the adjustments to the measurement setup and the adjustments to the measurement procedure are described for this experiment.
5. Liquid composition experiments  5.12. Liquid composition experiment number 12

5.12.2 Results

Data selection

Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which are selected manually. The focus during the selection is the compositions and not the temperature and pressure which remain more or less constant during the measurement. The chromatographies of the three data points will be discussed.

![Figure 5.51: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 29.2bar and a temperature of -30.5°C](image1)

In Figure 5.51 the measurement chromatographies of data point one are presented. The first few chromatographies indicate that impurities are present in the sample line. During the measurement the chromatographies have the tendency to go to a steady value of 96.0% (around sample number 20), which was caused by the fact that almost no leakage flow was present in that period. The pressure reducer screw was not tightened enough. In the initial stage of this measurement the desired leakage flow was set and reached, but apparently the leakage flow dropped after some time. After tightening the pressure reducer screw, the leakage flow reestablished and the CO₂ concentration increased to a new steady value. The last ten chromatographies are selected to be analyzed.

![Figure 5.52: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 29.1bar and a temperature of -39.9°C](image2)

![Figure 5.53: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 29.0bar and a temperature of -49.2°C](image3)

In Figure 5.52 and in Figure 5.53 the first few samples contains impurities. Eventually the CO₂
5. Liquid composition experiments  5.12. Liquid composition experiment number 12

content in the sample has the tendency to go a steady value. Sample numbers 20 till 30 are selected for data point 2. Sample numbers 32 till 42 are selected for data point 3. The chromatographies fluctuations of data point 3 are rather large in comparison with the chromatographies fluctuations of data point 2, which was a very steady measurement.

Overall result
The selected chromatographies of the data points are processed and compared with the phase calculation modeling.

![Figure 5.54: Fraction CO₂ in liquid phase versus temperature at a pressure of 29.1 bar.](image)

The measurement data points are positioned below the phase calculation modeling (see Figure 5.54). The process conditions which are used in the phase calculation modeling are the averages of the data points pressure and temperature presented in Table 5.24. In Table 5.23 the actual values of the measurements and model are given with the standard deviation and difference between the model and the measurements. The difference between the model and the measurements increases for decreasing temperature according to this experiment.

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂,meas [%]</th>
<th>CO₂,model [%]</th>
<th>Difference [%]</th>
<th>σCO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>96.90</td>
<td>97.38</td>
<td>0.47</td>
<td>0.03</td>
</tr>
<tr>
<td>#2</td>
<td>96.33</td>
<td>96.82</td>
<td>0.49</td>
<td>0.02</td>
</tr>
<tr>
<td>#3</td>
<td>95.84</td>
<td>96.43</td>
<td>0.59</td>
<td>0.06</td>
</tr>
</tbody>
</table>

In Table 5.24 the temperatures, pressures, their standard deviations and the chiller temperature are given. The average pressure over the whole experiment was quite uniform. Only the pressure in data point 2 is slightly higher. The pressure reducer of the gas bottle was set in the beginning
5. Liquid composition experiments  5.13. Liquid composition experiment number 13

of the experiment and it was not adapted during the experiment. The temperatures were steady during the measurements.

Table 5.24: Temperatures, pressures and standard deviations of the data points

<table>
<thead>
<tr>
<th>Data point</th>
<th>( p_{avg} ) [bar]</th>
<th>( \sigma_p ) [bar]</th>
<th>( T_{avg} ) [°C]</th>
<th>( \sigma_T ) [°C]</th>
<th>( T_{chill} ) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>29.22</td>
<td>0.46</td>
<td>-30.52</td>
<td>0.02</td>
<td>-34.0</td>
</tr>
<tr>
<td>#2</td>
<td>29.52</td>
<td>0.45</td>
<td>-39.92</td>
<td>0.03</td>
<td>-45.0</td>
</tr>
<tr>
<td>#3</td>
<td>29.03</td>
<td>0.46</td>
<td>-49.21</td>
<td>0.03</td>
<td>-56.0</td>
</tr>
</tbody>
</table>

5.12.3 Conclusion experiment

In this experiment liquid measurements at 29 bar were done with a 69.8-30.2 %CO\(_2\)-N\(_2\) mixture. The difference between the model and the results is about 0.5%, which is in the range of the maximum possible relative standard deviation of the GC (1%)[5]. Furthermore, possible errors in the phase calculation modeling are present. So, the experiment results are consistent with the phase calculation modeling.

The chromatographies of the data points are very steady over time. No large fluctuations are present anymore in the tendencies of the graphs. During a measurement the leakage flow may drop, which results in none reliable results, so the leakage flow should be frequently checked during measurements.

For this experiment the same process conditions are used as for liquid experiment number 10 (Section 5.10). The pressure in experiment 12 is 1 bar less than the pressure in experiment 10. The differences between the results and the model are consistent with each other. Only for a temperature of \(-30\) °C the differences differ, but only 0.1%. Small leakages were found during experiment number 10, which may be the reason for these small differences.

5.13 Liquid composition experiment number 13

The results of liquid experiment number 13 are described in this section. If necessary, adjustments to the measurement procedure and measurement setup are discussed.

5.13.1 Data points

A premixed gas bottle of 49.6-50.4 %CO\(_2\)-N\(_2\) mixture with an accuracy of ±2%. By using this gas bottle, condensation occurs at a lower pressure than when using a premixed gas bottle of 49.6-50.4 %CO\(_2\)-N\(_2\) mixture. Liquid samples are taken from the condensation cell to be analyzed with the GC. This experiment consists of in total of four measurement points. The temperature of all measurement points is about \(-50\) °C in the lower part of the condensation cell. The pressures of the measurement points are respectively 25 bar, 30 bar, 35 bar and 40 bar. At these pressures liquid should form in the condensation cell in which the liquid fraction in the cell should be higher than 25%. The measurement procedure described in Section 5.11.3 is used in this experiment. The only adjustment is that the pressure is the variable instead of the temperature, which is constant.

5.13.2 Results

Data selection

Not all the logged data is useful for data processing due to impurities in the sample line before and after a measurement. For each data point the best chromatographies are analysed, which are
5. Liquid composition experiments 5.13. Liquid composition experiment number 13

selected manually. The focus during the selection is the compositions and not the temperature and pressure which remain more or less constant during the measurement. The chromatographies of the four data points will be discussed.

![Overall graph](image1)

![Close-up of graph](image2)

Figure 5.55: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 25.2bar and a temperature of −50.5°C

In Figure 5.55 the measurement chromatographies of data point one are presented. The first 5 samples are not useful, because the sample line is filled with impurities which have to be flushed out of the system. When the impurities were removed, the tendency of the graph went to a steady value with small fluctuations. The last 15 samples are taken for data processing. The chromatographies of data point two (see Figure 5.28) have the same tendency as the chromatographies of data point one. First the impurities have to removed of the sample line and after which the results fluctuate around a steady value. At the end of the measurement all liquid was drained from the condensation cell, so gas samples were taken, which ended in a sharp drop in CO₂ concentration. The range of interest for data processing are sample 15 till 30.

![Overall graph](image3)

![Close-up of graph](image4)

Figure 5.56: Percentage CO₂ in liquid phase vs the corresponding sample number at a pressure of 30.4bar and a temperature of −50.6°C

In Figure 5.57 the measurement chromatographies of data point three are presented. Again the
first few chromatographies are results of impurities. In this case it was because of the remaining gas of the previous measurement. When watching closely to the graph a significant shift in concentration can be observed. The leakage flow to the GC dropped. The pressure reducer screw was tightened to increase the leakage flow, which resulted in a higher CO₂ concentration. The last 15 samples are taken for data processing.

After data point 3 the pressure was increased to reached the desired pressure for data point 4. It was noticed that in the temperature signal unusual fluctuations occurred. This is a consequence of that the thermocouples tip is in alternating contact with liquid and gas. Due to the position of the thermocouple in the cell, it was expected that not enough liquid was present for more measurements. This suspicion was strengthened by the fact that during data point 2 measurement the cell was drained from all its liquid. The gas in the cell has a very low CO₂ concentration, so the liquid fraction is low as well. About 10 bar of gas was deflated from the cell. Afterwards the condensation cell was filled with gas again up to the desired pressure of data point 4 from the premixed bottle. This procedure is allowed, because a CO₂-N₂ mixture is univariant. The
5. Liquid composition experiments  5.13. Liquid composition experiment number 13

chromatographies of data point 4 give a distinctive peak. Till that point all samples are still contaminated with impurities of previous measurement. When the impurities are removed out of the sample line, the chromatographies have the tendency to go to a steady value. The last 15 samples are taken for data processing.

Overall result

The selected chromatographies of the data points are processed and compared to the phase calculation modeling.

![Graph showing fraction CO₂ in liquid phase versus temperature at a temperature of -50.5°C](image)

Figure 5.59: Fraction CO₂ in liquid phase versus temperature at a temperature of −50.5°C

The measurement data points are positioned below the phase calculation modeling (see Figure 5.59). The process conditions which are used in the phase calculation modeling are the averages of the data points pressure and temperature presented in Table 5.25. In Table 5.26 the actual values of the measurements and model are given with the standard deviation and difference between the model and the measurements. The difference between the model and the measurements increases for increasing pressure according to this experiment.

Table 5.25: Comparison data points measurement with phase calculation modeling

<table>
<thead>
<tr>
<th>Data point</th>
<th>CO₂,meas [%]</th>
<th>CO₂,model [%]</th>
<th>Difference [%]</th>
<th>σCO₂,meas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>96.62</td>
<td>97.00</td>
<td>0.38</td>
<td>0.03</td>
</tr>
<tr>
<td>#2</td>
<td>95.60</td>
<td>96.16</td>
<td>0.56</td>
<td>0.04</td>
</tr>
<tr>
<td>#3</td>
<td>94.50</td>
<td>95.29</td>
<td>0.79</td>
<td>0.05</td>
</tr>
<tr>
<td>#4</td>
<td>93.50</td>
<td>94.34</td>
<td>0.85</td>
<td>0.05</td>
</tr>
</tbody>
</table>
5. Liquid composition experiments  5.13. Liquid composition experiment number 13

In Table 5.26 the temperatures, pressures, their standard deviations and the chiller temperature are given. The temperatures were steady during the experiments. Moreover the temperatures of the data points were almost identical. The deviations of the pressures is identical in comparison with previous measurements.

<table>
<thead>
<tr>
<th>Data point</th>
<th>$P_{avg}$ [bar]</th>
<th>$\sigma_p$ [bar]</th>
<th>$T_{avg}$ [°C]</th>
<th>$\sigma_T$ [°C]</th>
<th>$T_{chiller}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>25.23</td>
<td>0.63</td>
<td>-50.50</td>
<td>0.05</td>
<td>-57.0</td>
</tr>
<tr>
<td>#2</td>
<td>30.37</td>
<td>0.51</td>
<td>-50.57</td>
<td>0.02</td>
<td>-56.5</td>
</tr>
<tr>
<td>#3</td>
<td>35.74</td>
<td>0.54</td>
<td>-50.48</td>
<td>0.01</td>
<td>-56.3</td>
</tr>
<tr>
<td>#4</td>
<td>41.54</td>
<td>0.45</td>
<td>-50.31</td>
<td>0.02</td>
<td>-56.3</td>
</tr>
</tbody>
</table>

5.13.3 Conclusion experiment

In this experiment liquid measurements at $-50$ °C were done by using a 49.6-50.4 %CO$_2$-N$_2$ mixture. The difference between the model and the measurements increases for increasing pressure. This is still in the range of the maximum possible relative standard deviation of the GC (1%). Furthermore, possible errors in the phase calculation modeling are present. So the experiment results are consistent with the phase calculation modeling.

The chromatographies of the data points are very steady over time. No large fluctuations are present anymore in the tendencies of the graphs. During a measurement the leakage flow may drop, which results in unreliable results, so the leakage flow should be frequently checked during measurements.
Chapter 6

Conclusion liquid composition experiments

In this chapter equilibrium liquid composition experiments are discussed. A predefined binary mixture of CO\textsubscript{2} and N\textsubscript{2} is used for liquid composition experiments in the condensation cell. At predefined process conditions the mixture condensates in the cell to its equilibrium state. When the condensation cell is in its equilibrium state liquid samples are taken from the cell to analyze its composition. The results are compared to the phase calculation modeling. The liquid composition experiments are divided into two parts. The first part is liquid composition measurements at constant temperature in which the pressure is the variable. The second part is the opposite of the first part, which is liquid composition measurements at constant pressure in which the temperature is the variable.

A sample line is constructed from the bottom of the condensation cell to the inlet of the gas chromatographer. Initial experiment results were not consistent with the phase calculation modeling due to unwanted effects in the sample line. When the liquid from the cell enters the sample line, it starts to warm up by heat of the ambient air. The mixtures phase changes from liquid to gas. In the two phase region the formed gas has the tendency to flow back through the liquid into the condensation cell. The formed gas consists mainly of CO\textsubscript{2}. Eventually, the overall composition of the mixture in the sample line is different from the actual liquid composition in the cell. The measured CO\textsubscript{2} concentration was lower than predicted.

In order to reduce the back flowing of gas into the condensation cell, the sample line was reconstructed twice. A secondary valve, an inclined connecting pipe and insulation material were used to reduce the unwanted effects. The idea was to shift the two phase region more to the end of the sample line and to increase the mass flow in the sample line. Initial results gave an improvement about 1% CO\textsubscript{2} concentration in comparison with the prediction of the model. However new unwanted effects occurred in the sample line. First, the N\textsubscript{2} which was dissolved in the liquid was boiled out of the mixture. Due to the high mass flow rate the N\textsubscript{2} leaked to the ambient air by the secondary valve instead of being fed to the entrance of the GC. Second, the two phase flow region expanded till the end of the sample line. Liquid was deflated in the secondary valve, which leads to ice forming due to the Joule-Thomson effect.

A balance between enough mass flow for good results and unwanted effects near the end of the sample line had to be found. The leakage flow was increased by very small steps in order to get better results until ice forming in the secondary valve was observed. Eventually, the results were consistent with the phase calculation modeling. For low pressures at a temperature of −50°C, the experiment results were within 0.05% of the phase calculation modeling. For high pressures at a temperature of −50°C the experiment results were within 0.2% of the phase calculation modeling.
During these experiments the chromatographies were not steady. Fluctuations in concentration were large due to the unwanted effects described in the above paragraphs.

During the liquid composition measurement at constant pressure, the results differ a lot more from the phase calculation modeling. Moreover, no stability in the concentrations over time was reached. In order to overcome this problem, the sample line in the measurement setup had to be changed. A riser was introduced in the condensation cell from the top down to the bottom. Back flushing of gas is not possible anymore, because the gas will be transported to the top of the condensation cell. From that point the gas and liquid were transported to the entrance of the GC.

In the first experiments using the new constructed sample line, leakages were found in the sample line. The sample line was reconstructed and no leakages occurred anymore.

The concentrations of the samples were very steady after the impurities of previous experiment were out of the system. Minor fluctuations occurred around a steady value. The difference between the experiment results and the phase calculation modeling are larger than the previous method of taking samples from the floor of the cell. At 30 bar the differences were around 0.5%. At 40 bar the differences were around 0.8%. The differences have the tendency to get larger when the pressure increases. The results are still consistent with the model, because the difference is smaller than the GC maximum relative standard deviation of 1%. Furthermore, errors in the phase calculation modeling could be present. Moreover systematic errors in the temperature, pressure and concentrations have to be accounted for. These errors create a confidence interval in which most results are located.

A different method was used for the experiments at constant temperature than the experiments at constant pressure. The method used in the constant pressure experiments is applied in a 'check' experiment in which the temperature is constant. This is done to check if the found results are reliable. The concentration of the samples were very steady after the impurities of previous experiments were out of the system. The difference between the experiment results and the phase calculation modeling are larger than the previous method of taking samples from the floor of the cell. The difference increased for increasing pressure, but it is still beneath 1%.

The overall conclusion is that the phase calculation modeling is validated for temperatures at constant pressures and for pressures at constant temperatures. The experiments at constant temperatures are done by using two different methods. The results of both methods are reliable because it are located in the confidence interval. However, it has to be mentioned that the stability of the 'riser' method is much better than the stability of the 'bottom' method.
Part IV

Fog formation experiments
Chapter 1

Introduction

In this part the fog formation experiments will be discussed. The main goal of this project is to determine if fog is able to be formed in the condensation cell under specific process conditions. Fog formation occurs when the mixture of CO₂ and N₂ is cooled rapidly to create a non-equilibrium state which differs greatly from the actual equilibrium state at these process conditions. The equilibrium state can be determined by using the phase calculation modeling. That model is validated by the experiments described in Part II and Part III. Supersaturation is the ratio between the non-equilibrium state and the equilibrium state at specific process conditions. When the supersaturation is larger than one, fog formation will occur.

In order to get the fog formation in the condensation cell, the measurement set up and measurement procedure have to be optimized to diminish side effects like the freezing of cells glasses. Two initial experiments will be done in order to get the knowhow to perform these kind of measurements. The measurement procedure and if necessary the measurement set up will be constantly adjusted to prevent problems and to optimize the results. After the initial experiments background experiments with only N₂ gas in the cell will be done. These back ground experiments will provide an insight in the density fluctuations in the cell. These density fluctuations contaminate the actual fog formation experiments. When the averaged back ground intensity, obscuration and particle sizes are known, actual fog formation experiments will be performed.
Chapter 2

Measurement set up

A schematic representation of the measurement set up is given in Figure 2.1. A premixed gas cylinder is used for providing the gas for the condensation cell. The gas bottle is used for controlling the pressure in the cell with the pressure reducer. Before the gas enters the cell, it is cooled in a heat exchanger with coolant flow provided by the small chiller. The inlet temperature is measured with a T-type thermocouple positioned at the entrance of the cell. The outer shell of the condensation cell is filled with coolant liquid of the large chiller. The chiller is used for controlling the temperature in the cell. Its reference temperature is measured with a Pt100 thermometer (denoted with Pt in Figure 2.1) that is positioned in the cells lower part in a capillary. The inlet and outlet temperatures of the coolant flow is measured with two T-type thermocouples.

Two 10 cm T-type thermocouples positioned respectively in the lower part and in the upper part of the condensation cell are used to measure the temperature in the cell. In the upper part of the cell an absolute pressure transducer is positioned which measures the pressure in bars. A gas chromatographer (GC) is used to measure the composition of the gas which is connected to the cell with a so called sample line. In the beginning of the sample line a relative pressure sensor is positioned which is used during the filling of the condensation cell. A valve is placed in this part of the condensation cell to deflate the condensation cell after the experiments. Furthermore, at the top of the condensation cell a pressure relief valve is connected which opens when the pressure exceeds 50 bar. At the floor of the cell a second valve is placed in order to deflate the cell. Finally, a Spraytec laser system is placed to measure the laser light scattering in the cell in which two quartz glasses are used to make the condensation cell optical available for laser applications.

The condensation cell is heavily insulated with insulation material except for the cells optical windows. During the cooling process water will freeze onto the windows which distorts the laser scattering. In order to prevent this problem a purge system is introduced. In Figure 2.2 the purge system is schematically depicted. N$_2$ gas is used for this system. The gas flow rate is controlled with the pressure reducer. The purge is separated into two parts. The first part consists of blowing N$_2$ gas over the windows in order to prevent ice forming. The gas is cooled in the heat exchanger if necessary. The coolant flow of the heat exchanger is the outlet coolant fluid of the condensation cell. The temperature, which is measured by a T-type thermocouple, can be controlled by using the valves around the heat exchanger. The second part consists of blowing N$_2$ in the laser and detector head in order to prevent ice forming at the Spraytec glasses. This part can be closed by using the valve in the line.
2. Measurement setup

Figure 2.1: Measurement setup with all sensors without the purge system

Figure 2.2: Purge system of the measurement setup
Chapter 3

Measurement procedure

The measurement procedure for CO2 fog experiments has to be carefully performed in order to avoid unwanted effects, such as ice forming on the windows, condensation on the laser windows or no proper laser alignment. All these effects lead to no decent experiments. The measurement procedure is divided into three parts: preparations, actual measurements and the closure of the experiment.

3.1 Preparations

Each experiment starts with the cleaning of the condensation cell windows and the laser windows. The protectors of the windows have to be removed. With a flashlight the windows are inspected for clarity. Lens tissues are used to clean the windows. When the windows are very dirty, droplets of ethanol are dropped on the lens tissue and then the lenses are treated. After treating by using a lens tissue in ethanol the lenses are cleaned with a dry lens tissue. Sometimes the inside windows of the Spraytec have no clarity. The Spraytec has to be removed from the positioning beam and the windows have to be removed from the spraytec for cleaning. After the cleaning of the windows the isolation caps are positioned on the cells windows. The Spraytec is positioned at a distance from the condensation cell. The N2 is provided by the purge system. The valve in the purge system for providing N2 to the laser has to be closed, like the valve to the heat exchanger which cools N2. The bypass has to be openend, so hot N2 can be blown in the insulation caps which prevents ice forming on the windows. The N2 mass flow has to be set reasonably high, which is done at touch, to prevent the previous described unwanted effects. However the mass flow can not be too high due to the fact that the N2 bottle have to provide N2 to the experimental setup during the whole experiment.

The condensation cell is filled twice with a mixture of about 5 bar and the cell is deflated twice in order to remove impurities in the cell for the experiments. In these experiments the cell is filled with a mixture of about 1.5-3 bar. Higher pressures may result in problems during the laser alignment and background intensity analysis due to severe density fluctuations in the cell. The impeller is set at position 2, which is most of the time the starting position during the actual measurement. The large chiller has to be connected to the power station and to the water supply station. The temperature of the large chiller is set about ten to fifteen degrees under the desired temperature in the cell due to the low amount of gas in the cell. If necessary, the temperature and the pressure can be adjusted by the gas bottle and the chiller, which can not be done during measurements. The cooling down process takes about three hours.

When the gas chromatographer is used, the GC has to be put on first. The helium supply have to be set at a pressure of 5.5 bar. It is very important to send the real time clock and method to the GC, otherwise measurements are converted wrongly due to wrong methods and results get overwritten. A small leakage flow of about 1.2 bar has to be established by tightening the pressure
3. Measurement procedure

3.2 Actual measurement procedure

During the cooling down process the temperature and pressure are monitored by the software program Labview. Ice forming on the windows can be monitored by using the laser intensity with software program Spraytec. The laser is used to perform background analysis and an alignments procedure in order to determine the laser intensity. The common laser intensity through the cell is about 65%. When the laser intensity is too low, the software program will give an error which means that ice is formed on the cells windows.

3.2 Actual measurement procedure

When the desired temperature is reached the measurement can be started. The cell does not have to be in equilibrium. Due to the low amount of gas in the cell, the temperature change over time is very low. At first the purge N₂ mass flow is increased. It is also possible to open the heat exchanger valve a little bit in order to decrease the purge temperature, which will differ per experiment. The purge valve to the Spraytec is opened to blow N₂ in the chambers. The insulation caps are removed and the Spraytec is positioned as close as possible to the cells windows.

The background analysis and alignment of the laser are started. When the laser preparations are succeeded the measurement can start. Labview, Prostation and Spraytec are started at the same time. The pressure is set at the desired pressure with the pressure reducer screw mounted on the premixed gas bottle. The valve is opened until the desired pressure is reached. When the fluctuations in the signal are gone, the impeller positions can be adjusted in order to change the mass and heat transfer in the cell.

Additional measurements can be done. First the cell has to be deflated. The temperature in the cell will drop due to the Joule Thomson effect. The temperature can not be below −55°C, otherwise CO₂ ice will form. The big chiller temperature has to be set at −55°C in order to heat up the cell to balance the released heat of the Joule Thomson effect. The mass and heat transfers are increased to speed up the CO₂ evaporation. When the cell is empty, the cell is filled with 1.5-3 bar premixed gas. The chiller temperature is set at its original value. The temperature has to be reestablished to the original value over a certain time period. Then the procedure described in the previous paragraph is repeated.

3.3 Closure

After the experiment the premixed gas bottle, the N₂ gas bottle and the helium bottle are closed. The chillers are set at 0°C. The condensation cell is deflated by opening the valve positioned at the upper part of the cell. Due to the expansion of the gas the temperature in the cell will drop. The temperature has to be higher than −55°C otherwise solid CO₂ will form. When the cell is empty, the chillers have to be put off. If necessary, the premixed gas bottle and the N₂ bottle have to be replaced, when the bottle pressures are too low for the next experiment. The Spraytec is removed from the condensation cell and the window protectors are placed on the cell windows and laser windows.
Chapter 4

Experiment approach

Fog formation experiments are delicate to perform with this experiment setup. During experiments problems may occur when the measurement procedure is not done in the correct way. A slight deviation of the measurement procedure may cause a failed experiment. The largest problem is water freezing on the cells windows and Spraytec windows, which can be solved by using the purge system only if it is applied in the correct way. In order to get the necessary knowhow how to perform these experiments two initial experiments are done. The measurement procedure will be improved by findings during these experiments.

The initial pressure in the cell is about 1.5-3 bar. A CO$_2$-N$_2$ mixture is instantly fed to the condensation cell at a temperature of $-50^\circ$C to a pressure of 40 bar. The condensation cell is at that moment far from its equilibrium state resulting in supersaturation. The supersaturation is the highest at a low temperature and high pressure with a low inlet temperature. In this case a 50 - 50% CO$_2$-N$_2$ mixture is used to obtain a reasonable recovery of the gas. In combination with a working temperature of $-50^\circ$C and a pressure of 40 bar supersaturation will occur in the condensation cell according to the supersaturation modeling[11].

After the initial experiments background experiments are done. The CO$_2$-N$_2$ mixture bottle is replaced by a pure N$_2$ bottle. The concept remains the same. The only difference is that no condensation will occur in the cell. However the Spraytec system measures a so called particle distribution, which is a result of density fluctuations in the condensation cell. The back ground experiments have the purpose to gain insight in the density fluctuations and how these fluctuations distorts the supersaturation experiments. The process conditions are the same as described in the previous paragraph. For different impellor speeds the condensation cell will be filled at the process conditions. The results are used as reference signal for future supersaturation experiments.

When the density fluctuations effects on the measurements are known, the fog formation measurements are started. The measurement procedure is adjusted in such a way in the previous experiments that no problems will occur during these experiments. The initial pressure in the cell is about 1.5-3 bar. A 50 - 50% CO$_2$-N$_2$ mixture is fed instantly to the condensation cell at a temperature of $-50^\circ$C to a pressure of 40 bar. The condensation cell is at that moment far from its equilibrium state resulting in fog formation. The Spraytec laser system is used to measure the scattering during the experiment. The results are compared to the background measurements in order to determine if fog was formed. Finally the Spraytec laser system is replaced by a camera and a laserpointer. In this case the laserpointer provides the laser beam which is scattered in the cell. The scattering is recorded with the camera, which gives a good visualisation of the fog formation in the cell.
Chapter 5

Initial fog formation experiments

5.1 Initial fog formation experiment number 1

The results of the first initial fog formation experiment are described in this section.

5.1.1 Experiment approach

The premixed gas bottle used for this experiment is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. The condensation cell is filled till a pressure of 3 bar. The large chiller is set at −70 °C in order to lower the cells temperature. Initially the impeller speed is set at position 6. The measurement procedure described in Chapter 3 is used in this experiment. When the condensation cell is at the desired temperature which is about −45 °C, the impeller speed is set at position 2. The pressure is set at 40 bar by the pressure reducer, but the valve of the pressure reducer is closed. The composition of the gas is not measured in this experiment.

The protectors were removed and the glasses were clean. The Spraytec is positioned as close as possible to the cell. The background and alignment procedure of the laser failed due to a lack of background light measured by the detector. During the inspection of the windows it was noticed that ice was formed on the cells windows. With hot N₂ the windows were cleaned manually, but the ice forming still occurred. However the laser intensity was improved from 35% to 62%. It was decided to proceed with the experiment.

5.1.2 Experiment results

Obscuration is the amount of blockage of the laser intensity. When the laser intensity drops due to particles in the medium, the obscuration is high. The particles scatters the laser, which diffraction is measured by the detectors resulting in a particle distribution. In Figure 5.1 the obscuration as function of the time is given of the experiment. During the rapid filling of the cell the obscuration reaches a maximum. Then a sharp decrease occurs whereafter the obscuration has the tendency to go to a steady value of about 60%. When the steady value was reached it was decided to deflate the cell rapidly, which results in fog formation by expansion. The obscuration reaches a maximum whereafter it rapidly drops to its steady value again.

In Figure 5.2 the corrected light scattering per detector after 36 seconds is shown. The first ten detectors have the tendency to measure most light intensity. These detectors give a high particle diameter which is around 400 µm. Fog particles are usually to have a size of about 1-100 µm. The high particle diameter is caused by large density fluctuations in the cell. The light scattering caused by these density fluctuations are measured primarily by the first ten detectors. When these
5. Initial fog formation experiments  5.1. Initial fog formation experiment number 1

Figure 5.1: Obscuration in condensation cell

Figure 5.2: Corrected light scattering after 36 seconds during decay in obscuration

detectors are left out of the equation, the particle diameter becomes significantly lower. During the decay of obscuration detector number from 11 to 36 measures scattering, which is a result of fog in the condensation cell. After a couple of seconds the scattering on the high numbered detectors disappear, when the obscuration reaches its minimum. From that point onwards the Spraytec does not record the scattering (see Figure 5.3), because the data is in the so called error zone of the Spraytec. This error zone can be adjusted in the method setup. The obscuration is independent of the selected detectors.

From this data it can be concluded that fog formation occurred. For about 10 seconds during the decay of the obscuration, scattering is measured at high numbered detectors. However, most data
5. Initial fog formation experiments  

5.2. Initial fog formation experiment number 2

The results of the second initial fog formation experiment are described in this section.

Figure 5.3: Dp50 in condensation cell

is in the so called error zone of the Spraytec. Although, it can be stated that the averaged particle diameter is in the same order for the particle sizes if the first ten detectors are neglected.

5.1.3 Experiment conclusion

A supersaturation experiment with a premixed 49.6-50.4 %CO2-N2 gas bottle was performed at a temperature of −45 °C and a pressure of 40 bar. During the cooling process no ice was formed on the cells windows. The protectors were removed and the Spraytec was positioned near the cells windows. Water from the ambient air freeze on the cells windows, resulting in a laser intensity of 35%, which is not good enough. With hot N2 the windows were cleaned manually, resulting in a laser intensity of 65%.

The obscuration reaches its maximum during the initial filling of the condensation cell. After reaching the maximum the obscuration drops significantly whereafter the obscuration has the tendency to go a steady value of 60%. The cell was deflated rapidly to obtain a second time fog formation by expansion. Due to density fluctuations, the first ten detectors distorts the experiments. When these detectors are left out of the equation, the particle diameter is in the correct order. However due to the error zones of the Spraytec, most of the data is left out in the data processing. It can be concluded that fog formation occurred, because for about 10 seconds scattering was measured at high numbered detectors. In the next experiments the measurement procedure has to be performed with much more care in order to prevent ice forming on the windows. The error zones in the Spraytec method have to be adjusted in order to get more information about the detectors above number ten.

5.2 Initial fog formation experiment number 2

The results of the second initial fog formation experiment are described in this section.
5. Initial fog formation experiments  5.2. Initial fog formation experiment number 2

5.2.1  Experiment approach

The premixed gas bottle used for this experiment is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. The condensation cell is filled up to a pressure of 4 bar. The large chiller is set at −64 °C in order to lower the cells temperature. The impeller speed is set at position 6 initially. The measurement procedure described in Chapter 3 is used for this experiment, but it is performed with much more care. When the condensation cell is at the desired temperature which is about −50 °C, the impeller speed is set at position 2. The pressure is set at 40 bar by the pressure reducer, but the pressure reducer valve is closed. The composition of the gas is not measured in this experiment.

The protectors were removed and the glasses were clean. The Spraytec is positioned as close as possible to the cell. The background and alignment procedure of the laser failed due to a lack of background light measured by the detector. During the inspection of the windows it was noticed again that ice was formed on the cells windows. With hot N₂ the windows were cleaned manually, but the ice forming still occurred. The background and alignment procedure of the laser was started for the second time but failed again. During the second inspection of the cells windows it was confirmed that the windows were clean. The Spraytec windows were clean. The background and alignment procedure of the laser was started several times, but every time the procedure failed. It was decided to cancel the experiment.

5.2.2  Experiment conclusion

A supersaturation experiment with a premixed 49.6-50.4 %CO₂-N₂ gas bottle was performed at a temperature of −45 °C and a pressure of 40 bar. During the cooling process no ice was formed on the cells windows. The protectors were removed and the Spraytec was positioned near the cells windows. Water from the ambient air freezed on the cells windows, resulting in a laser intensity of 35%, which is not good enough. With hot N₂ the windows were cleaned manually, but the procedure failed again. The cells pressure was in this case 4 bar, which may result in large density fluctuations causing the failure of starting the laser procedure. In the previous experiment the starting pressure was 3 bar and the laser procedure succeeded. So, the starting pressure in the condensation cell can not exceed 3 bar in order to prevent failing of the laser procedure.

During every supersaturation experiment ice forming on the windows occurred when the protectors were removed and the Spraytec was positioned near the cell. The measurement procedure has to be improved in order to prevent ice forming. The premixed 49.6-50.4 %CO₂-N₂ gas bottle is quite expensive, so these gas bottles are replaced with pure N₂ gas bottles. The background experiments are started without condensation in the cell.
Chapter 6

Background analysis experiments

In this chapter the background signals in the condensation cells are measured. The start up procedure of the laser has to be succeeded before a measurement can be started. At ambient conditions the Spraytec will give no signals. In the initial measurements the Spraytec measured signals, especially at the first ten detectors. These signals are a consequence of density fluctuations in the cell. N₂ gas is fed to the condensation cell, so no condensation occurs. The measured signals are analyzed at for the length of the obscuration is, the particle size and which detectors are involved in density fluctuations. These measurements are repeated as much as possible until the results are reproducible. The other goal of these background analyses is to improve the measurement procedure in order to prevent the problems described in the previous chapter.

6.1 Obscuration experiment number 1

The results of background experiment number 1 are described in this section.

6.1.1 Experiment approach

The pure N₂ gas bottle is used in this experiment. The condensation cell is filled till a pressure of 2.5 bar. The large chiller is set at −64 ◦C in order to lower the cells temperature. The impeller speed is set at position 2. The measurement procedure described in Chapter 3 is used in this experiment. The desired cell temperature is about −50 ◦C. The pressure is set at 40 bar with the pressure reducer.

The protectors were removed and the glasses were clean. The Spraytec is positioned as close as possible to the cell. The background and alignment procedure of the laser failed due to a lack of background light measured by the detector. During the inspection of the windows it was noticed that ice was formed on the cells windows. With compressed air the windows were cleaned manually, but the ice forming still occurred. However the laser intensity was improved from 11% to 65%. It was decided to proceed with the experiment. The experiment consists of 3 measurements. The condensation cell will be filled three times at an impeller position of 2(R2). After 4 minutes the impeller position is changed to 4(R4) to investigate the obscuration change. After 6.30 minutes the impeller position is changed to 6(R6). Finally after 8.30 minutes the impeller position is changed back to 2(R2).

6.1.2 Experiment results

The pressure and temperature of the first measurement was not logged due to technical problems. The third measurement could not be performed due to ice forming on the windows of the cell and Spraytec. The laser intensity dropped to 20%. On the other hand the second measurement succeeded. In Figure 6.1 the lower cell temperature is shown. A sharp increase in temperature
occurred because the cell was filled hot gas. The hot gas cools down by the heat in the condensation cell until an equilibrium temperature is reached. In Figure 6.2 the pressure tendency is shown. The pressure is increased rapidly to about 40 bar. When the steady value is reached clear fluctuations are present in the signal. This phenomenon has also been noted in the equilibrium composition experiments.

The obscuration of the first measurement is shown in Figure 6.3. During the rapid filling the obscuration reaches a maximum value. After reaching the maximum value, the temperature decreases and also the obscuration decreases. The obscuration has the tendency to get to a steady value. The last 50 samples in this steady region are averaged and its standard deviation is calculated. After the steady region, the obscuration drops significantly due to the change in impeller speed. Again the last 50 samples are averaged. After 6.30 minutes the impeller speed is increased further resulting again in an obscuration drop. Eventually, the rotor speed is set at 2 which indicates an increase of obscuration. The averages and standard deviations are shown in Table 6.1 for both measurements.

The obscuration of the second measurement is shown in Figure 6.4. It has the same tendency as the obscuration of measurement 1. The only difference is that the obscuration tendency at rotor speed 2 around 150 seconds is more smooth in the second measurement. In the end, the averages are nearly the same. When the averages are compared to each other, it can be concluded that the obscuration for each impeller speed is in accordance with each other. The standard deviations decrease at higher impeller speeds. The obscuration is lower for higher impeller speeds because the mixing of density fluctuations is better than at a lower impeller speed.

The average particle diameters of the measurements are shown in Figure 6.5, which are different.
6. Background analysis experiments

6.1. Obscuration experiment number 1

Table 6.1: Averages of obscuration in relation to impeller speeds

<table>
<thead>
<tr>
<th></th>
<th>Max obs</th>
<th>Obs R2</th>
<th>Obs R4</th>
<th>Obs R6</th>
</tr>
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<tbody>
<tr>
<td>Exp 1: Obs mean [%]</td>
<td>94.87</td>
<td>44.85</td>
<td>24.26</td>
<td>16.03</td>
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<td>1.02</td>
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<tr>
<td>Exp 2: Obs mean [%]</td>
<td>94.29</td>
<td>45.16</td>
<td>25.34</td>
<td>17.41</td>
</tr>
<tr>
<td>Exp 2: Obs std [%]</td>
<td>-</td>
<td>3.32</td>
<td>1.93</td>
<td>1.39</td>
</tr>
</tbody>
</table>

The particle diameter of measurement 2 goes to its asymptote more smoothly in comparison to the tendency of the blue line. The particle diameter is dependent on the impeller speed like the obscuration. A higher impeller speed implies a larger particle diameter. The particle diameter is around 400-500 µm.

![Figure 6.5: Dp50 tendency versus time: red line is dp50 of measurement 2, blue line is dp50 of measurement 1](image)

In Figure 6.6 the corrected light scattering at two moments in measurement 1 are shown. After 40 seconds the obscuration is decreasing to its steady value. The density fluctuations of filling the cell are diminishing. Just after the maximum obscuration it is assumed that CO$_2$ fog is present, when a premixed CO$_2$-N$_2$ bottle is used. The first 10 detectors measure most light scattering due to density fluctuations. After 300 seconds when the obscuration is steady at impeller speed 2, the first 10 detectors still measure the most light scattering. However, the light scattering at detector numbers 11+ are increased, which indicate very small ice forming on the windows. In measurement 2 the light scattering at detector number from 11 was substantially higher than in measurement 1. After conducting measurement 2 it was noticed that ice was formed on the windows.
6. Background analysis experiments

6.2. Obscuration experiment number 2

6.1.3 Conclusion experiment

A background experiment with pure N₂ gas bottle was performed at a temperature of −50 °C and a pressure of 40 bar. During the cooling process no ice was formed on the cells windows. The protectors were removed and the Spraytec was positioned near the cells windows. Water from the ambient air froze on the cell windows, resulting in a laser intensity of 11%, which has to be about 65%. With compressed air the windows were cleaned manually, resulting in a laser intensity of 65%. The experiment consisted of three measurements. During the first measurement the pressure and temperature were not logged. The third measurement is not performed due to ice forming on the windows. The obscuration tendencies of measurement one and two are in agreement. The steady values and their standard deviations are nearly identical. The obscuration decreases when the impeller speed increases, because of the better mixing in the cell. The particle diameter increases when the impeller speed increases, because of the better mixing in the cell. During the filling of the cell hot gas enters the cell resulting in a sharp increase of the temperature. The gas cools rapidly until an equilibrium temperature is reached. The first 10 detectors measured the most corrected light scattering which is caused by the density fluctuations. High numbered detectors measured a higher scattering near the end of measurement 2, which is a result of ice forming on the windows.

6.2 Obscuration experiment number 2

The results of background experiment number 2 are described in this section.

6.2.1 Experiment approach

The pure N₂ gas bottle is used in this experiment. The condensation cell is filled up to a pressure of 2.5 bar. The large chiller is set at −64 °C in order to lower the cells temperature. The impeller speed is set at position 2. The measurement procedure described in Chapter 3 is used in this experiment. The desired cell temperature is about −50 °C. The pressure is set at 40 bar by the pressure reducer. The experiment consists of 3 measurements. The condensation cell will be filled three times at an impeller position of 2. After 4 minutes the impeller position is changed to 4 to investigate the obscuration change. After 6.30 minutes the impeller position is changed to 6. At last after 8.30 minutes the impeller position is changed back to 2.

The protectors were removed and the glasses were clean. The Spraytec is positioned as close as
possible to the cell. The background and alignment procedure of the laser failed due to a lack of background light measured by the detector. During the inspection of the windows it was noticed that ice was formed on the cells windows. With compressed air it was tried to clean the windows, but the ice growth rate was faster than the removal rate of the ice. Hot N₂ did not work either. So, it was decided to stop the experiment.

6.2.2 Conclusion experiment

A background experiment with pure N₂ gas bottle was performed at a temperature of −50°C and a pressure of 40 bar. During the cooling process no ice was formed on the cells windows. The protectors were removed and the Spraytec was positioned near the cells windows. Water from the ambient air freezeed on the cell windows. With compressed air and hot N₂ it was tried to clean the windows, but it failed. This was the fourth time that ice was formed on the cells windows after the placement of the Spraytec. Apparently the outside air enters the area in front of the cells windows when the protectors are removed. The area between the Spraytec and the windows has to be isolated to prevent that air containing water reaches the windows. This area has to be filled by using N₂ gas with the purge system.

6.3 Obscuration experiment number 3

The results of background experiment number 3 are described in this section.

6.3.1 Measurement procedure adjustments

The described measurement procedure in Chapter 3 is adjusted due to the ice forming on the cells windows. Ice forming occurs when the protectors of the cell windows are removed and the Spraytec system is positioned near the condensation cell. Ambient air flows into the window area, resulting in water freezing on the windows. In order to prevent this problem the Spraytec is positioned at the start of the cooling down process as close as possible near the windows instead of just before the measurement start. Isolation boxes are made to create an isolation chamber between the cells windows and the Spraytec windows. These isolation boxes are positioned over the frame of the Spraytec windows and over the frame of the cells windows.

N₂ at a high flow rate is blown into the isolation chambers to deflate all air. It takes about 30 seconds. The purge valve to the Spraytec has to be open to blow N₂ in the Spraytec chambers. Otherwise ice forming will occur on the Spraytec windows instead of on the cell windows. When the chambers are filled with N₂, the purge system is set at a lower flow rate (at touch) to constantly provide N₂ to the isolation and the Spraytec chambers. The cooling down process can be started only if the above mentioned steps are applied. During the cooling down process the lasers starting procedure can be started to check if the laser intensity dropped over time. If it has dropped, then most probably ice forming has occurred. However, appropriate measures can be taken on time to reduce the ice forming, for example by increasing the N₂ flow rate. All other aspects of the measurement procedure described in Chapter 3 remain the same.

6.3.2 Experiment approach

The pure N₂ gas bottle is used in this experiment. The condensation cell is filled till a pressure of 1.8 bar. The large chiller is set at −64°C in order to reduce the cells temperature. The impeller speed is set at position 2. The desired cell temperature is about −50°C. The pressure is set at 40 bar with the pressure reducer. The experiment consists of 3 measurements. The condensation cell will be filled three times at an impeller position of 2(R2). After 3.30 minutes the impeller position is changed to 4(R4) to investigate the obscuration change. After 6 minutes the impeller position is changed to 6(R6). Finally, after 8.30 minutes the impeller position is changed back to
2(R2). When 12 minutes are past the measurement is ended.

The cooling down process took about 3 hours before reaching the desired temperature. Every hour the starting procedure of the Spraytec was started in order to investigate the laser intensity. Due to isolation chambers the laser intensity increased from 65% to 72%. In the isolation chambers a temperature gradient is present resulting in N\textsubscript{2} density fluctuations. The N\textsubscript{2} flow in the isolation chambers have less impact on the measurement, because the N\textsubscript{2} flows over the Spraytec frame to the ambient, instead of flowing radially out when no isolation chambers were present. The flow is more turbulent in the isolation chamber resulting in better mixing and less density fluctuations. After two hours of cooling down the laser intensity dropped to 35%. The N\textsubscript{2} was increased, which improved to laser intensity to its original level of 72%.

### 6.3.3 Experiment results

Three measurements were performed. Each measurement was started with a laser intensity of 72%. After measurement 3 the laser background, the alignment procedure was started again and the laser intensity dropped to 50%, indicating that ice forming had occurred, so the last part of measurement 3 can be compromised. The N\textsubscript{2} purge bottle was almost empty, which resulted in a drop of the flow rate. So the N\textsubscript{2} flow rate was too low to prevent ice forming near the end of the measurement.

![Temperature tendency versus time](image)

**Figure 6.7:** Temperature tendency versus time

In Figure 6.7 the temperature tendencies of all measurements are shown. The tendencies are identical to each other. A small offset is present between the measurements due to the cooling of the cell. The starting temperature of measurement one is higher than the consecutive measurements. During the deflating of the condensation cell of each experiments the condensation cells temperature drops due to the Joule Thomson effect. This heat is stored in the interior of the cells material. The starting temperature of the consecutive measurement is therefore lower than the temperature of the previous experiment. In Figure 6.8 the pressure tendencies of all
6. Background analysis experiments  

6.3. Obscuration experiment number 3

![Graph of pressure tendency versus time](image)

**Figure 6.8:** Pressure tendency versus time

![Graph of obscuration tendency versus time](image)

**Figure 6.9:** Obscuration tendency versus time

Measurements are shown. The pressure is increased rapidly to about 40 bar. When the steady value is reached, clear fluctuations are present in the signal, which has also been noticed in the equilibrium composition experiments.
6. Background analysis experiments

6.3. Obscuration experiment number 3

The obscuration of all measurements are shown in Figure 6.9. During the rapid filling the obscuration reaches a maximum value. After reaching the temperature decreases and also the obscuration decreases. The obscuration has the tendency to reach a steady value. The last 50 samples in this steady region are averaged and its standard deviation is calculated. After the steady region, the obscuration drops significantly due to the change in impeller speed. Again the last 50 samples are averaged. After 6 minutes the impeller speed is increased further, resulting in an obscuration drop. Eventually the rotor speed is set at 2 which indicates an increase of obscuration. The averages and standard deviations of all regions are shown in Table 6.2. The obscuration in measurement 1 is slightly higher than in the other measurements. In every region the obscuration is in the same order. The standard deviations are the same. Moreover all measurements have the same obscuration tendencies. The dp50 of all measurements is shown in Figure 6.10. All measurements have the same dp50 tendencies. The particle diameter depends on the impeller speed like the obscuration. A higher impeller speed implies a higher particle diameter. The particle diameter is around 400-500 µm.

![Figure 6.10: Dp50 tendency versus time](image)

Table 6.2: Averages of obscuration in relation to impeller speeds

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</table>
6. Background analysis experiments

6.3. Obscuration experiment number 3

In Figure 6.11 the corrected light scattering at two moments in measurement 1 are shown. After 34 seconds the obscuration is decreasing to its steady value. The density fluctuations of filling the cell are diminishing. Just after the maximum obscuration it is assumed that CO₂ fog is present when a premixed CO₂-N₂ bottle is used. The first 10 detectors measure most light scattering due to the density fluctuations. After 205 seconds when the obscuration is steady at impeller speed 2, the first 10 detectors still measure most light scattering. However, the light scattering at detector number 19 is substantially higher than the light scattering at surrounding detectors, but still very small in comparison with the first 10 detectors. A possible reason for the peak at detector number 19 are small scratches on the quartz cell window at the Spraytec laser side. When detectors 1-10 are neglected, no substantial scattering is measured. When detectors 1-13 are neglected, the Spraytec measures no data that can be processed. Apparently detector number 11-13 still measure some scattering that is a result of density fluctuations. The corrected light scattering profiles of measurement 2 and 3 are identical to measurement 1.

6.3.4 Conclusion experiment

A background experiment with pure N₂ gas bottle was performed at a temperature of −50°C and a pressure of 40 bar. The measurement procedure was adjusted by positioning the Spraytec at the beginning of the measurement near the condensation cell. Isolation chambers are created to prevent air flowing to the windows. The purge has to be opened for the cell windows but also for the Spraytec windows. During the cooling down the laser intensity can be determined as measure for freezing of ice on windows. After two hours of cooling down, the laser intensity dropped, however this was restored by increasing the N₂ flow rate.

The experiment consisted of three measurements. At the end of measurement 3, the laser intensity was dropped to 50% which did not influence the results. The obscuration tendencies of the measurements are identical. The steady values and their standard deviations are in the same order. The obscuration decreases when the impeller speed increases, because of the better mixing in the cell. The particle diameter increases when the impeller speed increases. During the filling of the cell hot gas enters the cell resulting in a sharp increase of the temperature. The gas cools rapidly until an equilibrium temperature is reached. When looking at the corrected light scattering, the first 13 detectors measure most intensity, which are caused by density fluctuations. A substantial peak at detector number 19 is present throughout all measurements, which may be caused by scratches on the quartz cell window on the Spraytec laser side. No ice was formed on the windows during the measurements according to the corrected light scattering.
6.4 Obscuration experiment number 4

The results of background experiment number 4 are described in this section.

6.4.1 Experiment approach

The pure N\textsubscript{2} gas bottle is used in this experiment. The condensation cell is filled up to a pressure of 1.9 bar. The large chiller is set at $-64^\circ C$ in order to lower the cell's temperature. The impeller speed is set at position 2. The desired cell temperature is about $-50^\circ C$. The pressure is set at 40 bar by the pressure reducer. The experiment consists of 3 measurements. The condensation cell will be filled three times at a impeller position of 2(R2). After 3.30 minutes the impeller position is changed to 4(R4) to investigate the obscuration change. After 6 minutes the impeller position is changed to 6(R6). Finally after 8.30 minutes the impeller position is changed back to 2(R2). When 10 minutes are past the measurement it ended. The measurement procedure described in Chapter 3 is used with the adjustments described in subsection 6.3.1.

6.4.2 Experiment results

The cooling down process took about 3 hours before reaching the desired temperature. Every hour the background and alignment procedure of the Spraytec was started to investigate the laser intensity. The laser intensity was about 71% and it did not change over time. So no ice forming occurred during the whole experiment. Two of the three measurements were performed. The last measurement could not be performed, because the N\textsubscript{2} gas bottle was empty after two measurements. Apparently, the purge flow rate was too high to measure all desired measurements. The pressure was not logged by unknown reasons for the first 30 seconds of measurement 1. After the experiment the inside window of the Spraytec detector had traces of condensation which compromised the measurement. The temperature tendencies were the same, only a slight offset is present exactly like that is shown Figure 6.7.

The obscuration of all measurements is shown in Figure 6.12. During the rapid filling the obscuration reaches a maximum value. After reaching the temperature decreases and also the obscuration decreases. The obscuration has the tendency to get to a steady value. The last 50 samples in this steady region are averaged and the standard deviation is calculated. After the steady region, the obscuration drops significantly due to the change in impeller speed. Again the last 50 samples are averaged. After 6 minutes the impeller speed is increased further, resulting again in an obscuration drop. Eventually the rotor speed is set at 2 which indicates an increase of obscuration. The averages and standard deviations of all regions are shown in Table 6.3. The obscuration in measurement 1 is quite higher than in the other measurement. In every region the obscuration of measurement 1 is about 10% higher than the obscuration of measurement 2. However, the maximum obscuration is identical. Especially the obscuration of measurement 2 at impeller speed 4 is quite low. The condensation on the inside detector window influenced the measurement. The particle diameter in measurement 2 is about 100 $\mu$m larger than the particle diameter of measurement 1. It can be stated that the particle diameter is dependent on the impeller speed like the obscuration. A higher impeller speed implies a higher particle diameter, which was also concluded in the previous experiments. The corrected light scattering of measurement 1 is identical to the correct light scattering of the previous experiment (see Figure 6.11). In measurement 2 the condensation on the inside detector window scattered the laser light in such a way that detectors 1-10 measured that particular scattering, which resulted in a higher particle diameter.

6.4.3 Conclusion experiment

A background experiment with a pure N\textsubscript{2} gas bottle was performed at a temperature of $-50^\circ C$ and a pressure of 40 bar. Initially the experiment consisted of three measurements. The last
6. Background analysis experiments  

6.5. Obscuration experiment number 5

The results of background experiment number 5 are described in this section.
6. Background analysis experiments

6.5. Obscuration experiment number 5

6.5.1 Measurement setup adjustments

In most of the previous background experiments the cells windows were frozen due to a low N₂ flow rate. When the N₂ flow rate is too high the purge gas bottle will be empty before the whole experiment is performed. The N₂ flow rate is set at touch, which is not optimal. So in the purge system rotameters are introduced, which are depicted in Figure 6.13. One rotameter is positioned behind the pressure reducer, the second one is positioned after the T piece in the cells window purge. The rotameters range is quite large for the purge flow rate and it is measured in normal cubic meters air. Therefore the flow rate indication in the rotameters is in the lower part of the range, which is also not optimal. With the rotameters in the purge system it is possible to determine the correct amount of flow needed for preventing the above mentioned problems.

![Figure 6.13: Adjusted purge system](image)

In Obscuration experiment number 4 it was mentioned that the inside windows of the Spraytec had traces of condensation. This means that the introduction of isolation chambers have introduced the problem of possible condensation on the Spraytec window, but it has solved the problem of freezing cell windows. In order to maintain clean Spraytec windows the Spraytec purge part is heated with an open coil heat element. The heat element (denoted in Figure 6.13 as heater) can be set at a temperature from 0°C to 150°C. Hot N₂ in the Spraytec system gives more certainty that no condensation occurs at the windows without creating a temperature gradient into the condensation cell.

The measurement procedure described in Chapter 3 is used with the adjustments described in subsection 6.3.1. The N₂ purge flow rate can be controlled with the rotameters. An appropriate starting flow rate is about 3Nm³/h (empirical deduced). The heat element is set at 50°C.

6.5.2 Experiment approach

The pure N₂ gas bottle is used in this experiment. The condensation cell is filled till a pressure of 2 bar. The large chiller is set at −64°C in order to lower the cells temperature. The impeller speed is set at position 2. The desired cell temperature is about −50°C. The pressure is set at 40 bar by the pressure reducer. The experiment consists of 3 measurements. The condensation cell will be filled three times at an impeller position of 2(R2). After 3 minutes the impeller position is changed to 4(R4) to investigate the obscuration change. After 6 minutes the impeller position is changed to 6(R6). Finally after 8.30 minutes the impeller position is changed back to 2(R2). When 10 minutes are past the measurement it ended.
6.5.3 Experiment results

After one hour down in the cooling process the laser intensity dropped below 1%. Apparently the \( \text{N}_2 \) flow was zero. Initially it was set at a low flow rate of \( 2 \text{Nm}^3/\text{h} \). After a couple of minutes the membrane has positioned in an equilibrium position in which no flow was possible due to the hysteresis sensitive membrane in the pressure reducer. The Spraytec windows were frozen this time. The \( \text{N}_2 \) flow rate was increased to \( 4 \text{Nm}^3/\text{h} \). When the desired cell temperature of \(-50^\circ \text{C}\) was reached the laser intensity improved to 65%, which is appropriate enough to continue the measurements. However, more \( \text{N}_2 \) has been used to clean the windows, resulting in too less \( \text{N}_2 \) to perform the last (third) measurement.

![Obscuration tendency versus time](image)

**Figure 6.14**: Obscuration tendency versus time

The temperature tendencies of the two measurements are the same, only a slight offset is present exactly like Figure 6.7. The pressure tendencies are also the same exactly like Figure 6.8. In Figure 6.14 the obscuration of both measurements is shown. Measurement 1 is slightly shifted to the left. The maximum obscuration is positioned at the first sample point. The tendencies are identical for the measurements. After the sharp decrease in obscuration, the obscuration increases slightly until a steady value is reached. The steady value at impeller speed 2 of measurement 1 is about 7% higher than measurement 2. The other steady values at the other impeller speeds are the same. The averages and standard deviations of all regions are shown in Table 6.4. The particle diameter of both measurements are identical to each other. The particle diameter is dependent on the impeller speed like the obscuration. A higher impeller speed implies a higher particle diameter. The particle diameter is around 400-550 \( \mu \text{m} \). The corrected light scattering of both measurements is identical to the corrected light scattering of experiment number 1 (Figure 6.6). At the high numbered detectors scattering is measured, which is not desired. During the preparations of this experiment the laser intensity improved from 1% to 65%, but not all ice was removed from the windows. This resulted in scattering at high numbered detectors. However, the scattering at the
high numbered detectors decreased over the whole experiment and the laser intensity increased to about 68%.

Table 6.4: Averages of obscuration in relation to impeller speeds

<table>
<thead>
<tr>
<th></th>
<th>Max obs</th>
<th>Obs R2</th>
<th>Obs R4</th>
<th>Obs R6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp 1: Obs mean [%]</td>
<td>94.26</td>
<td>66.16</td>
<td>29.55</td>
<td>12.80</td>
</tr>
<tr>
<td>Exp 1: Obs std [%]</td>
<td>-</td>
<td>2.93</td>
<td>2.66</td>
<td>1.46</td>
</tr>
<tr>
<td>Exp 2: Obs mean [%]</td>
<td>94.51</td>
<td>59.23</td>
<td>25.02</td>
<td>14.69</td>
</tr>
<tr>
<td>Exp 2: Obs std [%]</td>
<td>-</td>
<td>2.97</td>
<td>1.81</td>
<td>1.05</td>
</tr>
</tbody>
</table>

6.5.4 Conclusion experiment

A background experiment with a pure N₂ gas bottle was performed at a temperature of −50°C and a pressure of 40 bar. Rotameters are positioned in the purge system to give an indication what the N₂ flow rate is in the system. Moreover, an open coil heat element is placed in the Spraytec purge part to heat the N₂ to prevent condensation in the Spraytec chambers.

During the cooling down process the N₂ flow rate was zero, which resulted in ice forming on cell and Spraytec windows. The N₂ flow rate was set substantially higher and eventually the windows were clean. Initially the experiment consisted of three measurements. The last measurement could not be performed due to an empty purge N₂ bottle. The temperature tendencies of the two measurements are the same with only a slight offset. The pressure functions are also identical. The obscuration signals are also nearly identical. Only the steady value differs a few percentages with each other, but these are in the same order. The obscuration decreases when the impeller speed increases, because of the better mixing in the cell. This has repeatedly been noticed in every experiment. The particle diameter increases when the impeller speed increases, because of the better mixing in the cell. During the preparations of this experiment the laser intensity improved from 1% to 65%, but not all ice was removed from the windows. This resulted in scattering at high numbered detectors. However the scattering at high numbered detectors decreased over the whole experiment and the laser intensity increased to about 68%. The largest scattering was measured by the first ten detectors, which indicates primarily, density fluctuations.

6.6 Obscuration experiment number 6

The results of background experiment number 6 are described in this section.

6.6.1 Experiment approach

The pure N₂ gas bottle is used in this experiment. The condensation cell is filled till a pressure of 1.6 bar. The large chiller is set at −64°C in order to lower the cells temperature. The impeller speed is set at position 2. The desired cell temperature is about −50°C. The pressure is set at 40 bar by the pressure reducer. The experiment consists of 3 measurements. The condensation cell will be filled three times at an impeller position of 2. After 5 minutes the impeller position is changed to 4 to investigate the obscuration change. After 10 minutes the impeller position is changed to 6. Finally after 15 minutes the impeller position is changed back to 2. When 20 minutes are past the measurement is ended. The impeller position is changed at different timepoints to prolong the period of time to obtain a steady obscuration and particle diameter. The measurement setup adjustments described in Chapter 6.5.1 are used in this experiment. The measurement procedure described in Chapter 3 is used together with the adjustments described in subsection 6.3.1. The N₂ purge flow rate can be controlled with the rotameters. An appropriate starting flow rate is about 3Nm³/h. The heat element is set at 50°C.
6.6.2 Experiment results

After one hour had passed in the cooling process the laser intensity dropped below 14%. The N\textsubscript{2} flow was zero. Initially it was set at a low flow rate of 2.5Nm\textsuperscript{3}/h. After a couple of minutes the membrane is positioned in an equilibrium position in which no flow was possible, because the membrane in the pressure reducer is hysteresis sensitive. The cells windows were frozen. The N\textsubscript{2} flow rate was increased to 5Nm\textsuperscript{3}/h. When the desired cell temperature of −50 \degree C was reached the laser intensity was improved to 65%, which is appropriate enough to continue the measurements. However, more N\textsubscript{2} has been used to clean the windows, resulting in too less N\textsubscript{2} to perform the last two measurements.

![Figure 6.15: Obscuration tendency versus time](image)

The temperature and pressure curve are identical to the temperature and the pressure curves of previous measurements. In Figure 6.15 the measurements obscuration is shown, which is a similar tendency compared to the previous measurements. It was chosen extend the periods of time between changing the impeller speed, to reach a clear steady value. The averages and standard deviations of all regions over the last 100 samples in each region are shown in Table 6.5. The steady values are in accordance with the steady values of the previous measurements. The measurements particle diameter has the identical tendency of the previous measurements. A higher impeller speed implies a higher particle diameter. The particle diameter has the order of around 400-550 µm. The corrected light scattering of measurement is identical to the correct light scattering of experiment number 3 (see Figure 6.11).

<table>
<thead>
<tr>
<th>Table 6.5: Averages of obscuration in relation to impeller speeds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max obs</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>Exp 1: Obs mean [%]</td>
</tr>
<tr>
<td>Exp 1: Obs std [%]</td>
</tr>
</tbody>
</table>
6.6.3 Conclusion experiment

A background experiment with pure N\textsubscript{2} gas bottle was performed at a temperature of $-50 \, ^\circ\text{C}$ and a pressure of 40 bar. During the cooling down process the N\textsubscript{2} flow rate was zero, which resulted in ice forming on the cell windows. The N\textsubscript{2} flow rate was set substantially higher and eventually the windows were clean. Initially the experiment consisted of three measurements. The last two measurement could not be performed due to an empty purge N\textsubscript{2} bottle. The temperature, the pressure, the obscuration and the particle diameter curves are identical to the temperature, the pressure, the obscuration and the particle diameter curves of previous measurements. The steady values are also in accordance with the steady values of previous measurements. The corrected light scattering of this measurement is identical to the correct light scattering of experiment number 3. The first 10 detectors measure most intensity, which are caused by density fluctuations. A substantial peak at detector number 19 is present throughout all measurements, which may be caused by scratches on the quartz cell window on the Spraytec laser side. No ice formed on the windows during the measurements according to the corrected light scattering.

6.7 Obscuration experiment number 7

The results of background experiment number 7 are described in this section.

6.7.1 Experiment approach

The pure N\textsubscript{2} gas bottle is used in this experiment. The condensation cell is filled till a pressure of 1.6 bar. The large chiller is set at $-64 \, ^\circ\text{C}$ in order to lower the cells temperature. The impeller speed is set at position 2. The desired cell temperature is about $-50 \, ^\circ\text{C}$. The pressure is set at 40 bar by the pressure reducer. The experiment consists of as many possible measurements done with one full N\textsubscript{2} purge bottle. The condensation cell will be filled one time at an impeller position of 2. In the other measurements the condensation cell will be filled at a impeller position of 4, which is done in order to investigate if the obscuration curve is identical to the obscuration curve at impeller position 2. The condensation cell is only filled with N\textsubscript{2} and after 6 minutes the measurement is ended. The impeller speed remains constant throughout the measurement. The measurement setup adjustments described in Section 6.5.1 is used in this experiment. The measurement procedure described in Chapter 3 is used together with the adjustments described in subsection 6.3.1. The N\textsubscript{2} purge flow rate can be controlled with the rotameters. The starting flow rate is about $4.5 \, \text{Nm}^3/\text{h}$. The heat element is set at 50°C.

6.7.2 Experiment results

During the cooling down process no problems occurred. The laser intensity was 71% when the condensation cell reached the desired temperature. Five measurements were done before the N\textsubscript{2} gas bottle was empty. In the first four measurements the impeller speed was set at position 4. In the last measurement the impeller speed was set at position 2.

The temperature and pressure curves are identical to the temperature and the pressure curves of previous measurements, only a slight offset is present exactly like Figure 6.7. In Figure 6.16 the measurements obscuration at impeller speed 4 is shown. During the filling of the condensation cell the obscuration reaches a maximum of about 94%, which is caused primarily by density fluctuations. The obscuration drops until it reaches a steady value. All four obscuration curves are identical to each other. The averages and standard deviations over the last 150 samples are shown in Table 6.6. The averages and the standard deviations are identical. In Figure 6.17 the obscuration signal of the last measurement at impeller speed position 2 is shown. During the filling of the condensation cell the obscuration reaches a maximum of about 94%, whereafter the obscuration drops to reach a steady value. The pressure, temperature and
6. Background analysis experiments

6.7 Obscuration experiment number 7

![Graph](image)

Figure 6.16: Obscuration tendency versus time of impeller speed 4 measurements

Particle diameter curves are identical to the pressure, temperature and particle diameter curves of previous measurements.

Table 6.6: Averages of obscuration in relation to impeller speeds, R4 is impeller speed position 4 and R2 is impeller speed position 2

<table>
<thead>
<tr>
<th></th>
<th>Max obs [%]</th>
<th>Obs mean R4 [%]</th>
<th>Obs std R4 [%]</th>
<th>Obs mean R2 [%]</th>
<th>Obs std R2 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp 1</td>
<td>94.20</td>
<td>31.57</td>
<td>2.36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Exp 2</td>
<td>94.66</td>
<td>32.49</td>
<td>2.17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Exp 3</td>
<td>93.94</td>
<td>32.18</td>
<td>2.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Exp 4</td>
<td>94.10</td>
<td>29.65</td>
<td>2.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Exp 5</td>
<td>94.91</td>
<td>-</td>
<td>-</td>
<td>64.23</td>
<td>3.10</td>
</tr>
</tbody>
</table>

In measurement 1 the first 10 detectors measured most light scattering due to density fluctuations. However, the light scattering at detector number 19 was substantially higher than the light scattering at surrounding detectors, but it was still very small in comparison with the first 10 detectors. A possible reason for the peak at detector number 19 are small scratches on the quartz cell window at the Spraytec laser side. When detectors 1-10 were neglected, no substantial scattering was measured. When detectors 1-13 were neglected, the Spraytec measured no data that can be processed. Apparently detector number 11-13 still measured some scattering which was a result of density fluctuations. The corrected light scattering profiles of the other four measurements are identical to measurement 1.

6.7.3 Conclusion experiment

A background experiment with pure N₂ gas bottle was performed at a temperature of −50 °C and a pressure of 40 bar. The impeller position was not changed during the measurement to reach a
steady obscuration over time. 5 measurements were performed. The first 4 measurements were performed at impeller position 4. The obscuration curves of these measurements were identical to each other. The last measurement was performed at impeller position 2. The pressure, the temperature and the particle diameter curves of all measurements were identical to the pressure, the temperature and the particle diameter curves of previous measurements. When looking at the corrected light scattering, the first 13 detectors measured most intensity, which were caused by density fluctuations. A substantial peak at detector number 19 was present throughout all measurements, which may be caused by scratches on the quartz cell window on the Spraytec laser side. No ice formed on the windows during the measurements according to the corrected light scattering. The corrected light scattering is identical for all measurements.

6.8 Summary background experiments

In this chapter multiple background experiments are described. N₂ gas is fed to the condensation cell under a pressure of 40 bar and a cell temperature of −50°C at primarily impeller speed position 2. No condensation will occur, but due to density fluctuations the Spraytec laser system will measure scattering. The measured signals are analyzed at the obscuration, the particle size and which detectors are involved in density fluctuations. During most experiments the impeller speed is changed in order to see what the effects are on the detectors. The other goal of these background analyses is to improve the measurement procedure, to prevent ice forming on the windows.

During the first two background experiments freezing of water on the cells windows occurred when the insulation caps were removed and the Spraytec was positioned near the condensation cell. This phenomenon was also noticed during the initial supersaturation experiments. In order to prevent ice forming on the windows, insulation caps were positioned over the Spraytec frame and the cell windows frame to create isolated chambers in which N₂ gas was fed constantly by the purge system. The amount of N₂ fed to the purge system is the key for preventing ice forming. The N₂
should be high enough to prevent ice forming, but low enough to prevent an empty gas bottle so that not the whole experiment could be performed. Rotameters were placed in the purge system and a open coil heat element was introduced to control the temperature of the mass flow. However the rotameters scale is not appropriate, so the rotameters have to be replaced by a controllable flow meter. All improvements prevent ice forming on windows only if the measurement procedure is performed with much care.

When the gas is fed rapidly to the condensation cell, the gas will cool down by the inlet heat exchanger. However the gas temperature is much higher than the cells temperature, resulting in a sharp increase of temperature. The gas cools down very rapidly due to the heat of the condensation cell until it reaches a constant temperature. This temperature curve occurred during every measurement. A small offset is present between the measurements due to the cooling of the cell. The starting temperature of a measurement is higher than the consecutive measurements. During the deflating of the condensation cell of each experiment, the condensation cells temperature drops due to the Joule Thomson effect. This heat is stored in the interior of the cells material. The starting temperature of the consecutive measurement is then lower than the temperature of the previous one. The pressure is increased rapidly to about 40 bar. When the steady value is reached clear fluctuations are present in the signal, which have also been noticed in the equilibrium composition experiments. The pressure curves occurred during every measurement.

The obscuration reaches a maximum when the gas enters the condensation cell. Then the obscuration drops and goes to a minimum in the curve, whereafter the obscuration goes to a steady value. When this steady value was reached the impeller speed increased and the obscuration dropped. After reaching the steady value, the impeller speed was further increased and the obscuration dropped further. The obscuration is dependent on the impeller speed. A high impeller speed implies a high mass and heat transfer which results in less density fluctuations and also in less obscuration fluctuations. In Table 6.7 the obscuration range for the impeller speeds and the maximum obscuration are given. An impeller speed gives a clear predefined obscuration range. The obscuration in the future fog formation measurements have to consistent with this obscuration range.

Table 6.7: Obscuration ranges in relation to impeller speeds

<table>
<thead>
<tr>
<th>Obscuration</th>
<th>Range [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum obscuration during filling of cell</td>
<td>94-95</td>
</tr>
<tr>
<td>Obscuration impeller speed 2</td>
<td>55-70</td>
</tr>
<tr>
<td>Obscuration impeller speed 4</td>
<td>22-35</td>
</tr>
<tr>
<td>Obscuration impeller speed 6</td>
<td>11-18</td>
</tr>
</tbody>
</table>

When looking at the corrected light scattering of the experiments the first 10 detectors measure the most scattered light, which are primarily density fluctuations. The scattered light can also be measured at detector numbers 11-13, especially during the filling of the cell, which are also density fluctuations. The light scattering at detector number 19 is substantially higher than the light scattering at surrounding detectors, but still very small in comparison with the first 10 detectors. A possible reason for the peak at detector number 19 are small scratches on the quartz cell window at the Spraytec laser side. When detector numbers 1-13 are neglected in the data processing, the Spraytec measures no data that can be processed. The ideal result when the laser intensity is above 70% indicating that no ice was formed on the windows. When ice has formed on the windows two possibilities exist. The first possibility is that the ice scatters the laser so that high numbered detectors measure light intensities, which will distort future supersaturation experiments. The second possibility is that the ice scatters the laser so that the low numbered detectors measure increased light intensities, which result in a higher and none representative par-
particle distribution. So the laser intensity has to be above 70% in order to be sure that the windows are ice free and that the experiments will not be distorted.

Directly from the corrected light scattering the particle distribution is determined. The averaged particle diameter (dp50) is in all experiment about 400 µm at impeller speed 2 to 550 µm at impeller speed 6. The particle diameter is dependent on the impeller speed like the obscuration. A higher impeller speed implies a higher particle diameter, which is just an indication for less density fluctuations. When fog formation will occur with a premixed CO₂-N₂ mixture, the droplet sizes should be near the 100 µm, which implies that high numbered detectors should measure substantially more scattering. In order to remove the density fluctuations in the cell, detectors 1 till 13 can be neglected during the data processing of supersaturation experiments.
Chapter 7

Spraytec fog formation experiments

In this chapter the Spraytec fog formation experiments are discussed. The condensation cell is cooled down to a temperature of $-50^\circ\text{C}$ at a low pressure around 2 bar with a 50-50% CO$_2$-N$_2$ mixture. When the desired temperature is reached, the pressure is rapidly increased to 40 bar, which results in a high supersaturation thus fog formation. The fog formation is measured with the Spraytec laser system which uses laser diffraction to measure the droplet sizes of the fog. Density fluctuations cause large laser diffractions which distort the measurements. The influence of the density fluctuations on the measurement results were investigated in the previous chapter. In combination with the results of the previous chapter it can be deduced if fog formation occurred during the Spraytec fog formation experiments.

Ice forming on the cells windows and to a lesser extent on the Spraytec windows causes unreliable Spraytec scattering signals. In the previous chapter the measurement setup was changed to avoid these problems. First insulation caps were positioned over the Spraytec and the cell windows frame to create an isolation chamber, which is filled with nitrogen. The N$_2$ is constantly provided by the purge system. The amount of N$_2$ provided to the purge system is key to a successful measurement. The N$_2$ should be high enough to prevent ice forming, but low enough to prevent an empty gas bottle so that not the whole experiment could be performed. The rotameters in the purge system (Figure 7.2) are replaced by a single calibrated rotameter with an appropriate range behind the pressure reducer. The N$_2$ flow rate can be controlled with the new flow meter, which will provide a constant (known) flow rate to the purge system. Furthermore, a totalizer is connected to the leakage flow of the GC in order to measure the flow rate in the sample line, which is used to determine the GC delay of measuring the gas composition (Figure 7.1). The detailed description of the measurement setup can be found in Chapter 2. The measurement procedure described in Chapter 3 is used together with the adjustments described in subsection 6.3.1.
7. Spraytec fog formation experiments

Figure 7.1: Measurement setup with all sensors without the purge system

Figure 7.2: Purge system of the measurement setup
7.1 Spraytec fog formation experiment 1

The results of fog formation experiment number 1 are described in this section.

7.1.1 Experiment approach

The premixed gas bottle used for this experiment is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. The condensation cell is filled up to a pressure of 3 bar. The large chiller is set at −64 °C in order to lower the cells temperature. Initially the impeller speed is set at position 4. When the condensation cell is at the desired temperature which is about −50 °C, the impeller speed is set at position 2. The pressure is set at 40 bar by the pressure reducer. The N₂ starting flow rate is set at 15LPM air. The heat element is set at 50 °C. The warning signals of the Spraytec were changed from 5% to 1% to obtain more information during the experiment. The composition of the gas was not measured in this experiment.

7.1.2 Experiment results

After half an hour the laser intensity dropped to 68% from initially 72%. The N₂ flow rate was too low so it was increased to 23LPM air. The laser intensity increased to its initial value. After 2 and a half hour the impeller speed was changed from position 4 to position 2, which is the desired impeller position for the fog formation experiments. When a lower cell temperature of −49 °C was reached the measurement was started. The laser intensity was 72%. The N₂ flow rate was increased to 30LPM air. Only one measurement was performed due to the fact that the N₂ purge bottle contained only 150 bar instead of a full N₂ gas bottle of 200 bar. After 2 minutes the pressure reducer was closed.

Temperature and Pressure

In Figure 7.3 the temperature in the cell is shown into the time for the experiment and a reference measurement with only N₂. The reference measurement consists of a combination of the background experiment results at impeller position 2. The figure on the left is the temperature in the upper part of the cell. When the pressure is rapidly increased the temperature increases to a maximum value around −23 °C. The incoming gas is cooled rapidly by the environment. In the figure on the right the temperature in the lower part of the cell is shown. Instant condensation occurs when the pressure is increased. The CO₂ liquid drops to the floor of the cell and absorbs more environmental heat, which results in a significant lower part temperature in comparison with the reference measurement. The CO₂-N₂ mixture cools down more slowly than pure N₂ gas, because of the condensation of CO₂ in the cell. When condensation occurs the pressure drops in the cell and more hot gas enters the condensation cell to maintain the pressure of 40 bar. When the equilibrium is almost reached the temperatures of the experiment and the reference measurement are almost equal. The experiment temperature reaches eventually a lower temperature than the reference experiment due to the higher heat capacity of a liquid-gas phase mixture in comparison with a gas phase mixture at the same large chiller set point.

In Figure 7.4 the pressure in the cell is shown into the time for the experiment and a reference measurement with only N₂. The pressure increases very rapidly until the equilibrium pressure is reached. The experiment reaches its maximum pressure a little bit later due to the condensation and the extra feeding of gas to maintain the pressure. The pressures set with the pressure reducer were not identical. The reference measurements pressure was set about 2 bar higher. After 2 minutes the pressure reducer was closed and the cell pressure drops due to condensation. Clear fluctuations in the pressures signal were present which were also noticed in the equilibrium composition experiments.
7. Spraytec fog formation experiments  7.1. Spraytec fog formation experiment 1

Figure 7.3: Temperature curves in the condensation cell with reference measurement

Figure 7.4: Pressure curves in the condensation cell with reference measurement

Obscuration

In Figure 7.5 the obscuration during the experiment is shown together with a reference measurement with pure N₂. The obscuration rises very rapidly due to the volume of gas entering the cell. Condensation occurs and the obscuration drops slowly in comparison with the reference measurement to a very low obscuration of about 10%. At this moment the pressure reducer is letting in extra hot gas into the cell to maintain the desired pressure. The obscuration rises until an equilibrium value is reached of about 45%, which is about 20% lower than the steady obscuration value of the reference measurement. The obscuration profile of a single gas phase mixture differs a lot with the obscuration profile of a liquid-gas phase mixture.
7. Spraytec fog formation experiments  

7.1. Spraytec fog formation experiment 1

Light scattering and associated particle diameter

The averaged particle diameter which is discussed in the following paragraphs is just an indication. The particle diameter is determined volume based, which is not yet validated. The averaged particle diameter of the reference measurement is steady in the period of time, which clearly differs from the averaged particle diameter of the experiment. During the filling of the condensation cell, instant condensation occurs. The scattering on the high detectors increases significantly resulting in a distinctive peak downwards. In Figure 7.7 the light intensities on the detectors are shown. The distinctive peak occurs after 11 seconds. The light intensities for this measurement are more than 60 % less than for the reference measurement. Significant light intensities are measured around detector number 10-15. However, the light intensities on the detector number higher than 15 are in the order 500, but due to the scale of the y axis these are not visible. Still, this is important because such intensities were not measured during the background experiments.

After the peak fog formation occurs and the high detector measures a steady light scattering. Meanwhile the density fluctuations cause higher scattering intensities on the low number light scattering (green line in Figure 7.7), which results in an increased averaged particle diameter. The dashed blue line in Figure 7.6 represents the averaged particle diameter when detector numbers 1-13 are not included in the data processing. For the reference measurement no data is logged when the low numbered detectors are not taken into account when the scattering intensities are below 200. During the first 90 seconds of the experiment, there is clear light scattering on the high numbered detectors. The pressure drops in the condensation cell by the condensation and so the hot gas is entering the cell. The hot gas blows the fog to the walls and it creates more density fluctuations. The light scattering at the low numbered detectors rises and therefore the averaged particle diameter also rises. Meanwhile the hot gas that entered cools down rapidly and condensates in a film but also in fog. However, this fog is not steady. The next batch of hot air to compensate the pressure blows again the fog to the walls. From that point onwards no significant scattering is measured at high numbered detectors and so no fog is present in the cell.
7. Spraytec fog formation experiments  
7.1. Spraytec fog formation experiment 1

Figure 7.6: Averaged particle diameter (dp50) with reference measurement

Figure 7.7: Corrected light scattering at various times

7.1.3 Conclusion experiment
A fog formation experiment with a 49.6-50.4 %CO₂-N₂ gas bottle was performed at a temperature of −50 °C and a pressure of 40 bar. During the cooling of the condensation cell no ice formed on
the cells windows or on the Spraytec windows. A N\textsubscript{2} flow rate of 30 LPM air is an appropriate set point to prevent ice forming. One measurement was performed. The pressure curve of the experiments is similar to reference curve. This experiment can not be considered isobar. The pressure is not maintained on the desired pressure for the whole experiment, because of the closing of the pressure reducer. The response time to reach a steady pressure is larger due to condensation in the cell. This is also noticed in the temperature curves. Hot gas enters the cell to maintain the desired pressure which keeps the temperature high in the cell. However the lower part cell temperature is significant lower than the reference measurement due to liquid forming in the cell.

The obscuration is very high during the filling of the cell. After the filling of the cell, obscuration drops to a minimum of 10%. At that point the pressure drops in the cell and hot gas enters the cell to maintain the pressure. The obscuration increases to its steady value which is about 20% lower than the steady value of the reference measurement.

During the filling of the condensation cell fog formation occurs, because at the detector number higher than 14 light intensities are measured for about 80 seconds. In the reference measurement no intensities at the detector numbers 14+ exceeded the Spraytec intensity limits. A distinctive downward peak is noticed in the overall particle diameter, which is a result of a combination of less light scattering at detector numbers 1-8 and more light scattering at detector numbers 9-15. Detector numbers 16+ do not influence the overall particle diameter due to the low light intensities measured at these detectors, but these are very important for the fog measurement. Around 80 seconds hot gas enters the cell to maintain the pressure, which results in blowing away the fog to the walls. However, a small part of the incoming gas condensates into fog. When the equilibrium is almost reached no light scattering is measured which exceeds the scattering intensity limits of the Spraytec.
7.2 Spraytec fog formation experiment 2

The results of fog formation experiment number 2 are described in this section.

7.2.1 Experiment approach

The premixed gas bottle used for this experiment is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. The condensation cell is filled up to a pressure of 3 bar. The large chiller is set at −64°C in order to lower the cells temperature. Initially the impeller speed is set at position 6. When the condensation cell is at the desired temperature which is about −50°C, the impeller speed is set at position 2. The pressure is set at 40 bar by the pressure reducer. The N₂ starting flow rate is set at 30LPM air. The heat element is set at 60°C. The warning signals of the Spraytec were changed from 5% to 1% to obtain more information during the experiment. The composition of the gas was not measured in this experiment. After 7 minutes the experiment was stopped.

The measurement is repeated as many times as possible. In order to repeat the measurements the large chiller is set at −55°C to heat up the condensation cell after completing a measurement. The impeller speed is increased from position 2 to position 6. The cell is deflated in such a way that the cell lower part temperature is at all times higher than −55°C in order to prevent CO₂ ice forming in the cell. Deflating the cell causes a temperature drop in the cell due to the Joule Thomson effect. A low deflation flow rate in combination with a higher cell temperature prevents CO₂ ice forming in the cell. The most critical part of the deflation is when all gas is removed from the cell and the liquid is evaporating. The JT effect is at that moment the largest. When the cell is deflated the large chiller is set at −58°C and the impeller speed is set at position 2. The cell is flushed twice with a mixture of 5 bar.

7.2.2 Experiment results

This experiment contains in total 4 measurements. During the whole experiment the laser intensity was steady around a value of 72%, so no problems occurred.

Temperature and Pressure

In Figure 7.8 the upper cell temperature is shown into the time for the experiment and a reference measurement with only N₂. The reference measurement is a combination of the background experiments results at impeller position 2. When the pressure is increased rapidly the temperature increases to a maximum value around −22°C. The incoming gas is cooled rapidly by the environment. In Figure 7.9 the lower cell temperature is shown. Instant condensation occurs when the pressure is increased. The CO₂ liquid drops to the cells floor and absorbs more environmental heat, which results in a significant lower part temperature in comparison with the reference measurement. The CO₂-N₂ mixture cools down more slowly than pure N₂ gas, because of the condensation of CO₂ in the cell, which is noted in all four measurements. When condensation occurs the pressure drops in the cell and more hot gas enters the condensation cell to maintain the pressure of 40 bar. When the equilibrium is almost reached the temperatures of the experiment and the reference measurement are almost equal. The experiment temperature reaches eventually a lower temperature than the reference experiment, because of the higher heat capacity of a liquid-gas phase mixture in comparison with a gas phase mixture at the same large chiller set point. All measurement temperature curves are similar to each other, but a small offset is present between the measurements due to the cooling of the cell.
7. Spraytec fog formation experiments 7.2. Spraytec fog formation experiment 2

Figure 7.8: Upper cell temperature curves in the condensation cell with reference measurement

Figure 7.9: Lower cell temperature curves in the condensation cell with reference measurement

In Figure 7.10 the pressure in the cell is shown into time for the measurements together with a reference measurement with only N₂ for the first 100 seconds. The pressure increases very rapidly until the equilibrium pressure is reached. The experiment reaches its maximum pressure a little
bit later than due to the condensation and the extra feeding of gas to maintain the pressure. The pressure curves of the measurements are identical to each other and all differ from the reference measurement. Clear fluctuations in the pressure signals are present which are also noticed in the equilibrium composition experiments. Small offsets in pressure are present due to the inaccurate settings of the pressure reducer.

![Figure 7.10: Pressure curves in the condensation cell with reference measurement](image)

**Obscuration**

![Figure 7.11: Obscuration curves in the condensation cell with reference measurement](image)

In Figure 7.11 the obscuration during the measurements is shown including a reference measurement with pure N₂. The obscuration rises very rapidly due to the gas volume entering the cell.
Condensation occurs and the obscuration drops slowly in comparison with the reference measurement to a very low obscuration of about 10%. At this moment the pressure reducer is letting extra hot gas entering the cell to maintain the desired pressure. The obscuration rises until an equilibrium value is reached of about 45%, which is about 20% lower than the steady obscuration value of the reference measurement. The obscuration profile of a single gas phase mixture differs a lot with the obscuration profile of a liquid-gas phase mixture. The obscuration curves of the measurements have to the same profile, but for every consecutive measurement the region of very high obscuration becomes shorter. This is caused by the lower cell temperature for each consecutive measurement. Condensation occurs more quickly and it reaches earlier its equilibrium position. The time period for controlling the pressure in the cell by feeding hot gas to the cell becomes larger for consecutive measurements (low obscuration region). Eventually all obscuration curves have the same the slope and the same equilibrium value in the last part of the measurements.

**Light scattering and associated particle diameter**

The averaged particle diameter which is discussed in the following paragraphs is just an indication. The particle diameter is determined volume based, which is not yet validated. The averaged particle diameter of the reference measurement is steady in the period of time, which clearly differs from the averaged particle diameter of the experiment. During the filling of the condensation cell, instant condensation occurs. The scattering on the high detectors increases significantly resulting in a distinctive peak downwards for measurement 1 (Figure 7.12), which is also noticed in the previous experiment. After the distinctive peak, fog formation occurs. At the high numbered detectors the light intensities increase, but in comparison with the low numbered detectors the increase has no effect on the averaged particle diameter. At a certain point hot gas enters into the cell to maintain the pressure, which causes severe density fluctuations. This results in a large increase in average particle diameter. Furthermore the fog is blown away, so at the high numbered detectors nothing is measured anymore. The dashed line in the Figure gives an indication of the particle diameter of the fog and the duration of the fog formation in the cell.

![Figure 7.12: Averaged particle diameter (dp50) of measurement 1 with reference measurement](image-url)
Figure 7.13: Averaged particle diameter (dp50) of measurement 2 with reference measurement

The average particle diameter curve of the second measurement is slightly different from the first one. The largest difference is that there is no significant downwards peak in the curve. Another difference is that the increase of average particle diameter occurs a few seconds earlier, which is the consequence of maintaining isobaric conditions. The averaged particle diameter of the fog is the same as in the previous measurement, but the duration of keeping the diameter is slightly less.
7. Spraytec fog formation experiments  

7.2. Spraytec fog formation experiment 2

Figure 7.14: Averaged particle diameter (dp50) of measurement 3 with reference measurement

In Figure 7.14 and Figure 7.15 the distinctive peak downwards is also not present. Furthermore, the period of fog formation gets smaller for each consecutive measurement, which is the consequence of maintaining isobaric conditions. Eventually, when the pressure is steady, no significant
fog volume is present anymore to be measured, so only density fluctuations are measured. The average particle diameter of every measurement goes to the same steady value around 400 µm, exactly like the reference measurement.

![Corrected light scattering at t=15 seconds](image)

**Figure 7.16:** Corrected light scattering at t=15 seconds for all measurement and reference measurement.

In Figure 7.16 the corrected light scattering on the individual detectors is shown at 15 seconds after increasing the pressure in the cell. At 15 seconds the averaged particle diameter in measurement 1 is much lower than the averaged particle diameter in the other measurements. The light scattering at detector number 1-5 is about 40-50% less for measurement 1 in comparison with measurements 2-4. The light scattering at detector number 10-15 is about 200-300% more for measurement 1 in comparison with measurements 2-4. However the light scattering at these detectors for measurement 2-4 is higher than the light scattering at these detectors of the reference measurement which are practically the same as the background intensity (100 µm). Relatively low intensities on low numbered detectors in combination with relatively high intensities on high numbered detectors results in a low particle diameter. So the distribution of light intensity over the detectors is different for measurement 1 in comparison with measurement 2-4. These light intensities are only caused by density fluctuations.

In Figure 7.17 the corrected light scattering, several seconds before the significant increase in dp50, for all measurements and reference measurements are shown. Density fluctuations cause most light scattering on the detectors 1-10, which are 10-20 % less than in the beginning of the measurements. In the figure on the right the corrected light scattering on detector numbers 10-20 is shown. The intensities are higher than the reference measurements, which are equal to the background intensity of 100. In this region fog is present in the condensation cell for all measurements. At detector number 19 a small peak is present which is caused by small scratches on the quartz cell window at the Spraytec laser side.
7. Spraytec fog formation experiments

7.2. Spraytec fog formation experiment 2

Figure 7.17: Corrected light scattering several seconds before significant increase in dp50 for all measurement and reference measurement

7.2.3 Conclusion experiment

A fog formation experiment with a 49.6-50.4 %CO₂-N₂ gas bottle was performed at a temperature of -50 °C and at a pressure of 40 bar. During the cooling of the condensation cell no ice formed on the cells windows or on the Spraytec windows. Four measurements were performed. Experiments pressure curves are similar to reference curve. The response time to reach a steady pressure is larger due to condensation in the cell. This is also noticed in the temperature curves. Hot gas enters the cell to maintain the desired pressure which reaches the temperature high in the cell. However the lower part cell temperature is significantly lower than the reference measurement due to liquid forming in the cell.

The obscurion is very high during the filling of the cell. After the filling of the cell, obscuration drops to a minimum of 10%. At that point the pressure drops in the cell and hot gas enters the cell to maintain the pressure. The obscuration increases to its steady value which is about 20% lower than the steady value of the reference measurement. For every consecutive measurement the region of very high obscuration becomes shorter due to the lower cell temperature for each consecutive measurement.

During the filling of the condensation cell fog formation occurs, because at the detector numbers higher than 14, light intensities are measured for about 80 seconds. For the consecutive measurements the fog formation time shortens to about 35 seconds. In the reference measurement no intensities at the detector number 14+ exceeded the Spraytec intensity limits. A distinctive downwards peak is noticed in the overall particle diameter of measurement 1, which is a result of a combination of less light scattering at detector numbers 1-8 and more light scattering at 9-15. Measurements 2 to 4 do not contain a peak, because the intensity distribution is more focussed to the detectors number 1-6. Detector numbers 16+ do not influence the overall particle diameter due to the low light intensities at these detectors, but these are very important for the fog measurement. After the peak hot gas enters the cell to maintain the pressure, which results in blowing away the fog to the walls. However a small part of the incoming gas condensates into fog. Just before the gas enters the cell, significant intensities are measured at detectors 10-20, which is fog. In the reference measurement no scattering is measured at these detectors. When the equilibrium is almost reached no light scattering is measured which exceeds the scattering intensity limits of the Spraytec.
7.3 Spraytec fog formation experiment 3

The results of fog formation experiment number 3 are described in this section.

7.3.1 Experiment approach

The premixed gas bottle used for this experiment is a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. The condensation cell is filled up to a pressure of 3 bar. The large chiller is set at −64°C in order to lower the cells temperature. Initially the impeller speed is set at position 6. When the condensation cell is at the desired temperature which is about −50°C the impeller speed is set at position 2. The pressure is set at 40 bar with the pressure reducer. The N₂ starting flow rate is set at 30LPM air. The heat element is set at 60°C. The composition of the gas is measured in this experiment. The total delay of the GC is determined by the totalizer positioned after the GC. After 7 minutes the experiment was stopped.

The measurement is repeated as many times as possible. In order to repeat the measurements the large chiller is set at −55°C to heat up the condensation cell after completing a measurement. The impeller speed is increased from position 2 to position 6. The cell is deflated in such a way that the cell lower part temperature is at all times higher than −55°C in order to prevent CO₂ ice forming in the cell. Deflating the cell causes a temperature drop in the cell due to the Joule Thomson effect. A low deflation flow rate in combination with a higher cell temperature prevents CO₂ ice forming in the cell. The most critical part of the deflation is when all gas is removed from the cell and the liquid is evaporating. The JT effect is at that moment the largest. When the cell is deflated the large chiller is set at −58°C and the impeller speed is set at position 2. The cell is flushed twice with a mixture of 5 bar.

7.3.2 Experiment results

This experiment contains 3 measurements in total. The laser intensity dropped to 66% during the deflating procedure after measurement 1. The N₂ gas flow was increased to 40LPM air. The laser intensity increased to 68% when the second measurement was started. In the beginning of measurement 3 the laser intensity was back at its original value of 72%. The gas composition is measured in measurement 1 and 3. The averaged leakage flow rate in measurement 1 had large fluctuations with a low mean. The leakage flow has to be set as high as possible to achieve a small delay.

Temperature and Pressure

In Figure 7.18 the upper cell temperature is shown into time for the experiment and a reference measurement with only N₂. The reference measurement is a combination of the background experiments results at impeller position 2. When the pressure is increased rapidly the temperature increases to a maximum value around −21°C. In Figure 7.19 the lower cell temperature is shown. The temperature of measurement 2 and 3 reaches eventually a lower temperature than the reference experiment due to the higher heat capacity of a liquid-gas phase mixture in comparison with a gas phase mixture at the same large chiller set point. All measurement temperature curves are identical to each other, but a small offset is present between the measurements due to the cooling of the cell, which is exactly like in the previous experiment (Section 7.2.2). The logging of the temperature data for measurement 2 and 3 started with a few seconds delay due to the processing time of Labview, which differs each time. Due to the delay the first process condition points are not logged.
7. Spraytec fog formation experiments

7.3. Spraytec fog formation experiment 3

In Figure 7.20 the pressure in the cell is shown into time for the measurements including a reference measurement with only N$_2$ for the first 100 seconds. The pressure increases very rapidly until the equilibrium pressure is reached. The experiment reaches its maximum pressure at little
bit later due to condensation and feeding of gas to the cell in order to maintain the pressure.

![Pressure curves in the condensation cell with reference measurement](image)

**Figure 7.20:** Pressure curves in the condensation cell with reference measurement

**Obscuration**

In Figure 7.21 the obscuration during the measurements is shown including a reference measurement with pure N₂. The obscuration curves are identical to the obscuration curves measured in the previous experiment (Section 7.2.2). The obscuration curves of the measurements have to same profile, but for every consecutive measurement the region of very high obscuration becomes shorter. This is caused by the lower cell temperature for each consecutive measurement. Condensation occurs more quickly and it reaches earlier its equilibrium position. The timeperiod for controlling the pressure in the cell by feeding hot gas to the cell becomes larger for consecutive measurements (low obscuration region). Eventually all obscuration curves have the same the slope and the same equilibrium value in the last part of the measurements.
7. Spraytec fog formation experiments  
7.3. Spraytec fog formation experiment 3

Figure 7.21: Obscuration curves in the condensation cell with reference measurement

**Light scattering and associated particle diameter**

The averaged particle diameter which is discussed in the following paragraphs is just an indication. The particle diameter is determined volume based, which is not yet validated. The averaged particle diameter of the reference measurement is steady in the period of time, which clearly differs from the averaged particle diameter of the experiment. During the filling of the condensation cell, instant condensation occurs. The scattering on the high detectors increases significantly resulting in a distinctive peak downwards for measurement 1 (Figure 7.22), which is also noticed in the previous experiments. After the distinctive peak fog formation occurs. At the high numbered detectors the light intensities increase, but in comparison with the low numbered detectors the increase has no effect on the averaged particle diameter. At a certain point hot gas enters the cell to maintain the pressure, which causes severe density fluctuations. This results in a large increase in average particle diameter. Furthermore the fog is blown to the walls, so at the high numbered detectors nothing is measured anymore. The dashed line in the Figure gives an indication of the particle diameter of the fog and the duration of the fog formation in the cell.

The average particle diameter curve of the second measurement is slightly different from the first one. The largest difference is that there is no significant downward peak in the curve. Another difference is that the increase of average particle diameter occurs a few seconds earlier, which is the consequence of maintaining isobaric conditions. The averaged particle diameter of the fog is the same as in the previous measurement, but the existence of the fog is slightly less. This measurement is exactly the same as the second measurement of the previous experiment (Section 7.2.2). The third measurement average particle diameter curve (Figure 7.23) is similar to the second measurement. The distinctive peak is also not present in the signal. The only difference is that the average particle diameter during the entering of hot gas to maintain isobaric conditions is about 100 µm lower. This is caused by the intensity distribution on the detectors. Near the end of measurement 3 ice forming on the windows occurred due to an empty purge bottle. Minor intensities were measured at high numbered detectors which is observed in the last 60 seconds of
7. Spraytec fog formation experiments

7.3. Spraytec fog formation experiment 3

Figure 7.22: Averaged particle diameter (dp50) of measurement 1 with reference measurement

Figure 7.23: Averaged particle diameter (dp50) of measurement 2 with reference measurement
Figure 7.24: Averaged particle diameter (dp50) of measurement 3 with reference measurement

In Figure 7.25 the corrected light scattering on the individual detectors is shown at 16 seconds after increasing the pressure in the cell. At 16 seconds the averaged particle diameter in measurement 1 is much lower than the averaged particle diameter in the other measurements. The light scattering at detector number 1-5 is about 30-40% less for measurement 1 in comparison with measurements 2 and 3. The light scattering at detector number 10-15 is the same for every measurement, but for the reference measurement the light scattering is almost zero. The density fluctuations caused less scattering in measurement 1 than in measurement 2 and 3. At this point of time no significant volume of fog is present in the cell because no significant scattering is measured at detector numbers 14+.
Figure 7.25: Corrected light scattering at t=16 seconds for all measurements and reference measurement

Figure 7.26: Corrected light scattering several seconds before significant increase in dp50 for all measurement and reference measurement

In Figure 7.26 the corrected light scattering several seconds before significant increase in dp50 for all measurement and reference measurement are shown. No significant intensities are measured at the detector numbers 25+ throughout the experiment, therefore these detectors are neglected. Density fluctuations cause most light scattering on the detectors 1-10, which are 10-20 % less than in the beginning of the measurements. In the figure on the right the corrected light scattering on the detector numbers 10-25 is shown. The intensities are higher than in the reference measurements, which are equal to the background intensity of 100. The intensities measured in measurement 2 are larger than the intensities measured in measurement 1 and 3, which indicates that more fog is
formed during this measurement. In all measurements fog was formed. At detector number 19 a small peak is present which is caused by small scratches on the quartz cell window at the Spraytec laser side.

Gas composition
In Figure 7.27 the CO$_2$ concentration in the gas phase is shown during the measurement. In measurement 2 the GC did not start because there was not a steady column temperature. In measurement 1 the leakage flow rate was 60Ncc/min CH$_4$ which is equal to about 0.03LPM 70-30 %CO$_2$-N$_2$. The CO$_2$ concentration dropped only 3% which is not in accordance with the phase calculation modeling, which states that at these process conditions the CO$_2$ concentration is about 20%. The flow rate in the sample line was too low to measure non equilibrium gas compositions. The flow rate in measurement 3 was set at a maximum leakage flow of about 300Ncc/minCH$_4$ which is equal to about 0.15LPM 70-30 %CO$_2$-N$_2$. The initial concentration in the sample line is affected by the impurities left by the previous measurements. A steep drop in CO$_2$ concentration is detected. This is caused by condensation of CO$_2$ in the cell. After 600 seconds the condensation in the cell is near its equilibrium. In this short period the equilibrium position will not reach, because the gas phase contains fog which is highly concentrated CO$_2$ that results in a slightly higher CO$_2$ concentration in the sample line.

![Figure 7.27: CO2 mole concentration in gas during measurement](image)

7.3.3 Conclusion experiment
A fog formation experiment with a 49.6-50.4 %CO$_2$-N$_2$ gas bottle is performed at a temperature of −50 °C and at a pressure of 40 bar. During cooling of the condensation cell no ice formed on the cells windows or on the Spraytec windows. Three measurements were performed. Experiments pressure curves are similar to reference curve. The response time to reach a steady pressure is larger due to condensation in the cell. This is also noted in the temperature curves. For measurement 2 and 3 the first seconds of the process conditions are not logged due to a delay in the start
up procedure of Labview.

The obscuration curves are identical to each other. First, a significant rise in obscuration is noticed due to the filling of the cell. Second after the filling of the cell, an obscuration drop is present in which fog is formed. Third, a low region of obscuration is established which is the starting point for maintaining isobaric conditions by adding hot gas to the condensation cell. At last, the obscuration rises to a steady value which is the equilibrium position for these process conditions. The obscuration curves differ a lot from the reference measurement. For every consecutive measurement the region of very high obscuration becomes shorter due to the lower cell temperature for each consecutive measurement.

During the filling of the condensation cell fog formation occurs, because at the detector numbers higher than 14, light intensities are measured for about 80 seconds. For the consecutive measurements the fog formation time shortens to about 35 seconds. In the reference measurement no intensities at the detector number 14+ exceeded the Spraytec intensity limits. A distinctive downwards peak is noticed in the overall particle diameter of measurement 1, which is a result of a combination of less light scattering at detector numbers 1-8 and more light scattering at 9-15. Measurements 2 to 4 do not contain a peak, because the intensity distribution is more focussed to the detectors number 1-6. Detector numbers 16+ do not influence the overall particle diameter due to the low light intensities at these detectors, but these are very important for the fog measurement. After the peak hot gas enters the cell to maintain the pressure, which results in blowing away the fog to the walls. However a small part of the incoming gas condensates into fog. Just before the gas enters the cell, significant intensities are measured at detectors 10-25, which is fog. Especially in measurement 2 the intensities were quite high which indicates (in comparison with other measurement) a large volume of fog. In the reference measurement no scattering was measured at these detectors. When the equilibrium was almost reached no light scattering was measured which exceeded the scattering intensity limits of the Spraytec.

The gas composition is measured for measurements 1 and 3. In measurement 2 the GC did not start because there was not a steady column temperature. In measurement 2, the CO₂ concentration in the sample line did not drop, because the leakage flow was too low. The leakage flow rate in measurement 3 was set at a maximum which resulted in a delay of 105 seconds in the sample line. The CO₂ concentration drops very fast in the beginning due to the condensation. In the end the CO₂ concentration is almost steady, which means that the equilibrium position is reached. Fog can be present in the sample line, which will increase the CO₂ concentration in the gas.

### 7.4 Spraytec fog formation experiment 4

The results of fog formation experiment number 4 are described in this section.

#### 7.4.1 Experiment approach

The premixed gas bottle used for this experiment was a 49.6-50.4 %CO₂-N₂ mixture with an accuracy of ±2%. The condensation cell is filled up to a pressure of 3 bar. The large chiller is set at −64°C in order to lower the cells temperature. Initially the impeller speed is set at position 6. When the condensation cell is at the desired temperature which is about −50°C, the impeller speed is set at position 2. The pressure was set at 40 bar with the pressure reducer. The N₂ starting flow rate was set at 30 LPM air. The heat element was set at 60°C. The composition of the gas was measured in this experiment. The total delay of the GC is determined by the totalizer positioned after the GC. After 7 minutes the experiment was stopped.

The measurement is repeated as many times as possible. In order to repeat the measurements the large chiller is set at −55°C to heat up the condensation cell after completing a measurement.
The impeller speed is increased from position 2 to position 6. The cell is deflated in such a way that the cell lower part temperature is at all times higher than $-55^\circ C$ in order to prevent CO$_2$ ice forming in the cell. Deflating the cell causes a temperature drop in the cell due to the Joule Thomson effect. A low deflation flow rate in combination with a higher cell temperature prevents CO$_2$ ice forming in the cell. The most critical part of the deflation is when all gas is removed from the cell and the liquid is evaporating. The JT effect is at that moment the largest. When the cell is deflated the large chiller is set at $-58^\circ C$ and the impeller speed is set at position 2. The cell is flushed twice with a mixture of 5 bar.

### 7.4.2 Experiment results

This experiment contains of 4 measurements in total. During the whole experiment the laser intensity remained steady around a value of 72%, so no problems occurred.

Temperature and Pressure

![Graph showing temperature curves](image)

In Figure 7.28 the upper cell temperature is shown into time for the experiment and a reference measurement with only N$_2$. The reference measurement is a combination of the background experiments results at impeller position 2. When the pressure is increased rapidly the temperature increases to a maximum value around $-23^\circ C$. In Figure 7.29 the lower cell temperature is shown. The temperature of measurement 2 and 3 reaches eventually a lower temperature than the reference experiment due to the higher heat capacity of a liquid-gas phase mixture in comparison with a gas phase mixture at the same large chiller set point. All measurement temperature curves are identical to each other, but a small offset is present between the measurements due to the cooling of the cell, which is exactly like in the previous experiment (Section 7.2.2). The logging of the temperature data for measurement 2 and 3 started with a few seconds delay due to the processing time of Labview, which differs each time. Due to the delay the first process condition points are
Figure 7.29: Lower cell temperature curves in the condensation cell with reference measurement not logged.

Figure 7.30: Pressure curves in the condensation cell with reference measurement
In Figure 7.30 the pressure in the cell is shown into time for the measurements including a reference measurement with only N\textsubscript{2} for the first 50 seconds. The pressure increases very rapidly until the equilibrium pressure is reached. The experiment reaches its maximum pressure at little bit later due to condensation and feeding of gas to the cell in order to maintain the pressure.

**Obscuration**

In Figure 7.31 the obscuration during the measurements is shown including a reference measurement with pure N\textsubscript{2}. The obscuration curves are identical to the obscuration curves measured in the previous experiment (Section 7.2.2). The obscuration curves of the measurements have to same profile, but for every consecutive measurement the region of very high obscuration becomes shorter. This is caused by the lower cell temperature for each consecutive measurement. Condensation occurs more quickly and it reaches earlier its equilibrium position. The timeperiod for controlling the pressure in the cell by feeding hot gas to the cell becomes larger for consecutive measurements (low obscuration region). Eventually all obscuration curves have the same the slope and the same equilibrium value in the last part of the measurements.

![Figure 7.31: Obscuration curves in the condensation cell with reference measurement](image)

**Light scattering and associated particle diameter**

The averaged particle diameter which is discussed in the following paragraphs is just an indication. The particle diameter is determined volume based, which is not yet validated. The averaged particle diameter of the reference measurement is steady in the period of time, which clearly differs from the averaged particle diameter of the experiment. During the filling of the condensation cell, instant condensation occurs. The scattering on the high detectors increases significantly resulting in a distinctive peak downwards for measurement 1 (Figure 7.32), which is also noticed in the previous experiments. After the distinctive peak fog formation occurs. At the high numbered detectors the light intensities increase, but in comparison with the low numbered detectors the
increase has no effect on the averaged particle diameter. At a certain point hot gas enters the cell to maintain the pressure, which causes severe density fluctuations. This results in a large increase in average particle diameter. Furthermore the fog is blown to the walls, so at the high numbered detectors nothing is measured anymore. The dashed line in the Figure gives an indication of the particle diameter of the fog and the duration of the fog formation in the cell.

The average particle diameter curve of the second measurement is identical to the first one. The downward peak is present in the curve. The only difference is the time when hot gas enters the cell to maintain the isobaric conditions (high dp50). For the first measurement it is 70 seconds and the seconds measurement it is 60 seconds. The averaged particle diameter of the fog is the same as in the previous measurement, but the duration is slightly less. The average particle diameter curve of the third measurement (Figure 7.33) is identical to the second measurement of the previous experiments (Section 7.2.2). The distinctive peak is not present in the signal. The increase of average particle diameter occurs a few seconds earlier, which is the consequence of maintaining isobaric conditions. The averaged particle diameter of the fog is the same as in the previous measurement, but the existence of the fog is slightly less. Near the end of the measurement ice forming on the cells windows occurred. The N2 purge flow rate was set at 35LPM air. After 5 minutes the laser intensity was 71.8%.

![Graph](image)

Figure 7.32: Averaged particle diameter (dp50) of measurement 1 with reference measurement
7. Spraytec fog formation experiments

The average particle diameter curve of the fourth measurement (Figure 7.34) is identical to the previous. The distinctive peak is not present in the signal. The increase of the average particle diameter occurs a few seconds earlier, which is the consequence of maintaining isobaric conditions.
7. Spraytec fog formation experiments 7.4. Spraytec fog formation experiment 4

The averaged particle diameter of the fog is the same as in the previous measurement, but the duration is slightly less. In the first 20 seconds the averaged particle diameter with only detectors 14-36 has a lower average with large fluctuations in comparison with the reasonably steady particle diameter in the first two measurements.

![Diagram](image)

Figure 7.35: Averaged particle diameter (dp50) of measurement 4 with reference measurement

In Figure 7.36 the corrected light scattering on the individual detectors is shown at 17 seconds after increasing the pressure in the cell. At 17 seconds the averaged particle diameter in measurement 1 and 2 is much lower than the averaged particle diameter in the other measurements. The light scattering at detector numbers 1-5 is about 30-40% less for measurement 1 in comparison with measurements 2 and 3. The light scattering at detector numbers 10-15 is about 200-300% more for measurement 1 and 2 in comparison with measurements 3 and 4, but for the reference measurement the light scattering is almost zero. The density fluctuations caused less scattering in measurement 1 than in measurement 2 and 3. At this point of time no significant volume of fog is present in the cell because no significant scattering is measured at detector number 14+.

In Figure 7.37 the corrected light scattering several seconds before significant increase in dp50 for all measurement and reference measurement are shown. No significant intensities are measured at the detector numbers 25+ throughout the experiment, therefore these detectors are neglected. Density fluctuations cause most light scattering on the detectors 1-10, which are 10-30 % less than in the beginning of the measurements. In the figure on the right the corrected light scattering on the detector numbers 15-25 is shown. The intensities are quite higher than the reference measurements, which is equal to the background intensity of 100. The intensities measured in measurement 4 are larger than the intensities measured in measurement 1,2 and 3, which indicates that more fog is formed during this measurement. For all measurements fog was formed. At detector number 19 a small peak is present which is caused by small scratches on the quartz cell window at the Spraytec laser side.
Figure 7.36: Corrected light scattering at t=17 seconds for all measurement and reference measurement

Figure 7.37: Corrected light scattering several seconds before significant increase in dp50 for all measurement and reference measurement

Gas composition
In Figure 7.38 the CO₂ concentration in the gas phase is shown during the measurement. The flow rate in all measurements was set at a maximum leakage flow of about 0.4LPM 70-30 %CO₂-N₂. The initial concentration in the sample line is affected by the impurities left by the previous measurements. A steep drop in CO₂ concentration is observed due to the condensation of CO₂ in the cell. After 450 seconds the condensation cell is near its equilibrium. In this short period the equilibrium position will not be reached, because the gas phase contains fog which is highly concentrated CO₂ that results in a slightly higher CO₂ concentration in the sample line.
7.4.3 Conclusion experiment

A fog formation experiment with a 49.6-50.4 %CO$_2$-N$_2$ gas bottle was performed at a temperature of $-50^\circ$C and at a pressure of 40 bar. During cooling of the condensation cell no ice formed on the cells windows or on the Spraytec windows. Four measurements were performed. Experiments pressure curves were near identical to reference curve. The response time to reach a steady pressure is larger due to condensation in the cell. This was also noted in the temperature curves. For measurement 1 the first seconds were not logged due to a delay in the start up procedure of Labview.

The obscuration curves are identical to each other. First, a significant rise in obscuration is noticed due to the filling of the cell. Second after the filling of the cell, an obscuration drop is present in which fog is formed. Third, a low region of obscuration is established which is the starting point for maintaining isobaric conditions by adding hot gas to the condensation cell. At last, the obscuration rises to a steady value which is the equilibrium position for these process conditions. The obscuration curves differ a lot from the reference measurement. For every consecutive measurement the region of very high obscuration becomes shorter due to the lower cell temperature for each consecutive measurement.

During the filling of the condensation cell fog formation occurs, because at the detector numbers higher than 14, light intensities are measured for about 80 seconds. For the consecutive measurements the fog formation time shortens to about 35 seconds. In the reference measurement no intensities at the detector number 14+ exceeded the Spraytec intensity limits. A distinctive downwards peak is noticed in the overall particle diameter of measurement 1 and 2, which is a result of a combination of less light scattering at detector numbers 1-8 and more light scattering at 10-15. Measurements 3 and 4 do not contain a peak, because the intensity distribution is more focussed to the detector numbers 1-6. Detector numbers 16+ do not influence the overall particle diameter due to the low light intensities at these detectors, but these are very important for the
fog measurement. After the peak hot gas enters the cell to maintain the pressure, which results in blowing away the fog to the walls. However a small part of the incoming gas condensates into fog. Just before the gas enters the cell, significant intensities are measured at detectors 10-25, which is fog. Especially in measurement 4 the intensities were high which indicates (in comparison with other measurement) a large volume of fog. In the reference measurement no scattering was measured at these detectors. When the equilibrium was almost reached no light scattering was measured which exceeded the scattering intensity limits of the Spraytec.

The leakage flow rate in measurement 3 was set at a maximum which resulted in a mean delay of 55 seconds in the sample line. The CO₂ concentration drops very fast in the beginning due to the condensation. Finally, the CO₂ concentration becomes almost steady which means that the equilibrium position is reached. In the sample line fog can be present which will increase the CO₂ concentration in the gas. All CO₂ concentration curves are in accordance with each other.

7.5 Summary Spraytec fog formation

In this chapter the Spraytec fog formation experiments were discussed. 49.6-50.4 %CO₂-N₂ mixture was fed to the condensation cell under a pressure of 40 bar and a cell temperature of -50°C at primarily impeller speed 2. During the filling of the condensation cell condensation (fog formation and film formation) in combination with density fluctuations will cause scattering on the Spraytec laser. The scattering was measured with the Spraytec detector. Fog formation can be deduced from the scattering intensity distribution in combination with the pressure, the temperature and the obscuration curves. Four experiments were conducted with in total 12 measurements, in which during five measurements the CO₂ concentration in the gas was successfully measured.

All measurement results were compared to a reference measurement with only N₂. The pressure increased very rapidly until the equilibrium pressure is reached. The experiment reached its maximum pressure at little bit later due to the condensation and feeding extra gas to maintain the pressure. The pressures set with the pressure reducer were not identical, because of the inaccurate settings of the pressure reducer. For some measurements the first seconds of the pressure and temperature curves were not logged due to a delay in the start up procedure of Labview. The upper cell temperature increased to a maximum value around -22°C. The incoming gas was cooled down rapidly by the environment. Instant condensation occurred when the pressure was increased. The CO₂ liquid dropped to the cells floor and absorbs more environmental heat, which resulted in a significant lower part temperature in comparison with the reference measurement. The CO₂-N₂ mixture cooled down more slowly than pure N₂ gas, because of the condensation of CO₂ in the cell. When condensation occurred the pressure drops in the cell and more hot gas entered the condensation cell to maintain the pressure of 40 bar. When the equilibrium was almost reached the temperatures of the experiment and the reference measurement were almost equal. The experiment temperature reached eventually a lower temperature than the reference experiment due to the higher heat capacity of a liquid-gas phase mixture in comparison with a gas phase mixture at the same large chiller set point.

The obscuration rised very rapidly due to the gas volume entering the cell. Condensation occurred and the obscuration dropped slowly in comparison with the reference measurement to a very low obscuration of about 10%. At this moment the pressure reducer was letting in extra hot gas into the cell to maintain the desired pressure. The obscuration rose until an equilibrium value was reached, which was about 20% lower than the steady obscuration value of the reference measurement. The obscuration profile of a single gas phase mixture differed a lot with the obscuration profile of a liquid-gas phase mixture. The obscuration curves of the measurements had to same profile, but for every consecutive measurement the region of very high obscuration became shorter. This was caused by the lower cell temperature for each consecutive measurement. Condensation occurred more quickly and it reached earlier its equilibrium position. The region for controlling the
pressure in the cell by feeding hot gas to the cell became larger for consecutive measurements (low obscuration region). Eventually all obscuration curves had to the same the slope and equilibrium value in the last part of the measurements.

The averaged particle diameter is just an indication. The particle diameter is determined volume based, which is not yet validated. During the filling of the condensation cell, instant condensation occurred in the first 20 seconds. Due to density fluctuations and fog formation scattering intensities were measured on the detectors. Throughout the whole measurement the density fluctuations were more pronounced in the averaged particle diameter than the fog formation due to higher scattering intensities of the density fluctuations. In the first 20 seconds no fog was formed due to the high cell temperature and the inlet temperature. The scattering measured was purely density fluctuations of the filling. Its intensity distribution differed for each measurement. When high intensities were measured at detector numbers 10-15 then a significant downward peak was present in the averaged particle diameter. This was noticed in every first measurement of each experiment. For each consecutive measurement after the first measurement in one experiment high intensities were measured at detector numbers 1-10 instead of detector numbers 10-15, which prevented the peak in the signal. Moreover the time until hot gas entered the cell to maintain isobaric conditions reduced for every consecutive measurement in a single experiment due to a lower cell temperature. Especially the walls were colder due to the Joule Thomson effect by the deflation of the condensation cell. This point of time gave an indication of the particle diameter of the fog and the duration of the fog formation in the cell. Clear intensities were measured at detector number 14-25 which are associated with fog scattering. After this point of time the hot gas that entered the cell blew the fog to the walls, so no fog was present anymore. Finally the cell reached its equilibrium position and the averaged particle diameter was the same as the reference measurement. In every measurement fog formation occurred, however the amount of fog is very small, which is deduced from the intensity ratio between detector numbers 1-13 intensities and the detector numbers 13-25.

The CO₂ concentration in the gas was measured by the gas chromatograph during the measurement. The GCs delay was determined with the totalizer which is positioned after the GC. The leakage flow had to be set at a maximum to diminish the delay. The initial concentration in the sample line was affected by the impurities left by the previous measurements. A steep drop in CO₂ concentration was present due to the condensation of CO₂ in the cell. After some time the cell reached its equilibrium and the change over time in CO₂ concentration went to zero. In the short runtime of the measurement the equilibrium position will not be reached due to that the gas phase contains fog. The fog is highly concentrated CO₂ that results in a slightly higher CO₂ concentration in the sample line.
Chapter 8

Fog formation camera experiments

In this chapter the fog formation camera experiments will be discussed. The condensation cell is cooled down to a temperature of \(-50^\circ C\) with a 50-50% CO\(_2\)-N\(_2\) mixture or with pure N\(_2\) gas at a low pressure around 2 bar. When the desired temperature is reached the pressure is rapidly increased to 40 bar, which results in a high supersaturation thus fog formation. These experiments are the same as the previous experiments but the Spraytec laser system is replaced by a laserpointer and a ccd camera.

The laserpointer is just a simple green laser pen with an intensity of 5mW. The laser is positioned in such a way that the laser beam enters high from a high level through the cell window and that it is pointed to the left below the second cell window. At first a JAI camera was used for the recording of the fog. However the JAI camera is a black and white camera that could not record the laser and its background light. Moreover, the focus of the lens system was too narrow for the amount of volume that had to be filmed. Eventually, the ccd camera was replaced by a 12 megapixel household photo camera. The cell windows still have to be purged and only the camera side have to be purge with hot N\(_2\). The supply lines of the hot N\(_2\) are connected to the isolation cap of the camera side.

Two experiments with each two measurements are performed. In the first experiment 50-50% CO\(_2\)-N\(_2\) mixture is used to create fog formation. Also fog formation by expansion is measured. In the second experiment pure N\(_2\) gas is fed to the condensation cell to obtain a reference measurement for the condensation movies. The measurement procedure described in Chapter 3 is used with the adjustments described in subsection 6.3.1.

8.1 Fog formation camera experiment 1

The results of camera fog formation experiment number 1 are described in this section.

8.1.1 Experiment approach

The premixed gas bottle used for this experiment is a 49.6-50.4% CO\(_2\)-N\(_2\) mixture with an accuracy of \(\pm 2\%\). The condensation cell is filled up to a pressure of 3 bar. The large chiller is set at \(-64^\circ C\) in order to lower the cells temperature. Initially the impeller speed is set at position 6. When the condensation cell is at the desired temperature which is about \(-50^\circ C\), the impeller speed is set at position 2. The pressure is set at 40 bar by the pressure reducer. The N\(_2\) starting flow rate is set at 30LPM air. The heat element is set at 60\(^\circ\)C. The composition of the gas was not measured in this experiment. Two measurements were performed. After the second measurement fog was created by expansion for three short moments, in which the temperature and pressure were not logged.
8. Fog formation camera experiments  

8.1. Fog formation camera experiment 1

8.1.2 Experiment results
During the whole experiment no ice formed on the cells windows. In Figure 8.1 the pressure in the cell is shown into time for the experiment. The pressure increases very rapidly until the equilibrium pressure is reached. The experiment reaches its maximum pressure at little bit later due to the condensation and the feeding of extra gas to maintain the pressure in comparison with an experiment with pure N\textsubscript{2} gas.

![Pressure curve](image)

Figure 8.1: Pressure curves in the condensation cell

In Figure 8.2 the temperature in the upper cell is shown into time. The temperature rises rapidly to a maximum of $-22^\circ$C. The incoming gas is cooled rapidly by the environment until it reaches its equilibrium condition. In Figure 8.3 the temperature in the lower cell is shown into time. The temperature peak is much lower than the temperature peak in the upper part due to instant condensation in the cell. The liquid CO\textsubscript{2} drops to the bottom and the liquid keeps the lower part of the cell at a low temperature. The temperature curves are identical to the temperature curves of the previous experiments.
8. Fog formation camera experiments

8.1. Fog formation camera experiment 1

Camera snapshot measurement 1

Before starting the measurement a reference movie is recorded at a pressure of 2 bar. The laser is pointed left downwards into the cell. On the windows two green laserdots are noticed. No
laserbeam can be seen. The laser intensity gives a clear background light in the cell which is shown in Figure 8.4.

![Figure 8.4: Reference snap shot movie at p=2 bar and T=−50°C of measurement 1](image)

In Figure 8.5 the situation at 30 seconds after the filling of the cell is shown. When the pressure is rapidly increased in the cell, instant condensation occurs. At the left side of the window CO$_2$ liquid in a film is present. Due to density fluctuations and fog formation the background intensity from the cell reduces, which is exactly the obscuration increase in the Spraytec experiment. A clear laser beam is noticed in the cell. In this laser beam particles are moving through the beam which cause scattering of the laser beam. Small high light bursts in the laser beam are noticed in the first 100 seconds of the movie. Near the end of the movie (Figure 8.6) the background intensity increases and the overall laser beam intensity drops a little, but it is still present. The film condensation on the windows is gone. During this measurement fog is formed, but in a small volume. In comparison with the reference movie a laser beam was visible and the background light in the cell is lower, indicating a higher obscuration.

![Figure 8.5: Snap shot movie t=30 seconds at p=40 bar of measurement 1](image)
8. Fog formation camera experiments  

8.1. Fog formation camera experiment 1

Figure 8.6: Snap shot movie t=300 seconds at p=40 bar of measurement 1

Camera snapshot measurement 2

The measurement procedure is repeated and again a reference measurement is done. The reference measurement is identical to the previous one. The laser beam is not visible in the cell. In Figure 8.7 the situation at 15 seconds after the filling of the cell is shown. The pressure is increased very rapidly in the cell and film and fog formation occur. The film formation happens at the wall and partly at the inside of the cells windows. A small liquid CO₂ volume at the bottom of the cells windows can be clearly seen in the snapshot. The laser beam becomes visible and it is being scattered by fog particles and droplet falling from the cells ceiling. The scattering intensity of falling droplets is much higher than the scattering intensity of the fog particles. Furthermore, the background intensity drops in the beginning of the measurement. After 100 seconds the background intensity steadily increases to its reference state (reference measurement). The laser beam intensity slightly drops, but it is still visible due to density fluctuations. Eventually the liquid CO₂ dropped to the bottom of the cell and only density fluctuations were present. In this measurement fog was formed, which was only a small volume.
8. Fog formation camera experiments

8.1. Fog formation camera experiment 1

Camera snapshot expansion

Immediately after the execution of measurement 2 fog formation by expansion is performed three times. The starting pressure is about 40 bar. Three times the cell is deflated rapidly for about 5 seconds, which is about 5 bar reduction in pressure every time. Instant fog is formed. In Figure 8.9 and Figure 8.10 the intensity of the laser beam is very bright. A large amount of fog is produced and it causes high laser beam scattering. In the third expansion so much fog is created that the scattering intensities are immens, which is shown in Figure 8.11.
8. Fog formation camera experiments  

8.1. Fog formation camera experiment 1

Figure 8.9: Snap shot movie fog formation by expansion number 1

Figure 8.10: Snap shot movie fog formation by expansion number 2

Figure 8.11: Snap shot movie fog formation by expansion number 3

8.1.3 Conclusion experiment

A fog formation experiment with a 49.6-50.4 %CO₂-N₂ gas bottle was performed at a temperature of −50°C and at a pressure of 40 bar. The condensation process was recorded with a 12 megapixel camera. The experiment contains two measurements, which both have a runtime of 6 minutes. For each measurement a reference movie was produced. In general the background
intensity drops, which indicates that the obscuration increases. Instant condensation occurs in the form of film and fog formation. On the windows a clear liquid CO_2 film is noticed in the beginning of each measurement. The laser beam becomes visible due to scattering of the laser beam by fog particles. The intensity is quite low. When a CO_2 droplet falls from the ceiling which causes a high scattering intensity. Near the end of the measurement the background intensity increases and the film formation on the windows disappear. The remaining CO_2 liquid on the window flows to the bottom of the cell. The laser beam intensity drops a little but it is still visible due to density fluctuations in the cell. Fog is formed in both measurements but in a small unsteady volume.

Immediately after the execution of the second measurement fog formation by expansion was performed three times. About a 5 bar of pressure was released from the cell rapidly, which resulted in instant fog formation. A large volume of fog was formed in comparison with fog formation by rapid cooling. The large volume of fog scattered the laser beam enormously, which caused severe light intensities. Especially at attempt number three massive light intensities were observed.

8.2 Fog formation camera experiment 2

The results of camera fog formation experiment number 2 are described in this section.

8.2.1 Experiment approach

The premixed gas bottle used for this experiment is a N_2 gas. The condensation cell is filled up to a pressure of 3 bar. The large chiller is set at -64°C in order to lower the cells temperature. Initially the impeller speed is set at position 6. When the condensation cell is at the desired temperature which is about -50°C, the impeller speed is set at position 2. The pressure is set at 40 bar by the pressure reducer. The N_2 starting flow rate is set at 30LPM air. The heat element is set at 60°C. The composition of the gas is not measured in this experiment.

8.2.2 Experiment results

During the whole experiment no ice formed on the cells windows. In Figure 8.12 the pressure in the cell is shown into time for the experiment. The pressure increases very rapidly until the equilibrium pressure is reached. The experiment reaches its maximum pressure at little bit faster, because no condensation occurs in the cell.
8. Fog formation camera experiments  

8.2. Fog formation camera experiment 2

In Figure 8.14 the temperature in the upper cell is shown into time. The temperature rapidly rises to a maximum of \(-22^\circ\text{C}\). The incoming gas is cooled rapidly by the environment until it reaches its equilibrium condition. In Figure 8.15 the temperature in the lower cell is shown as function of
8. Fog formation camera experiments  

8.2. Fog formation camera experiment 2

time. The temperature peak is slightly lower than the temperature peak in the upper part. The temperature and pressure in the cell reaches much faster its equilibrium conditions when N₂ gas is fed to the cell instead of the CO₂-N₂ mixture, because no condensation occurs in the cell.

![Figure 8.14: Lower cell temperature curves in the condensation cell](image)

Camera snapshot measurement 1

Before starting the measurement a reference movie is recorded at a pressure of 2 bar. The laser is pointed left downwards into the cell. On the windows two green laserdots are noticed. No laser beam can be seen. The laser intensity gives a clear background light in the cell which is shown in Figure 8.15.

In Figure 8.16 the situation at 15 seconds after the filling of the cell is shown. When the pressure is rapidly increased in the cell, the background intensity drops in the cell. Clear density fluctuations are visible in the cell, so also a very low intensity laser beam is visible. After just 20 seconds the background intensity rises to its original value. The laser beam remains visible throughout the whole measurement due to density fluctuations.
8. Fog formation camera experiments  

8.2. Fog formation camera experiment 2

Figure 8.15: Reference snapshot movie at p=2 bar and −50°C of measurement 1

Figure 8.16: Snapshot movie t=15 seconds at p=40 bar of measurement 1

Camera snapshot measurement 2

The measurement procedure is repeated and again a reference measurement is done. The laser intensity dropped due to low battery. The measurement is performed but no significant laser beam was noticed. The background intensity in the cell was too low for a measurement. This measurement is not suitable as a reference measurement.

8.2.3 Conclusion experiment

A fog formation experiment with a pure N₂ gas bottle is performed at a temperature of −50°C and at a pressure of 40 bar. The condensation process is recorded with a 12 megapixel camera. The experiment contains two measurement, which both have a runtime of 6 minutes. For each measurement a reference movie is produced. The laser intensity in measurement 2 dropped due to empty batteries. The background intensity in the cell was too low to observe the events in the condensation cell. The laser beam was throughout the whole measurement not visible. In
8. Fog formation camera experiments

The first measurement the laser intensity was high enough for a good measurement. The laser beam was visible throughout the measurement at a low intensity due to density fluctuations. In the beginning the background intensity dropped but after 20 seconds it rose back to its original value.

8.3 Summary fog formation camera

In this chapter the camera fog formation experiments were discussed. During these experiments the Spraytec laser system was replaced by a 12 megapixel camera. Two experiments with each two measurements were performed. For each measurement a reference movie was recorded at a pressure of 2-3 bar. In the first experiment a 49.6-50.4 %CO₂-N₂ mixture was fed to the condensation cell under a pressure of 40 bar and a cell temperature of −50 °C at impeller speed position 2. The events in the cell were recorded with the camera. In the initial seconds the background intensity dropped in the cell. After 100 seconds the background intensity rose to its original value. A CO₂ film was formed on the window and the CO₂ liquid dropped to the bottom. The laser beam became visible and small moderate scattering intensities were noticed in the beam by fog particles. After 100 seconds no scattering was noticed anymore in the laser beam, however the laser beam remained visible due to the density fluctuations. During this experiment in both measurements fog was formed, but in a small volume.

In the second experiment pure N₂ gas was fed to the condensation cell under a pressure of 40 bar and a cell temperature of −50 °C at impeller speed position 2. The events in the cell were recorded with the camera. In the initial seconds the background intensity dropped in the cell. After 30-50 seconds the background intensity rose to its original value, which was similar to the CO₂-N₂ experiment. The laser beam also became visible due to density fluctuations, but the intensity was less than in the CO₂-N₂ experiment. The laser intensity dropped because of empty batteries, so the background light in the second measurement was too low to make the event clearly visible.

After the 49.6-50.4 %CO₂-N₂ mixture experiment fog was created by expansion. About 5 bar of gas was rapidly released from the cell, which resulted in instant condensation. This was performed three times. The first two tries the scattering of the laser beam intensity was very high. A large amount of fog was created and it had been observed with the unaided eye. The third try the scattering of the laser beam intensity was enormous. The whole condensation cell was illuminated and a huge amount of fog was created. The fog volume created with rapid cooling is very small in comparison with the fog volume created by expansion.
Chapter 9

Fog formation by expansion experiment

In this chapter an experiment will be discussed wherein fog is formed by expansion. In the previous chapter it was stated that the volume of the fog formed by cooling was very small in comparison with the volume of the fog formed by cooling. Fog by expansion in the condensation cell is not measured with the Spraytec system. Therefore one experiment is performed in order to measure the scattering signals on the detectors when fog is formed by expansion.

9.1 Experiment approach

The condensation cell is cooled down to a temperature of $-50 \degree C$ with a 49.6-50.4\% CO$_2$-N$_2$ mixture. The starting pressure is about 3 bar. When the pressure is increased in the cell, the Spraytec will not pass the optical background analysis during the startup. This is caused by severe density fluctuations in the cell. When the optical background analysis is succeeded, the pressure is increased to about 42 bar. Thereupon fog is formed by cooling, which is identical to the experiments in the previous two chapters. Over a timeperiod the mixture reaches an equilibrium state, which is highly saturated. The cell is deflated for 5 short moments. In each moment the pressure drop is about 5 bar. During these moments fog is formed by expansion. The fog droplets scatters the laser beam, which is measured at the detectors.

The large chiller is set at $-60 \degree C$. The initial impeller speed is set at position 6, which is changed to position 2 when the actual fog formation experiment is started. The purge flow rate is set at 40 LPM air and the heat element in the purge system at 60\degree C. The process conditions were not logged and the compositions were not measured, because of during the expansion of gas the process conditions give no valuable information.

9.2 Experiments results

The Spraytec start up procedure failed several times due to an alignment error. The position of the Spraytec was adjusted multiple times. Eventually the start up procedure succeeded. The windows of the cell and Spraytec were clean. A laser intensity of 68\% was measured.

In Figure 9.1 the obscuration during the experiment is shown together with a Spraytec reference experiment (Section 7.4. The measured curve tendency is positioned below the curve of the reference measurement, which may be caused by a slightly higher impeller speed in combination with
a higher equilibrium pressure of 42 bar. The 5 peaks near the end in the signal is caused by the deflation of the cell. Fog is formed by expansion during these peaks.

In Figure 9.2 the averaged particle diameter is shown over the course of the experiment. The average particle diameter is an indication of the particle size, which is determined volume based. This is not yet validated. The tendency of the graph is not identical to the tendency of the reference graph. First the peak at circa 50 seconds is a consequence of density fluctuations, which scattering is measured at the low numbered (1-6) detectors. Thereupon the scattering is measured at the intermediate numbered detectors (7-13). In this area no fog is present anymore. The particle diameter increases due to entering hot gas for maintaining isobaric conditions. Thereupon the condensation cell reaches its equilibrium state.

The first expansion resulted in severe density fluctuations and so in an upwards peak. The duration of the expansion was 2 seconds. The consecutive expansions resulted in downward peaks. During the expansions scattering at the detector numbers 14+ are measured, which proves that fog droplets are formed.

In Figure 9.3 the corrected scattering at the detectors is shown. The red and blue lines represent fog formation by cooling. The green and magenta lines represent fog formation by expansion during the first 2 deflations. As discussed in the previous chapters, the first 14 detectors measures primarily density fluctuations. The scattering intensities of the fog particles are measured with the detector numbers 15+. The scattering intensities of the fog droplets are very small in comparison with the scattering intensities of the density fluctuations for fog formation by cooling and for fog formation by expansion.

In the close up of Figure 9.3 the intensities on the detectors associated with fog droplets are shown. The intensities of fog formed by expansion are 2-3 times higher than the intensities of fog formed by cooling. Moreover, the intensity distribution of fog formed by expansion is significant up to
detector number 25. The intensity distribution of fog formed by cooling reaches up to detector number 20. Therefore, the volume of fog created by expansion is larger than the volume of fog created by cooling. This is also observed during the camera experiments in the previous chapter.

9.3 Conclusion experiment

In this experiment fog was formed by expansion with a 49.6-50.4% CO₂-N₂ gas bottle at a temperature of −50 °C. In the start of the experiment the Spraytec gave multiple alignment errors, which was solved by repositioning the Spraytec. The scattering intensities of the density fluctuations
were much larger than the scattering intensities of the fog droplets. The measured intensities of fog formation by expansion was about 2-3 times higher than the measured intensities of fog formation by cooling. Moreover, the intensity distribution over the detectors was much larger for fog formation by expansion. This is in accordance with the results of the previous chapter, wherein it is stated that the fog volume formed by expansion is much larger than the fog volume formed by cooling.
Chapter 10

Conclusion fog formation experiments

In this part the fog formation experiments are discussed. Fog formation occurs when a mixture of CO₂ and N₂ is cooled rapidly to create a non-equilibrium state which differs greatly from the actual equilibrium state at these process conditions. The process conditions are a pressure of 40 bar and a cell temperature of −50 °C at primarily impeller speed position 2.

In order to get the fog formation in the condensation cell, the measurement set up and measurement procedure had to be optimized to diminish side effects like freezing of the cells glasses. Two initial fog formation experiments were done to optimize the measurement procedure. In both experiments water froze on the cells windows at the moment when the windows protectors were removed and the Spraytec was positioned near the cell. It was decided to go on with the background experiment with only N₂ gas. First, the protectors were replaced by insulation caps that isolated the area between the Spraytec and the cell. The Spraytec had to be purged in order to prevent ice forming on the Spraytec windows. The Spraytec is used during the whole experiment to measure the amount of ice forming which is related to the laser intensity. The laser intensity is about 72%. When the laser intensity dropped, ice formed on the windows. The N₂ flow rate proved to be the key to prevent the ice forming. Eventually a calibrated rotameter with the right scale was placed in the purge system. A N₂ flow rate of 30 LPM air is enough to maintain clean windows throughout the experiments. Furthermore, an open heat coil element was placed in the purge in order to heat up the purge to the Spraytec windows.

In the background analysis the main goal was to get an insight in the obscuration and averaged particle diameter with the corresponding scattering distribution at three different impeller speeds, which determines the mass and heat transfer in the cell. The impeller speed position 2 is the most important because during the fog formation experiments the mass transfer should be low in order to prevent the fog from moving to the walls. The obscuration is about 55-70% stationary. The scattering intensities are a consequence of density fluctuations in the cell. The averaged particle diameter is about 400 µm, which corrected scattering distribution on the detectors is more focussed at the detector numbers 1-10. When only detector numbers 14+ are observed no information is obtained. The scattering at these detectors is below the Spraytec measuring limit. These intensities are in the same order than the background light intensity.

The fog formation experiments with a 49.6-50.4 %CO₂-N₂ mixture are 12 times performed. Large scattering intensities on the low numbered detectors are measured which are in fact density fluctuations. Moderate scattering intensities are measured at detector numbers 14+ which are fog particles. These intensities were not measured during the background experiments. In every measurement fog formation occurred, however the amount of fog is very small, which is deduced from
10. Conclusion fog formation experiments

the intensity ratio between the detector number 1-13 intensities and the detector number 14-25. The duration of the fog shortened for each consecutive measurement in one experiment due to a lower cell temperature and maintaining isobaric conditions.

The Spraytec system is replaced by a 12 megapixel camera and a green laser pen. During the filling of the condensation cell instant film and fog formation occurred. The background intensity dropped and the laser beam became visible. In the laser beam moderate scattering intensities were observed which were fog particles. Near the end of the measurement the background intensity increased to its original value and the laser beam remained visible due to density fluctuations. When fog was created by expansion high scatter intensities were observed and the fog was observed with the unaided eye. The fog volume created with rapid cooling is very small in comparison with the fog volume created by expansion.

This statement is verified with an experiment wherein fog is formed by expansion. The scattering intensities of the fog formed by expansion are 2-3 times higher than the scattering intensities of the fog formed by cooling. Moreover the intensity distribution is larger for fog formed by expansion. Therefore it is stated that the fog volume formed during expansion is larger than the fog volume formed during cooling, which verifies the observations of the camera experiments.
Bibliography


