On the Solubility of Acid and Sour Gases in Water and Brines Under Reservoir Conditions

Imperial College
London

Rayane Hoballah

Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy and the Diploma of Imperial College London

Imperial College London
Department of Chemical Engineering
London, SW7 2AZ, United Kingdom
December 2016
Declaration of Originality

I herewith certify that all material in this dissertation which is not my own work has been properly acknowledged.

January 20th 2017, London

Rayane Hoballah

Copyright Declaration

"The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work."
To my best friend and wife, Emily Zinn Hoballah.
"Two things define you: Your patience when you have nothing and your attitude when you have everything."

- Unknown
Acknowledgements

I remember the day I first visited Imperial College, dreams in my head about this world-renowned academic centre where some of the greatest minds were shaped, transitioning from youth to adulthood. Fast forward five years later, I am writing this thesis to be granted the title of Doctor of Philosophy from this wonderful institution that is IC. It is only with humility that I look back into this thousand-mile journey where I took the first step as a different man than I am today.

I would like to thank the man who put his trust in me after a year as a research student in his laboratory, and offered me the chance to live this life-altering opportunity that is a PhD, Prof. Martin Trusler. Through his seemingly infinite knowledge, I grew as a researcher. An hour passed with Martin was equivalent to weeks in the library. His staggering work ethic during these five years has been contagious and his capacity to lead by the example never ceased to amaze me. I will also always be grateful to have personally experienced that, behind his back-breaking responsibilities, is a kind man who stepped up more than once to offer a generous hand in moments of disarray. I am thankful for his incredible teachings, his precious advises and for his priceless vision.

A man needs to be versed in poetry to describe the kind and caring man that is Prof. Geoffrey Maitland. His immeasurable capacity to care for and understand a heavy heart have been a lifesaver to me during this long journey. Countless times have I been galvanised by his support and his encouragements. Having Geoff on your team felt like no mountain was too high to climb. He has been a wonderful supervisor to me, but even more so, he will remain in my memory as a man who has lived every success in life, yet still inhabited a vibrant tolerance, patience and open-mindedness.

The outcome of this thesis would have been very different without the fantastic people whom I have met through these years, some of whom I am lucky to call friends and family. I cannot thank enough Kevin Kim, Shane Cadogan, Cheng Peng, Jonathan Schmidt, Hao Bian, Chidi Effika, Saif Al Ghafri, Claudio Calabrese, Paulius Viskaitis, Francois Delucas and Geraldine Torin-Alvarez for the joy, the laughters and the support you brought to my days
all these years. I am grateful to every single one of you and can only hope that life will not take you away from me so soon as it did for some of you.

A personal thank you to Ian MacDonald, who has always supported me in my future career endeavours.

Love is the best vector of knowledge, and in this regard I have had the best teachers one can dream of and the best childhood partners. I am grateful beyond words and actions to my father Yssam and my mother Hanane, who sacrificed their life by moving to a land far away from their family and all they knew in order to offer the best education and future opportunities to their children. Your unconditional love has always been my lighthouse in the storm, and your unshaken support my reason to always stand back up.

Durant toutes ces années ce sont tes conseils avisés, papa, qui m’ont montré la route à suivre dans les moments où les choses ont le moins de sens et c’est ta voix douce, maman, qui m’appaisait le coeur dans ces moments où le doute s’établit. Jamais je n’oublierais ce que vous avez sacrifié pour ma réussite et mon bonheur. Ma2 fe ahel mitilkone bi kilel dounia.

Thank you to my brother Nadime and my sister Mayla, for their precious affection and kindness during these years.

If the proverb "behind every great man there’s a great woman" is true, then I am set up to fantastic successes, as I have won at the lottery of love. No words can describe the support my wife has provided to me during this bumpy journey. She has been my air when I gasped and my caring partner who selflessly stood by me. This work is as much hers as it is mine, for she went through every turn along side me, holding my hand and encouraging me to reach forward. I love you eternally my sweet friend.

This work was carried out as part of the activities of the Qatar Carbonates & Carbon Storage Research Centre (QCCSRC). I gratefully acknowledge the funding of QCCSRC provided jointly by Qatar Petroleum, Shell, and the Qatar Science and Technology Park.
Abstract

Carbon Capture and Storage (CCS) has been identified as a central technology to reduce CO₂ emissions, but it is burdened by unoptimised economics. The capture and compression activities of a CCS plant represent the largest portion of the added cost of the generated electricity. Reducing the extensiveness of the separation process, in other words lowering the purity of the captured CO₂ stream has the potential to substantially cut the energy penalty resulting from this process thus making it more economically viable. Presence of impurities in the captured CO₂ stream introduces unknowns that must be understood in order to accurately predict the sequestration process. Thermodynamic properties and, in particular, phase-behaviour measurements, are the keystones to quality understanding of the reservoir performances. It provides scientific proof of the behaviour of injected fluids and their mixtures in the in-situ reservoir components. This thesis focuses on the former.

During the first part of this work, the phase-behaviour of binary mixtures composed of impurities (namely O₂ and C₃H₈) and water, were experimentally investigated at pressures and temperatures encountered in deep reservoir conditions, \( p = (0.1 - 60) \text{ MPa} \) and \( T = (348.15 - 398.15) \text{ K} \). Two equipments were exploited during part of this work: a synthetic apparatus (for brines binaries bubble point measurement over a wide range of temperatures and pressures, \( T = (298.15 - 473.15) \text{ K} \) and \( p = (0.1 - 50) \text{ MPa} \)) and a static analytical apparatus (for pure-water based systems at temperatures ranging from (298.15 to 473.15) K and pressures up to 20 MPa).

The synthetic equipment produced reliable solubility for the (CO₂+H₂O) system (1% Absolute Average Deviation with the literature data) during the validation phase. However, due to internal dead-volume issues which introduced large uncertainties for very low solute solubilities, as it is the case for C₃H₈ in H₂O, the apparatus failed to generate satisfactory measurements for the (C₃H₈+H₂O) system.

The (O₂+H₂O) was investigated at two isotherms with the analytical equipment: \( T = (308.15 \text{ and } 348.15) \text{ K} \), and up to 17.95 MPa. The use of Thermal Conductivity Detector proved not to be adapted to the analysis of this binary system as measurements did not give satisfactory accuracy.
The water-rich phase composition of the \((\text{C}_3\text{H}_8+\text{H}_2\text{O})\) binary generated good results through the parallel use of a Thermal Conductivity Detector and an Flame Ionised Detector. The isotherm \(T = 308.15\) K was measured up to 17 MPa. Measurements for isotherm \(T = 348.15\) K could only be obtained up to \(p = 2.8\) MPa. The solubilities obtained for both isotherms were in very good agreement with the literature (average standard deviation of 2%).

Experimental limitations encountered with the aforementioned apparatus were overcome in the second part of this work. To do so, a novel semi-analytical equipment was designed, assembled and validated for High Pressure High Temperature (HPHT) phase behaviour analysis. It offers the dual capabilities of solubility measurements for pseudo-binary mixtures composed of sour gases (\(\text{CO}_2, \text{H}_2\text{S}, \text{SO}_2\)) as well as sparingly soluble gases (\(\text{C}_3\text{H}_8\)) in highly concentrated brines and for a wide range of temperatures and pressures: \(T = (298.15 - 473.15)\) K and \(p = (5 - 70)\) MPa. The new semi-analytical apparatus operates in a new laboratory for exclusive use of High Pressure High Temperature (HPHT) sulphuric gases, partially built and commissioned under this work.

To validate the new apparatus, the composition of the water-rich phase of the \((\text{CO}_2+\text{H}_2\text{O})\) binary was obtained for two isotherms: \(T = (348.15, 398.15)\) K for pressures \(p\) up to 50 MPa and \(p\) up to 60 MPa, respectively. Isotherm \(T = 348.15\) K was experimentally obtained, which subsequently lead to the statistical re-appraisal of an older data set: isotherm, \(T = 398.15\) K. The two isotherms were consistent with the Spycher-Pruess (SP) solubility model as the AADs was 2% for both temperatures.

The \(\text{CO}_2\) solubility in the water-rich phase of the \((\text{CO}_2+\text{H}_2\text{O}+\text{NaCl})\) binary was studied at \(T = 348.15\) K and \(p\) up to 50 MPa, and with a salt concentration of \(m = 3\) mol/kg. This isotherm, which had not been explored in the literature at these conditions, presented good agreements with the SP predictions (AAD of 1%). This therefore verified the capacity of the new equipment to deliver good quality HPHT solubility measurements for pseudo-binaries composed of gases and concentrated brine.

New water-rich phase composition measurements for the \((\text{CO}_2 + \text{H}_2\text{O} + \text{NaHCO}_3)\) system were obtained at two isotherms: \(T = 348.15\) K with \(p = (0.1 - 60)\) MPa and \(T = 398.15\) K with \(p = (0.1 - 50)\) MPa and with a salt concentration of \(m = 0.8\) mol/kg. These studies
led to highly repeatable data sets for both isotherms, with an average deviation of 2.7% at 348.15 K and 2.2% at 398.15 K. As expected for highly concentrated brines, a salting-out effect is noticeable at all temperatures and pressures with less CO$_2$ dissolved in the saline solution than for pure H$_2$O. However this salting-out effect was not correctly predicted by the SP solubility model.

A modification of the SP solubility model was performed in terms of an addition to their Pitzer activity-coefficient formulation. A linear dependency in the bicarbonate molality was introduced, which resulted in a better prediction of the CO$_2$ mole fraction obtained for this system at the conditions of study.

For isotherm $T = 398.15$ K, over the pressure range 5 to 60 MPa and with the optimised Pitzer model, the computed CO$_2$ solubility in the bicarbonate brine agreed with the data reported here with an average absolute deviation of 2% and a maximum deviation of 6%. For isotherm $T = 398.15$ K, the average absolute deviation was 1% and the maximum deviation was 2%. For both isotherms, the agreements between the modified SP solubility model and the measured data were within the uncertainty of the experiments, which is a satisfactory conclusion.

The new results obtained in this work illustrate the potential of the new semi-analytical apparatus to provide previously unstudied solubility data of sour gases in highly concentrated brines for a wide range of pressures and temperatures: $T = (298.15 - 398.15)$ K and $p = (0.1 - 60)$ MPa. Low-hanging fruits for future high-impact measurements have been also identified.
## Contents

Acknowledgements

Abstract

1 Introduction

1.1 Energy and Global Warming Background

1.2 The Role of Carbon Capture and Storage

1.3 Project Motivations

1.4 The Qatar Carbonates and Carbon Storage Research Centre

1.5 Scope and Objectives

1.6 Thesis Outline

2 Phase Diagrams and Literature Review

2.1 Phase Diagrams

2.1.1 Phase Diagram of a Pure Component

2.1.2 Phase Diagram of a Binary System

2.2 Literature Review of Phase Equilibria of (CO\textsubscript{2} + Water/Brine) systems

2.2.1 Available Data for (CO\textsubscript{2}+H\textsubscript{2}O+salts) system

2.3 Literature Review of Phase Equilibria of the (N\textsubscript{2}+H\textsubscript{2}O) system

2.3.1 Available Data for (N\textsubscript{2}+H\textsubscript{2}O) system

2.3.2 Discussion and Evaluation of the Data

2.4 Literature Review of Phase Equilibria of the (O\textsubscript{2}+H\textsubscript{2}O) system

2.4.1 Available Data for (O\textsubscript{2}+H\textsubscript{2}O)

2.4.2 Discussion and Evaluation of the Data

2.5 Literature Review of Phase Equilibria of (H\textsubscript{2} + H\textsubscript{2}O) systems

x
2.5.1 Available Data for (H₂+H₂O) ......................................................... 33
2.5.2 Discussion and Evaluation of the Data .............................................. 36
2.6 Literature Review of Phase Equilibria of the (H₂S+H₂O) system .......... 37
  2.6.1 Available Data for (H₂S+H₂O) ....................................................... 37
  2.6.2 Discussion and Evaluation of the Data .............................................. 40
2.7 Literature Review of Phase Equilibria of the (SO₂+H₂O) system .......... 43
  2.7.1 Available Data for (SO₂+H₂O) ....................................................... 43
  2.7.2 Discussion and Evaluation of the Data .............................................. 44
2.8 Conclusions of the Literature Gap Analysis ........................................ 45

3 Thermodynamic Properties Modelling ................................................. 47
  3.1 Thermodynamic Equilibrium ............................................................... 48
    3.1.1 Introductory Concepts ................................................................. 48
    3.1.2 Quantifying the Thermodynamic Equilibrium in an Ideal System ... 51
    3.1.3 Quantifying the Thermodynamic Equilibrium in a Real Mixture ... 52
  3.2 Cubic Equation of State ................................................................. 56
    3.2.1 Ideal Gas Law ............................................................................. 56
    3.2.2 Van der Waals’ Equation of State ................................................. 56
    3.2.3 Cubic Equations of State ............................................................. 58

4 Presentation of the Existing Apparatus in the Thermophysics Laboratories 61
  4.1 The Synthetic Apparatus ................................................................. 62
    4.1.1 Description of the Apparatus ...................................................... 63
    4.1.2 Operating Procedure ................................................................. 63
    4.1.3 Volume Calibrations and Calculations ............................................ 64
    4.1.4 Dead-Volumes Discussion ............................................................. 65
    4.1.5 Validation using the (CO₂+H₂O) System ........................................ 69
    4.1.6 Attempts on the (C₃H₈+H₂O) System ........................................... 70
    4.1.7 Synthetic Apparatus - Conclusions ............................................ 71
  4.2 The Analytical Apparatus ............................................................... 73
    4.2.1 Description of the Apparatus ...................................................... 73
    4.2.2 Operating Procedure ................................................................. 76
    4.2.3 The (O₂+H₂O) System ................................................................. 77
4.2.4 The (C₃H₆+H₂O) System ............................................. 80

5 The New Semi-Analytical Apparatus - Presentation .......................... 85
  5.1 Working Principle .................................................. 86
  5.2 Design ............................................................. 90
    5.2.1 Unlocking Previous Pressure Limitations ....................... 91
    5.2.2 The Circulation Pump .......................................... 95
    5.2.3 The Gas Chromatograph ........................................ 99
    5.2.4 Material Compatibility and Reactor Design ..................... 102
    5.2.5 The Flash Vessel ............................................... 105
    5.2.6 Volume Considerations ........................................ 108
  5.3 Standard Operating Procedure ....................................... 111
    5.3.1 Filling R ....................................................... 112
    5.3.2 Filling F ....................................................... 112
    5.3.3 Bleeding F ..................................................... 113
    5.3.4 GC Sampling ................................................... 113
    5.3.5 R Content to Waste ............................................. 114
    5.3.6 F Content to Waste ............................................. 114
    5.3.7 Evacuate F ..................................................... 115
    5.3.8 Evacuate R ..................................................... 115
    5.3.9 Cleaning F ..................................................... 115
    5.3.10 Cleaning R .................................................... 117
    5.3.11 Brine Bottle Degasing ......................................... 118
    5.3.12 Brine Bottle to Atmospheric Pressure .......................... 118
  5.4 Calibration Methods ................................................ 118
    5.4.1 Method 1 ....................................................... 119
    5.4.2 Method 2 ....................................................... 121
    5.4.3 Method 3 ....................................................... 123
    5.4.4 Uncertainty Analysis .......................................... 125

6 The Semi-Analytical Apparatus - Solubility Measurements ................ 127
  6.1 Validation of the New Semi-Analytical Apparatus: The (CO₂+H₂O) System . 127
    6.1.1 Sampling Protocol ............................................. 129
E SolidWorks Drawings of the New Semi-Analytical Apparatus
List of Tables

1.1 Concentrations of impurities in dried CO₂, % by volume. 8

2.1 Bubble point data for the (CO₂+H₂O) system. 21
2.2 Bubble point data for the (CO₂+H₂O+NaCl) system. 22
2.3 Bubble point data for the (N₂+H₂O) system. 27
2.4 Bubble point data for the (N₂+H₂O) system. 28
2.5 Bubble point data for the (O₂+H₂O) system. 32
2.6 Bubble point data for the (H₂+H₂O) system. 34
2.7 Dew point data for the (H₂+H₂O) system. 35
2.8 Bubble point data for the (H₂S+H₂O) system. 38
2.9 Dew point data for the (H₂S+H₂O) system. 39
2.10 Bubble point data for the (SO₂+H₂O) system. 44

3.4 Redlich & Kwong (1949) Equation of State (RK EoS) 59
3.6 Soave-Redlich-Kwong Soave (1972) and Peng-Robinson Peng & Robinson (1976) Equations of State 60

4.1 Calibration of the Effective Volume of the Cell. 65
4.2 Result of measurements for (C₃H₈+H₂O) at \( T_{\text{ref}} = 398.15 \) K. 71
4.4 Result of measurements for (C₃H₈+H₂O) at \( T = 308.15 \) K. 83
4.5 Result of measurements for (C₃H₈+H₂O) at \( T = 348.15 \) K. 83

5.1 Filling R, valves set up. 112
5.2 Filling F, valves set up. 113
5.3 Bleeding F, valves set up. 113
5.4 GC Sampling, valves set up. 114
5.5 R content to waste, valves set up. 114
5.6 R content to waste, valves set up. .......................................................... 114
5.7 F to vacuum, valves set up. ............................................................... 115
5.8 R to vacuum, valves set up. ............................................................... 115
5.9 Cleaning the Flash Vessel F, valves set up. ................................................ 117
5.10 Cleaning R, valves set up. ............................................................... 117
5.11 Solvent bottle degasing, valves set up. .................................................... 118
5.12 Solvent bottle to atmosphere, valves set up. ............................................... 118
5.13 TCD response in function of column temperature with same size sample. .... 121
5.14 Calibration Uncertainty Analysis. ............................................................ 126

6.1 Mathematical function used to fit the ratio of partial mole fraction over full mole fraction. Fit illustrated in Figure 6.3. ................................. 135
6.2 Establishing the relationship between premature mole fraction calculation and full mole fraction. .......................................................... 136
6.3 Combined expanded uncertainty, \( U(x_{CO_2}) \) for the solubility measurement of CO\(_2\) in water for the \((CO_2+H_2O)\) system at \( T = (348.15, 398.15) \) K, using a coverage factor \( k = 2 \). ................................................ 141
6.4 Documentation of the actions taken toward the overall improvement of quality and repeatability of the sampling protocol for the new semi-Analytical rig. 144
6.5 Combined expanded uncertainty, \( U(x_{CO_2}) \) for the solubility measurement of CO\(_2\) in brine for the \((CO_2+H_2O+NaCl[3mol/kg])\) system at \( T = 348.15 \) K, using a coverage factor \( k = 2 \). ................................................ 152
6.6 Analysis of the \((H_2O+NaHCO_3[3mol/kg])\) brine at 3 isobars. ................... 157
6.7 Combined expanded uncertainty, \( U(x_{CO_2}) \) for the solubility measurement of CO\(_2\) in brine for the \((CO_2+H_2O+NaHCO_3[0.8mol/kg])\) system at \( T = (348.15, 398.15) \) K, using a coverage factor \( k = 2 \). ................................................ 159
6.8 CO\(_2\) mole fraction calculation in the \((CO_2+H_2O+NaHCO_3[0.8mol/kg])\) system at \( T = 348.15 \) K. .......................................................... 160
6.9 CO\(_2\) mole fraction calculation in the \((CO_2+H_2O+NaHCO_3[0.8mol/kg])\) system at \( T = 398.15 \) K. .......................................................... 160
6.10 CO\(_2\) solubility measurement \((CO_2+H_2O+NaHCO_3[0.8mol/kg])\) for isotherm \( T = 348.15 \) K ................................. 160

xvi
6.11 CO$_2$ solubility measurement (CO$_2$+H$_2$O+NaHCO$_3$[0.8mol/kg]) for isotherm $T = 398.15$ K. .................................................. 160

6.12 Addition of bicarbonate parameter in the SP Pitzer activity coefficient: effect on agreement with measured CO$_2$ solubility in sodium bicarbonate brine [0.8 mol/kg] at $T = 348.15$ K. .................................................. 168

6.13 Addition of bicarbonate parameter in the SP Pitzer activity coefficient: effect on agreement with measured CO$_2$ solubility in sodium bicarbonate brine [0.8 mol/kg] at $T = 398.15$ K. .................................................. 169

6.14 Dependence of $A$ in temperature. ................................................. 170

D.1 Health effects of respiratory exposure to H$_2$S. ........................................... 209
D.2 Health effects of respiratory exposure to SO$_2$. ........................................... 209
# List of Figures

1.1 Contribution of CCS to global emissions reductions .......................... 4  
1.2 CCS in the power and industry sector in the 2°C scenario .................. 6  
1.3 Impurities in the different capture technologies ............................. 8  
2.1 Generic Phase Diagram of a Pure Component ................................. 16  
2.2 Pressure-Temperature ($p$-$T$) Phase Diagram of a Binary Mixture .......... 17  
2.3 The phase behaviour of (CO$_2$ + H$_2$O) binary is a type IIIb according to the Van Konynenburg & Scott (1980) classification ........................................... 18  
2.4 Distribution in pressure and temperature for the bubble point measurements for the (CO$_2$+H$_2$O) system .............................................. 20  
2.5 Distribution in pressure and temperature for the bubble point measurements for the (CO$_2$+H$_2$O+NaCl) system ........................................... 21  
2.6 CO$_2$ mole fraction in NaHCO$_3$ aqueous solution at $T = (323.15$ and $373.15)$ K. 24  
2.7 Distribution in pressure and temperature of the bubble point measurements for the (N$_2$+H$_2$O) system .............................................. 26  
2.8 Distribution in pressure and temperature of the water content in N$_2$ in the literature ................................................................. 27  
2.9 N$_2$ solubility in water ............................................................... 29  
2.10 Water content of N$_2$ .................................................................... 30  
2.11 Distribution in pressure and temperature of the bubble point measurements for the (O$_2$+H$_2$O) system .............................................. 31  
2.12 Distribution in pressure and temperature of the bubble point measurements for the H$_2$-Water system .............................................. 33  
2.13 Distribution in pressure and temperature of the dew point measurements for the (H$_2$ + H$_2$O) system .............................................. 35
2.14 $H_2$ solubility in water. ........................................ 35
2.15 Dew point for the ($H_2+H_2O$) system at $T = 366.15$ K. ........................................ 36
2.16 Distribution in pressure and temperature for the bubble point measurements for the ($H_2S+H_2O$) system. ........................................ 38
2.17 Distribution in pressure and temperature for the dew point measurements for the ($H_2S+H_2O$) system. ........................................ 39
2.18 $H_2S$ solubility in water. ........................................ 41
2.19 Dew point for the ($H_2S+H_2O$) system at $T = 375$ K. ........................................ 42

4.1 P&ID for the Synthetic Rig. ........................................ 62
4.2 Synthetic Apparatus View Cell. ........................................ 66
4.3 Diffusion of gas in the capillaries of the cell. ........................................ 67
4.4 Cross-sectional view of the window assembly. ........................................ 68
4.5 ($CO_2+H_2O$) bubble point measurement at 1.05 MPa. ........................................ 69
4.6 Deviation introduced by 0.1 mL internal dead-volume on the theoretical bubble pressure. ........................................ 71
4.7 Example of density profiles with pressure and Henry's constant evolution with temperature for the gases of interest in this research. ........................................ 72
4.8 P&ID Analytical Apparatus in Thermophysics Lab ........................................ 75
4.9 Calibration of the TCD on the Analytical rig for $O_2$ and $H_2O$. ........................................ 77
4.10 Deans Switching System from Agilent Technologies. ........................................ 80
4.11 $C_3H_8$ mole fraction in pure water at $T = (308.15$ and $348.15)$ K in function of pressure. ........................................ 84

5.1 Simplified P&ID for the semi-analytical equipment. ........................................ 87
5.2 Full P&ID for the Semi-Analytical Apparatus. ........................................ 88
5.3 Exploded view of an HPLC Cheminert valve. ........................................ 92
5.4 The heat exchangers design. ........................................ 93
5.5 Circulation Pump Assembly, Back and Front. ........................................ 96
5.6 The T-piece/check valve, a novel design from this research. ........................................ 98
5.7 The Gas Chromatography used in the Semi-Analytical Apparatus, SRI 8610C. ........................................ 99
5.8 The valve box. ........................................ 101
5.9 The Power supply part of the Amplification Board. ........................................ 102
5.10 Rendering of the Semi-Analytical rig sitting outside the extracted enclosure.  104
5.11 The main vessel R. .............................................. 106
5.12 T-seal from Greene-Tweed. ...................................... 107
5.13 The Flash Vessel F. .............................................. 108
5.14 Control Panel for the Semi-Analytical Apparatus. .............. 111
5.15 Sample vaporisation in the Transfer line. .......................... 116
5.16 TCD calibration for water and CO₂ - Methods used. ............... 120
5.17 TCD calibration for water and CO₂ ............................... 123
5.18 The TCD Calibration for water with the steam-generator addition. 124
5.19 TCD calibration for water and CO₂ - Coefficients Summary. .... 125

6.1 CO₂ mole fraction in pure water. ................................ 128
6.2 CO₂ mole fraction evolution in function of the number of samples. 131
6.3 Mathematical function used to fit the ratio partial mole fraction over full mole fraction. .............................................. 138
6.4 CO₂ concentration in water-rich phase for the two isotherms \( T = (348.15; 398.15) \) K. ..................................................... 139
6.5 CO₂ mole fraction evolution with each liquid sample for each isobar studied at \( T=398.15 \) K. .............................................. 143
6.6 The particulates from the T-seals and one of the damages it generated on this apparatus - HPLC leakage. .......................... 147
6.7 CO₂ mole fraction in brine (CO₂+H₂O+NaCl) at \( m = 3 \) mol/kg and \( T = 348.15 \) K in function of pressure. ..................... 151
6.8 CO₂ mole fraction in brine (CO₂+H₂O+NaHCO₃) at \( m = 0.8 \) mol/kg and \( T = 348.15 \) K in function of pressure. ................. 161
6.9 CO₂ mole fraction in brine (CO₂+H₂O+NaHCO₃) at \( m = 0.8 \) mol/kg and \( T = 398.15 \) K in function of pressure. .......................... 162
6.10 Spycher-Pruess deviation from measured CO₂ solubility in sodium bicarbonate data. .............................................. 167

A.1 Bubble point (in mole fraction) for the (N₂+H₂O) system. ........ 199
A.2 Dew point (in mole fraction) for the (N₂+H₂O) system. ............ 199
A.3 Dew point (in mole fraction) for the (H₂+H₂O) system. ............. 200
A.4 Bubble point (in mole fraction) for the \((H_2+H_2O)\) system. ................. 200
A.5 Dew point (in mole fraction) for the \((H_2S+H_2O)\) system. ..................... 201
A.6 Bubble point (in mole fraction) for the \((H_2S+H_2O)\) system. ..................... 201
A.7 Bubble point (in mole fraction) for the \((O_2 + H_2O)\) system. ..................... 202

B.1 Oxygen Material Compatibility. .................................................. 203
B.2 Oxygen Ignition Mechanisms. ..................................................... 204
B.3 Oxygen Ignition Risk Assessment for the Analytical Rig. ..................... 205

E.1 Main Vessel - Vessel ................................................................. 211
E.2 Main Vessel - Cap ................................................................. 212
E.3 Main Vessel - Plug ................................................................. 213
E.4 Flash vessel - Body ................................................................. 214
E.5 Flash vessel - Lid ................................................................. 215
E.6 Flash vessel - Assembly .......................................................... 216
E.7 In-house gas stirrer ................................................................. 217
Chapter 1

Introduction

1.1 Energy and Global Warming Background

The pressing matter of energy demand and availability is a burning issue on a planet where the ever-limited resources are being shared by an exponentially growing population, thirsty for power consumption (The World Bank (2016)). Finding an equilibrium between these two forces has proven to be challenging for many governments around the world. Since the end of the 19th century the use of fossil-fuel as the dominant energy source has proved to be a reliable, although sometimes agitated, solution to this equation. In the past decade, a third constrain has been added to this equation, making the mathematics even harder to solve: global warming and the need for alternative decarbonised energy sources.

Fossil-fuels, a generic name used for coal, gas and oil, possess unique sets of advantages which explain our societal dependence upon them. This power source is abundant (boundaries of exploitable sources are pushed farther every day) and relatively available, which makes it, in comparison to other technologies in the start 20th century, cheap. Fossil-fuels also offers an advantageously-high calorific value, as they emit 35-48 MJ per kg through the simple process of burning them (wood (15% water) in comparison contains 15 MJ/kg (Laby & Kaye (1995))). The science developed from over 150 years of intensive usage and the range of industries developed from it are vast. Today, the production of pharmaceuticals, solvents, fertilisers, pesticides, paraffin/kerosene, jet fuel, asphalt, polymers and lubricants are still overwhelmingly petroleum originated. However, fossil-fuels and their mass-scale exploitations come at a great cost (as described later) and it seems that no one-solution will contain so
many advantageous features as this "black-gold." For the sake of the future of humanity, another energy balance needs to be established: a decarbonised one.

Upon examining the distribution of the conventional fossil-fuel reserves, their direct access is strikingly exclusive to a selected few countries (WEC (2013)). This setting lead to a global imbalance of hydrocarbon producers and saw the world turn dependent upon their controlled supply of the precious power source. Considering the tight link between energy security and the prosperity of a nation, this energy monopole has been generating geopolitical turmoil around the world (International Security Advisory Board (2014)). A telling example of the possible political impact resulting from the energy-market influence are the oil shocks in the 1970’s which forced nations around the world to reconsider the dependence of their economies on fossil fuel. Awareness rose that, in order to best shield oneself from unforeseen shortages of hydrocarbon supply, one had to diversify its energy portfolio and distance oneself from the reliance on this heavily siphoned energy source. For example, in the US, the President Jimmy Carter passed the Energy Security Act in 1980 which aimed at developing renewable energies on all fronts (Department of Energy (2012)), and in 1975, Brasil established a government-funded ethanol production program to phase out their dependency on fossil fuels. This desire to expand the array of energy sources was the first historical drive behind renewable energies and sustainable innovations.

Thirty-five years later, the worldwide energy portfolio has indeed evolved, although few would qualify this change as stark. According to WEC (2016), energy from fossil fuel has decreased 5% in the last 45 years, from 86% in 1970 to 81% in 2014. Fossil fuels are still the overwhelmingly dominant source of energy around the world, and future predictions draw a picture with little difference (IEA (2006)). However, the drive to move away from fossil fuel is of a different nature today than it was in the end of the 1970’s. In 2007, the International Panel for Climate Change (IPCC) published their AR4 in which they laid out unequivocal proofs that the mass-scale burning of fossil fuels, resulting in a yearly average of 30 Gt emissions of CO₂ worldwide, was the main source behind the warming of the planet (IPCC (2005)). A global rise in temperature resulting from a 20 million-year high CO₂ concentration in the atmosphere is associated with dire risks for the ecosystem of the planet, as well as human life. With a projected 4.5°C temperature increase, the IPCC predicts the following
risks with a high confidence (80 percent chance):

- Large fraction of species will face increased risk of extinction as most small mammals and freshwater molluscs, as well as most plants species, will not have the natural ability to adapt to the sudden change of landscape and resources.
- Ocean acidification magnitudes will lead to lower oxygen levels, putting the highly vulnerable coastal ecosystems at risk.
- Food security will be jeopardised as the global population increases and food reserves shorten.
- Groundwater reserves and their renewal will be challenged in most dry subtropical regions.
- Human health conditions will be exacerbated.
- Occurrences of natural cataclysms will be increased. Those include, but are not limited to: extreme precipitations leading to flooding, storm surges, air pollution, droughts and a sea level rise.

It goes without saying that, in the event of such scenarios, human nature and its way of living will be challenged to its core. Fully avoiding this future seems unlikely as allowances for carbon emissions that would limit global warming to 1.5°C will be spent in the next 5 years if no extraordinary actions are taken. In order to effectively avoid harmful climate impacts, the societies of the world will be required to drastically cut out CO₂ emissions (as well as CH₄ and other pollutants in a lesser extent) in addition to adapting to these climate changes.

Time is of the essence and action cannot be taken soon enough. An encouraging note in this bleak scene is that between 2008 and 2015, the levelised cost of electricity from solar PV and land-based wind power has decreased by 80% and by 35%, respectively (IEA (2016)). These technologies are now competitive with hydrocarbon-generated electricity. Divestments from the fossil fuel industry are happening worldwide and market-driven investments in the now cost-effective solar and wind power plants seem unstoppable (Hirtenstein (2016)).

Although clean energies do play a key role in emissions mitigations (predictions put CO₂ abatement resulting from solar PV and wind energy at 32% of global targets - see Figure 1.1), they are not the only champion to root for, nor will their sole efforts be enough to meet crucial emissions objectives. In their Energy Technology Perspectives 2016 (ETP) 2DS, the
CHAPTER 1. INTRODUCTION

Figure 1.1: Contribution of CCS to global emissions reductions (IEA (2016)). Renewable 32%, CCS 12%, Power generation efficiency and fuel switching 1%, End-use fuel switching 10%, End-use efficiency 38%, Nuclear 7%.

International Energy Agency (IEA) outlines a blueprint of the roles to be taken by available and emerging technologies in order to tackle Green-House Gas (GHG) emissions and maintain CO₂ level in the atmosphere under 450 part-per-million (ppm). To achieve this scenario, which would limit temperature rise to 2°C, nations worldwide will have to work hand-in-hand and nurture as quickly as possible a boundary-free energy technology revolution. The World Energy Council describes this extraordinary shift as the grant transition (WEC (2016)). The exact mix of technologies is difficult to predict with precision, but the energy revolution will be fuelled by the large-scale expansions of energy efficiency, of renewable energies (including nuclear power) and of the decarbonisation of power generation from fossil fuel.

1.2 The Role of Carbon Capture and Storage

To efficiently make a deep cut in the fossil fuel emissions, Carbon Capture and Storage (CCS) is a vital technology. In their 450 Scenario, the ETP predicts that global warming mitigation efforts will require the support of CCS, which will be responsible for the capture of 94 Gt of CO₂ by 2050, corresponding to nearly one-fifth of the necessary GHG emissions cuts (see Figure 1.1). Additionally, the IPCC provided a study of the potential impacts from the mitigation scenarios if specific decarbonising technologies were absent. The scenario that was the most unlikely to succeed resulted not from the phasing-out of nuclear energy nor from curtailing solar and wind energy or limiting the use of biofuel. Indeed, it is the absence of CCS and its implications on tackling global warming that would jeopardise the 2°C ambition the most, as well as generate the highest increase in the cost of CO₂ abatement efforts by far (IPCC (2014)).
CHAPTER 1. INTRODUCTION

Carbon Capture and Storage is usually presented as a three-step process. Firstly, in the capture stage, the CO₂ is stripped from the selected source of GHG using the appropriate capture technology. The most common of these methods are post-combustion, pre-combustion and oxy-fuel capture. Oxy-fuel combustion is still to be demonstrated for commercial use, while the maturity of pre-combustion and post-combustion capture are fully established (IEA (2016)). The carbon source point could be a power generation plant, an industry based facility or any other source emitting highly concentrated CO₂ in their operations. The second step is the transportation, in which the captured CO₂ is compressed to a liquid state and sent to a storage site (usually via pipelines), which can be an aquifer or a depleted oil/gas field. The final step is the sequestration, where the CO₂ is methodically injected into the reservoir several miles underground for safe geological storage. This trapping is the result of four different processes taking place at different time-scales (in general, geologically stored CO₂ becomes more securely trapped with time):

1. Structural/stratigraphic trapping: It is the dominant trapping mechanism, during which the supercritical CO₂ buoyant through the porous reservoir and rises to the top of the formation where it is contained by an impermeable cap-rock.

2. Residual trapping: This phase takes place early on after injection. As CO₂ is displaced through the pores of the rocks, some is disconnected from the bulk and remains trapped in the pore space in droplet-like form.

3. Solubility trapping: CO₂ dissolves in the fluids within the reservoir, thermodynamically sequestrating the gas. The heavier CO₂-rich brine or hydrocarbon sinks to the bottom of the reservoir. Consequently, fresh fluid is brought to contact with the CO₂ plume increasing the effect of this trapping phase.

4. Mineral trapping: It is the longest occurring trapping mechanism, in which the carbonic acid resulting from CO₂ dissolution in water/brine reacts with the reservoir rocks to form solid carbonate mineral.

The two most commonly encountered storage processes are Enhanced Oil Recovery (EOR) and Saline Aquifer Storage. EOR is currently the only commercial operation that brings economical value to the CCS process. It is the process of injecting supercritical CO₂ into a depleted hydrocarbon reservoir in view of increasing its yield by changing the physical properties of the underground fluid: principally interfacial tension, wettability, mobility,
viscosity and phase-behaviour. Injecting CO$_2$ in saline aquifer is investigated for the sole purpose of geological sequestration, as their potential capacity for storage could be extremely large (for example, in the Alberta basin, Bachu & Adams (2003) estimated that up to 4000 Gt of CO$_2$ could be ultimately sequestrated, equivalent to over 100 years of CO$_2$ emissions).

Due to popular misconception, CCS is too often perceived as a perpetuation of the business-as-usual for the fossil fuel industry (ENGO (2015)). In addition to saving precious GHG emissions from the coal or gas power plants (thus buying a little more time to reach full implementation of cleaner energies), CCS is also essential in tackling industry emissions. In fact, some industrial processes, such as the production of chemicals, iron, steel and cement, are heavy carbon emitters and CCS remains one of the only ways to decarbonise these industrial activities. According to the 450 scenario from the IEA, by 2050, 29 Gt of CO$_2$ will have been captured from industrial processes thanks to CCS (the close equivalent to one year of global current CO$_2$ emissions). As illustrated by Figure 1.2, this technology offers unique CO$_2$ abatement features across multiple sectors, and is key to the achievement of net zero emissions (or negative via the use of Biological CCS- BECCS).

Unfortunately, despite its central role in CO$_2$ mitigations and its international recognition, CCS is backed by little support around the world. In fact, only 15 industrial-scale CCS plants are under operation, capturing overall 31 Mt of CO$_2$ per year (Global CCS Institute (2015)), which by 2050 would only amount to nearly 1 Gt of captured CO$_2$. Thus, the current
implemented capture capacity would only achieve 1.1% of the potential 94 Gt advocated by the ETP.

The main hurdle to the large-scale awakening of CCS likely resides in its cost (although other barriers have been identified, such as the lack of legal framework in place, especially in terms of liability with regard to the fate of the CO$_2$). The technology is still too expensive to be attractive to investors. Although a lot of research is available in this domain, there is still a need to identify cost inefficiencies at commercial-scale. Such advancements cannot take place without a larger fleet of CCS demonstration plants, as available reports on the electricity costs to operate the few plants in existence today vary too greatly depending on the source of the cost analysis (MIT (2007)). CCS is a technology that is now considered proven (ENGO (2012)). Its burden is economical and, similar to PV and wind after the second oil crash, it needs the push from governmental incentives and regulations to increase its attractiveness to the market. How to achieve this goal is subject to other stimulating discussions.

1.3 Project Motivations

The capture and compression activities of a CCS plant can represent from 75% up to 90% of the full cost of capturing, transporting and storing the CO$_2$ (Herzog (2011)). Thus, it makes sense to investigate economical improvements regarding the way in which CO$_2$ is captured. In particular, leaving impurities in the captured CO$_2$ stream is a proposition that is generating great interest as it could lower the energy penalty resulting from the current extensive separation process. Depending on the origin of the fuel, the capture technology and other plant design details, various concentrations of certain species may be found in the final flue gas stream (see Table 1.1). These impurities can be classified in two categories:

- **Inert Gases**: N$_2$, O$_2$, Ar, H$_2$, CO and NO$_x$.
- **Sour Gases**: H$_2$S and SO$_2$.

As can be seen from Figure 1.3, each capture technology incorporates one to two impurity stripping units. For example, the oxy-fuel technology requires a cryogenic purification step to remove N$_2$, Ar, O$_2$ and NO$_x$ from the CO$_2$ stream. Suppressing the need for this unit would improve the overall cost of the process, but would be detrimental to the CO$_2$ purity (Metz
Table 1.1: Concentrations of impurities in dried CO₂, % by volume. (Metz et al. (2005))

<table>
<thead>
<tr>
<th></th>
<th>SO₂</th>
<th>H₂S</th>
<th>H₂</th>
<th>CO</th>
<th>CH₄</th>
<th>N₂/Ar/O₂</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>COAL FIRED PLANTS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-combustion capture</td>
<td>&lt;0.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Pre-combustion capture</td>
<td>0</td>
<td>0.01 - 0.6^a</td>
<td>0.8 - 2.0</td>
<td>0.03 - 0.4</td>
<td>0.01</td>
<td>0.03 - 0.6</td>
<td>2.1 - 2.7</td>
</tr>
<tr>
<td>Oxy-fuel</td>
<td>0.5^a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.7</td>
<td>4.2</td>
</tr>
<tr>
<td><strong>GAS FIRED PLANTS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-combustion capture</td>
<td>&lt;0.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Pre-combustion capture</td>
<td>0</td>
<td>&lt;0.01</td>
<td>1.0</td>
<td>0.04</td>
<td>2.0</td>
<td>1.3</td>
<td>4.4</td>
</tr>
<tr>
<td>Oxy-fuel</td>
<td>&lt;0.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.1</td>
<td>4.1</td>
</tr>
</tbody>
</table>

^a: The mentioned concentrations are deliberately left in the captured stream to reduce cost. The concentrations shown are based on use of coal with a sulphur content of 0.86%. The SO₂ and H₂S concentration is a linear function of the fuel sulphur content.

b: For clarity, the NO₂ concentration data has been removed as it is negligible.

Figure 1.3: Impurities in the different capture technologies. Courtesy of CO2CRC.
et al. (2005)). Leaving sulphur in the CO₂ stream could also be economically rewarding. An SO₂ concentration between 0.5 - 3.0% could generate savings of US$ 13 - 25 /t CO₂ avoided compared to pure CO₂ capture itself, which costs around US$ 55 /t CO₂ avoided (IEAGHG (2004)).

This potential 50% cost cut seems promising, but more research is needed as impacts on the compression, transport and storage must be understood. For example, the potential corrosion from the acid combination (H₂S+SO₂+CO₂) during transportation must be quantified to help estimate additional costs arising from material compatibility issues. The largest unknowns when it comes to impurities in the CO₂ stream are concerned with the storage. It is, therefore, where most research efforts must be invested to help improve CCS cost reduction. The following thesis subscribes to this momentum as it focuses on the technicalities behind the sequestration of the impure CO₂ and the thermodynamic details behind the fate of the gases involved. This work is part of a research effort from an academic group funded by industrial parties, the essence of which is to provide reliable data and accurate models for the properties of reservoirs and the fluids within them: the Qatar Carbonates and Carbon Storage Research Centre.

1.4 The Qatar Carbonates and Carbon Storage Research Centre

Carbonate reservoirs play a central role in the production of fossil-fuels around the world, as more than 60 % of the world’s oil and 40 % of the world’s gas reserves are held in carbonates (IEA (2006)). These formations are chemically active and their structures, especially their pore distributions, vary greatly in terms of depth, as well as from site to site. These features resulted in challenges when transferring technologies from the sandstone-optimised EOR techniques directly to carbonate reservoir applications. Injecting CO₂ in sandstone has proven to recover up to 20 % of the original capacity of a depleted reservoir (Energy.gov - Office of Fossil Energy (2010)). The recoveries are expected to be lower for carbonates, but if successful, EOR could unlock enormous volumes of high-quality fuel. Qatar is at the centre of these challenges as while the nation posses one of the greatest gas reserves in the world (14 %), most of these are trapped in carbonate formations. It is from this need to optimise oil and
gas recovery from these carbonate reservoirs that the Qatar Carbonates and Carbon Storage Research Centre (QCCSRC) was born in 2008.

QCCSRC is the result of a 10-year, US$ 70 million strategic collaboration between Imperial College London, Qatar Petroleum, Shell and the Qatar Science and Technology Park (part of Qatar Foundation). The original research programme set out to characterise carbonate reservoirs in detail and develop advanced computer modelling and simulations to establish an in-depth knowledge of rock structures and the way fluids, like oil, water, and natural gas and CO$_2$, move within them. This will in turn improve understanding of how these rocks trap gasses and fluids. The focus of the centre is set on Qatar and the Middle East, where significant quantities of the world’s fossil fuels and potential saline aquifer storage reservoirs are located in carbonate reservoirs (hence the name). To develop this multidisciplinary knowledge, the centre has established five laboratories with the following purposes:

- The Qatar CCS Multiscale Imaging Laboratory: This lab specialises in CO$_2$ injection and trapping in carbonate reservoirs using state of the art imaging techniques, including micro-CT and medical CT which provide visual evidences at different length scales, pore to core.

- The Qatar Complex Fluids Laboratory: This lab focuses on the fluid, pore-space and pore-surface interactions for CO$_2$ storage and EOR applications.

- The Qatar Stable Isotope Laboratory: This lab uses mass spectrometers to measure clumped isotopes, which is a new method to accurately determine the temperature of precipitation of carbonate minerals. This helps in understanding the reservoir’s geological history and thus improving its management.

- The Qatar Complex Porous Media Laboratory: This lab studies fluid properties and behaviour, as well as fluid-fluid and fluid-rock interactions in porous and confined media. These properties are key to the characterisation of new challenging systems, including reactive environments (e.g., carbonates), nanoporous (e.g., mudrocks) and fractured rock systems, for which conventional single- and multi-phase concepts are not well defined and the corresponding data set is rather scarce.

- The Qatar Thermophysical Properties Laboratory: This lab is dedicated to studying the fundamental physics and chemistry for improving the understanding of carbon sequestration and CO$_2$-driven enhanced oil recovery. Thanks to customised high-pressure,
high-temperature (HPHT) equipments, high-accuracy experimental data (such as phase equilibria, density, interfacial tension, contact angle, viscosity and diffusion coefficients) for brine/CO2/hydrocarbon systems under reservoir conditions are measured. These data are key as they are the basic input parameters for reservoir simulators and the building blocks of quality predictive simulations of CO2 storage.

The research work from this thesis was carried under the umbrella of the Qatar Thermophysical Properties Laboratory under the Task 2.2.1E.b Impurities in the CO2 stream: Phase behaviour. Obtaining accurate phase-behaviour measurements for systems involved in impure CO2 injections is the keystone to quality understanding of the reservoir performances.

1.5 Scope and Objectives

The end goal of the task to which this thesis belongs is to reliably obtain the thermodynamic properties and phase behaviour of any one multi-components system at any one pressure and temperature of interest in CO2 sequestration operations. Fulfilling this target by using exclusively experimental input is essentially impossible due to the discontinuous nature of measurements, while the range of components composition (pressure and temperature) for each system is itself continuous. To match this need for continuity, models must be built. They reproduce the trend of trusted data sets in a bounded range of pressure and temperature and offer simulated values for other conditions in this range. These mathematical formulations can either be empirical or based on sound theory, the latter usually being more effort-intensive to establish, yet possessing a broader predictive capacity.

Thermodynamic theory for phase-behaviour is well-established. More specifically, models have been developed and proven to be applicable to pure CO2 injections (see Chapter 3). However, the addition of impurities to the stream of CO2 brings handicapping unknowns to this theory, prohibiting any predictions without experimental input. The thermodynamic formulation of the mutual solubilities of the components of a phase is based on the pair-interaction coefficient of each pair of components. Therefore, to quantify the extent to which the phase-behaviour of a well understood system is changed when augmented by one component, the pair-interaction parameter of this component with each species in the
system must be obtained. For example, the phase-behaviour change from adding \( N_2 \) to the well-understood \((CO_2+H_2)\) system can be fully described for any original concentration of \( N_2 \) if one obtains the \( N_2/CO_2 \) and the \( N_2/H_2O \) interaction parameter. These parameters are accessed through the study of the phase-behaviour of the systems composed of the pair of interest, the \((N_2+CO_2)\) system and the \((N_2+H_2O)\) system (these two-components systems are called binaries).

Following this logic, the purpose of this work was to obtain the phase behaviour of binaries mixtures involving \( N_2, O_2, H_2, H_2S, SO_2, CO_2 \) (the injected fluids), water and salts (the reservoir fluids) from which the pair-interaction parameters could be obtained. In other words, the goal of this thesis was to study the phase-equilibria of the \((impurities+water)\) binaries as well as the \((impurities+(water+salts))\) binaries (called pseudo-binaries) under reservoir conditions. These data sets were to complement the scope of prediction provided by the established thermodynamic models, which in turn would grant new understanding of the solubility changes brought by the introduction of impurities in the captured CO\(_2\) stream.

The chosen systems to be studied were the \((N_2+H_2O)\), the \((O_2+H_2O)\), the \((H_2+H_2O)\), the \((H_2S+H_2O)\), the \((SO_2+H_2O)\) and the \((C_3H_8+H_2O)\) binaries at pressures up to 70 MPa and temperatures from (298.15 to 473.15) K. Considering the large number of systems to investigate, it was admitted that time might be limited to gather pseudo-binaries measurements, hence the focus on pure water binaries. Systems for which literature data were scarce were favoured. Due to the highly toxic nature of sulphuric gases, experience was to be gathered with more "inert" systems. It was therefore decided that the \((CO_2+H_2O)\) for the validation of the apparatus, the \((O_2+H_2O)\) and the \((C_3H_8+H_2O)\) binaries were the primary focus for solubility measurements which would, upon success, be followed by the study of the \(((H_2S/SO_2)+H_2O)\) binaries. Due to the high strain such systems put on an apparatus at the conditions of interest, three equipments were exploited for the aforementioned investigations: a synthetic apparatus for brines binaries bubble point measurement for a wide range of temperatures and pressures, \( T = (298.15 - 473.15) \) K and \( p = (0.1 - 50) \) MPa; a static analytical apparatus for pure-water based systems at temperatures ranging from (298.15 to 473.15) K and pressures up to 20 MPa; and a newly designed and constructed semi-analytical apparatus for sour-gases solubility measurements in brines along an extended range of temperatures and pressures, \( T = (298.15 - \)
473.15) K and $p = (0.1 - 70) \text{ MPa}$. 

The first objective of the present research was to validate the synthetic apparatus housed in the Qatar Thermophysical Properties Laboratory. From this gathered knowledge, investigations were to be carried out in regard to dead-volumes in the system which were suspected to cause potential error in solubility measurements of sparingly soluble gases in water. The bubble pressure of the $(C_3H_8+H_2O)$ was to be obtained for a large range of temperature and pressure: $T = (298.15 - 473.15) \text{ K} \text{ and } p = (0.1 - 50) \text{ MPa}$. 

The second objective was to assess the material compatibility between the static analytical apparatus available in the Qatar Thermophysical Properties Laboratory and pure $O_2$. If deemed compatible, the equipment was to be used to obtain the phase behaviour of the $(O_2+H_2O)$ system at temperatures from $(298.15 \text{ to } 473.15) \text{ K} \text{ and pressures up to } 20 \text{ MPa}$. Additionally, the composition of the saturated gas and liquid phase for the $(C_3H_8+H_2O)$ was to be measured for the same temperature and pressure range. 

The third objective of this thesis was to build a new apparatus which would provide solubility measurements of $H_2S$ and $SO_2$ in water and brines for a wide range of pressures and temperatures: $T = (298.15 - 473.15) \text{ K} \text{ and } p = (0.1 - 70) \text{ MPa}$. This new equipment was to be operated in a lab dedicated to the safe handling of high-pressure and high-temperature sulphuric gases. Designing and building this new laboratory with the help of other researchers was also part of the third objective. 

Finally, the last objective of this work was to adapt/develop a new solubility model based on the systems studied. Semi-empirical models, such as a $\gamma - \phi$ method (Orbey & Sandler (1998)), were to be investigated first before moving on to more predictive statistical dynamic models, such as an adapted SAFT version to water binaries (Chapman et al. (1990)). Due to the ambitious list of objectives, little expectation was placed on developing a fully predictive model like SAFT, and successfully obtaining a semi-fitted model was deemed satisfactory. 

This thesis was, therefore, set to be heavily oriented toward hands-on experimentations, involving great equipments and means from which pioneer high-pressure, high-temperature, phase-equilibria data could be generated.
1.6 Thesis Outline

This document starts with the assessment of the literature for the binaries at stake, as well as the appraisal of the available data sets (Chapter 2). From these studies, the systems for which fewer amounts of data were available were highlighted, and thus set as a priority in the ranking of the measurement campaigns. Introduced in Chapter 3 are thermodynamic notions and definitions relevant to the present work, as well as a brief background on the state of modern Equations of State. Both the synthetic and the analytical apparatus are introduced in Chapter 4. Conclusions gathered for the synthetic equipment, as well as results and set-backs encountered with the analytical apparatus, are found in this chapter. The new semi-analytical equipment and its design are discussed at length in Chapter 5. The challenges faced with the semi-analytical apparatus during the measurement campaigns, the results obtained and some data modelling are discussed in Chapter 6. The conclusions of this thesis with the recommendations for future work are compiled in Chapter 7.
2.1 Phase Diagrams

Phase behaviour provides information about what changes a fluid undergoes when thermodynamic variables (temperature, pressure and composition for the non-pure systems) are altered. Phase behaviour is graphically represented through phase diagrams, where the phase boundaries between phases and conditions for their presence are reported. The extractable information from these diagrams are key for numerous industries, and their thermodynamic theory has been largely covered in numerous textbooks, such as that of Prausnitz, Lichtenthaler & Azevedo (1999), to which the curious reader is encouraged to refer.

An interesting property of the phase behaviour of systems composed of a large number of components (sometimes many thousands) is that it is somewhat related to the simpler behaviour of the binary, ternary and other multi-component systems of which it is constituted. Therefore, understanding the phase diagrams of binaries is a necessary initial step to the better understanding of the phase behaviour of complex multi-component systems.

2.1.1 Phase Diagram of a Pure Component

The phase equilibria of a pure component is described by the pressure-temperature \((p, T)\) and the pressure-volume \((p, V)\) diagrams (a generic version of these diagrams for a pure fluid are presented in Figure 2.1). In Figure 2.1a, the line AC is commonly known as the *vapour pressure curve*, as it provides information on the pressure of the vapour phase while
in presence of liquid. The line AB is the solid-liquid equilibrium line or the melting point curve. The vapour-liquid and liquid-solid curves join at the triple point A. For a pure system, it is exclusively at these conditions that the three phases (liquid, solid and vapour) can coexist at equilibrium. At the critical point, C, the phase becomes indistinguishable. The conditions at which this state can exist are called critical. The critical temperature and the critical pressure are the maximum temperature and pressure where vapour and liquid phases can coexist for a pure fluid. In Figure 2.1b, the curve separating the phases is called the phase envelope of the fluid, and is formed by the apparition of the first bubble (bubble point) on the liquid end and the condensation of the first droplet of liquid on the vapour side (dew point). A compressed liquid (in a liquid phase, away from the envelope and from its critical temperature) undergoing pressure reduction will slowly expand (increase its molar volume) until reaching the envelope, where the first gas bubble is formed in the bulk of the liquid. From there, further expansion of the fluid results in more bubbles being generated (at constant pressure) and a vapour phase taking over the liquid phase. If the fluid expansion is continued, the vapour curve of the envelope is reached and the last drop of liquid evaporates while only vapour remains at these conditions. This is the dew point. At the critical point, these phase changes happen without any volume change for the system. Moreover, an isothermal expansion of a pure fluid at a temperature higher than its critical temperature does not result in any phase change. Under these conditions, the fluid is called supercritical.

Figure 2.1: Generic Pressure-Temperature (pT) and Pressure-Volume (pV) Phase Diagram of a Pure Component.
2.1.2 Phase Diagram of a Binary System

The phase equilibria of a multi-component system is more complex than that of a pure system, especially when the components present large differences in their physical properties. In the case of a two-component system (or binary), a description of the phase behaviour is obtained through the temperature, pressure and composition variables. Three-dimensional diagrams are less convenient to read than two-dimensions graphics, which is why it is common practise to plot the phase diagram for binaries in a \((p, T)\) as well as \((p, V)\), \((T, x)\) and \((p, x)\). As an example of these plots, the \((pT)\) phase diagram of a generic binary is plotted in Figure 2.2. Similar to a pure fluid, the phase envelope separates pure phases and is bounded by the bubble curve and the dew curve. However, unlike the pure component systems, the liquid and gaseous phases can coexist past the critical conditions. The highest pressure and highest temperature on the phase envelope are called cricondenbar and cricondentherm, respectively. For binaries and multi-component mixtures, at constant temperature, crossing the phase envelope does not translate to an isobaric expansion.

Van Konynenburg & Scott (1980) published a classification of the six main types of phase behaviour found experimentally for binary systems. These categories are obtained from van der Waals' Equation of State (apart from type VI). Extensive work on this subject can be found in the literature (Van Konynenburg & Scott (1980), Rowlinson & Swinton (1982), Sadus (1992), Bolz et al. (1998)) and the curious reader is invited to refer to them. In this work, it is the Type III phase behaviour which was encountered.

---

**Figure 2.2:** Pressure-Temperature \((pT)\) Phase Diagram of a Binary Mixture.
Type III mixtures have two critical curves that never meet. One critical curve starts from the critical point of the pure component with the higher critical temperature and goes to high pressures. The other critical curve starts from the critical point of the second component (lower critical temperature) and extends to the Upper Critical End Point (UCEP), on the end of the three-phase line. Five sub-classes of Type III behaviour are found, depending on the location of the main critical locus (Sadus (1992)). For example, similarly to other water binaries, the (CO₂+H₂O) system exhibits a type IIIb phase behaviour, with a discontinuous vapor-liquid critical curve, a wide $T_p$ range for liquid-liquid coexistence (below the critical temperature of CO₂), and sparse mutual solubility in the regions of the two- and three-phase equilibria (Hou et al. (2013b)).

(a) The different sub-types of Type III Phase Behaviour. 
(b) ($pT$) projection of the phase diagram for (CO₂ + H₂O) binary system in the vicinity of the water critical point. Extracted from the work of Aparicio-Martínez & Hall (2007).

Figure 2.3: The phase behaviour of (CO₂ + H₂O) binary is a type IIIb according to the Van Konynenburg & Scott (1980) classification.
2.2 Literature Review of Phase Equilibria of (CO$_2$ + Water/Brine) systems

The (CO$_2$+H$_2$O) system has been extensively studied under the pressure and temperature range of interest in this study: $p = (0.1$ to $70)$ MPa and $T = (273.15$ to $473.15)$ K. Many reviews have been published, and assessments of available data sets along with them (Mao et al. (2013), Hu et al. (2007), Qin et al. (2008), Mohammadi et al. (2004), Duan & Sun (2003), Duan et al. (2006)). Numerous models providing the mutual solubility of these species were developed, with the most famous being that of Duan & Sun (2003), and more recently that of Spycher & Pruess (2010). Data evaluation is usually made easier in such scenarios where accurate solubility models are available. Many authors have provided evaluations of the published models and alternatively developed their own versions of a High Pressure High Temperature (HPHT) solubility model (Mao et al. (2013), Diamond & Akinfiev (2003), Hu et al. (2007) Koschel et al. (2006)).

However, in the case where no solubility model is available, one must be able to evaluate the measurements in the literature and identify reliable data sets for future solubility models to be implemented onto. In this Chapter and in the rest of this thesis, the logic followed for experimental data will be similar to the one found in the work of Diamond & Akinfiev (2003) where consistency with other data sets and uncertainty are the relevant selection criterion. As there was no ad-hoc solubility model construction resulting from this analysis, it was deemed sufficient for the purpose of this work.  

Figure 2.4 illustrates how well-distributed the measurements for the (CO$_2$+H$_2$O) system are. Across the range of pressure and temperature of interest, data are densely present at low-pressure, low-temperature. They become a little scarcer at higher pressures in general, and absent at high-pressures and low-temperatures, which are conditions for hydrates formations. There seems to be little interest for new data in this $p$-$T$ range due to the availability of measurements, but also because most studies are consistent with each other (Duan & Sun (2003), Duan et al. (2006), Mao et al. (2013)), with some exceptions depending on the solubility model used for reference. The most used and cited authors for HPHT CO$_2$ solubility

---

1 Although a good way to check the validity of sparse data sets is to compare this latter to a theoretically sound HP solubility model such as the Krichevsky-Kasarnovsky Equation of State, this process was not followed in this work as, where confusion needed to be lifted, other proven and more accurate solubility models were used.
measurements in water are listed in Table 2.1. The purpose of this thesis was to generate new measurements to help shine a light on the behaviour of impure CO₂ storage in reservoirs. To fulfil this goal, the (CO₂+H₂O) binary could therefore be seen to contain little potential (which is why no analysis is done regarding the dew point for this system). On the other hand, some pseudo-binaries derived from this system do hold a high capacity for new measurements, as shown in the next subsection.

2.2.1 Available Data for (CO₂+H₂O+salts) system

In the quest to evaluate an aqueous CO₂ pseudo-binary, one has to firstly consider the (CO₂+H₂O+NaCl) system, as the NaCl brine represents a satisfying general case for saline aquifer (Koschel et al. (2006)). It quickly appears that, even if this system is not as thoroughly explored as the (CO₂+H₂O), authors have largely contributed with measurements in the range of pressure and temperature of interest here (Li et al. (2004)), as can be seen from Table 2.2. Some areas of the pT data distribution graph (Figure 2.5) could be explored more extensively (fewer data sets at pressure higher than 20 MPa), but little mystery lies within them as no phase transition happens in their vicinity. To complete the experimental knowledge, numerous HPHT solubility models have been developed (Koschel et al. (2006)). While they all do present their sets of advantages and drawbacks, a model that seems to stand out for its range of application, accuracy and relative simplicity is that of Spycher &
Table 2.1: Bubble point data for the (CO$_2$+H$_2$O) system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$T$ range /K</th>
<th>$p$ range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wiebe &amp; Gaddy (1939)</td>
<td>323 - 373</td>
<td>2.5 - 71.0</td>
</tr>
<tr>
<td>Wiebe &amp; Gaddy (1940)</td>
<td>285 - 313</td>
<td>2.5 - 51.0</td>
</tr>
<tr>
<td>Malinin (1959)</td>
<td>473 - 603</td>
<td>9.8 - 49.0</td>
</tr>
<tr>
<td>Tödheide &amp; Franck (1963)</td>
<td>323 - 623</td>
<td>20 - 350</td>
</tr>
<tr>
<td>Takenouchi &amp; Kennedy (1964)</td>
<td>383 - 623</td>
<td>10 - 150</td>
</tr>
<tr>
<td>Müller et al. (1988)</td>
<td>373 - 473</td>
<td>3 - 80</td>
</tr>
<tr>
<td>King et al. (1992)</td>
<td>288 - 298</td>
<td>6.0 - 25.0</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1982)</td>
<td>304 - 366</td>
<td>0.7 - 20.3</td>
</tr>
<tr>
<td>Bamberger et al. (2004)</td>
<td>323 - 353</td>
<td>4 - 13.1</td>
</tr>
<tr>
<td>Teng et al. (1997)</td>
<td>278 - 293</td>
<td>64 - 295</td>
</tr>
<tr>
<td>Chapoy et al. (2004)</td>
<td>274 - 351</td>
<td>0.2 - 9.3</td>
</tr>
<tr>
<td>Koschel et al. (2006)</td>
<td>323 - 373</td>
<td>2.1 - 19.5</td>
</tr>
<tr>
<td>Qin et al. (2008)</td>
<td>323 - 376</td>
<td>10.6 - 50</td>
</tr>
<tr>
<td>Liu et al. (2011)</td>
<td>308 - 328</td>
<td>2.1 - 16</td>
</tr>
<tr>
<td>Hou et al. (2013a)</td>
<td>298 - 448</td>
<td>1.5 - 18.0</td>
</tr>
</tbody>
</table>

Figure 2.5: Distribution in pressure and temperature for the bubble point measurements for the (CO$_2$+H$_2$O+NaCl) system. Data gathered from DECHEMA (2004)
Table 2.2: Bubble point data for the (CO$_2$+H$_2$O+NaCl) system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$T$ range /K</th>
<th>$p$ range /MPa</th>
<th>$m_{NaCl}$ / (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rumpf &amp; Maurer (1993)</td>
<td>313 - 433</td>
<td>0.5 - 9.6</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Bando et al. (2003)</td>
<td>300 - 333</td>
<td>10 - 20</td>
<td>0.18 - 0.53</td>
</tr>
<tr>
<td>Nighswander et al. (1989)</td>
<td>353 - 474</td>
<td>2.1 - 10.0</td>
<td>0.17</td>
</tr>
<tr>
<td>Kiepe et al. (2002)</td>
<td>313 - 353</td>
<td>0.0 - 10.1</td>
<td>0.5 - 4.3</td>
</tr>
<tr>
<td>Koschel et al. (2006)</td>
<td>323, 373</td>
<td>5 - 20</td>
<td>1 - 3</td>
</tr>
<tr>
<td>Yan et al. (2011)</td>
<td>323 - 413</td>
<td>5 - 40</td>
<td>0 - 5</td>
</tr>
<tr>
<td>Liu et al. (2011)</td>
<td>318</td>
<td>2.1 - 15.8</td>
<td>1.93 - 1.98</td>
</tr>
</tbody>
</table>

Pruess (2010). It provides a solubility correlation for the (CO$_2$+H$_2$O+NaCl$[m]$) which is valid for a wide range of temperatures and pressures ($T = (285.15 - 573.15)$ K and $p = (0.1 - 60)$ MPa), and for highly concentrated brines (salinities up to $m = 6$ mol/kg NaCl). They also report a Root Mean Square Deviation between their model and the selected literature of 7%. The success of their parametrisation of the solubility of this system leaves little room for ground-breaking measurements under the aforementioned pressure and temperature range. Therefore, similar conclusions can be drawn for these pseudo-binaries than for CO$_2$ and pure water: HPHT Vapor-Liquid-Equilibrium (VLE) experimental efforts should be invested in other pseudo-binaries.

Duan et al. (2006), thanks to their formulation of the Pitzer activity coefficient, built a CO$_2$ solubility model which accommodates for several salts found in marine brines. Based on this advancement, Snycher et al. (2003) extended the range of application of their model, which can be applied to highly concentrated brines composed of ($Na^{2+}$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$) ions (Spycher & Pruess (2010)). Thus, only limited interest lies within additional measurements for these systems. However, a pseudo-binary that remains un-studied at reservoir conditions is the (CO$_2$+H$_2$O+NaHCO$_3$). Experiments for this salt-species are both needed and valuable, as this compound can be highly concentrated in water formations at depths in the Atlantic, Gulf Coastal Plains and South China Sea (Foster (1950), Gao et al. (1997)).
The work from Gao et al. (1997) is the only available set of measurements to be found for HPHT solubility data for the (CO$_2$+H$_2$O+NaHCO$_3$) system. They measured the solubility of carbon dioxide in aqueous sodium bicarbonate solutions (2, 5 and 7% massic concentration) up to 58 MPa and (323, 373 and 403) K. Albeit the first and, to this date, the only data set available for this system at these pressures and temperatures, their measurements are surprising. Two of their measured isotherms are plotted in Figures 2.6a and 2.6b, as well as the CO$_2$ mole fraction in pure water, computed from the Spycher-Pruess (SP) model. One can generally expect a salting-out effect from salt presence on the CO$_2$ concentration (Duan et al. (2006)). Some salts might introduce the opposite: a salting-in effect. However, to our knowledge, no addition of species generates at the same time, for a set section of its phase diagram, a decrease in the CO$_2$ concentration in comparison to the pure water value, and for another section, an increase in this concentration. In that regard, the analysis of the isotherms resulting from the 2 m% measurements from Gao et al. (1997) show the data to behave singularly. In fact, their measurement present a strong salting-out effect at low-to mid-pressures, but intersects the bubble curve from the (CO$_2$+H$_2$O) system before overtaking it at higher pressures and showing a salting-in effect.

Moreover, their data, at any concentration or temperature chosen, seem not to show the characteristic change of slope from the CO$_2$ phase change, which can clearly be seen for $T = 323.15$ K in the case of the saturation curve of CO$_2$ in pure water. Finally, from their data sets at $T = 373.15$ K and $p \approx 50$ MPa, one can notice the inflexion in the solubility trend. This phenomenon finds no explanation in their work, nor in the rest of the literature, and behaves dissimilarly to what was experienced for many other similar systems.

Bicarbonate ions are known in Acid-base homoeostasis in the biology field for their property of body pH buffer (see Equation 2.1).

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+$$ (2.1)

One might wonder if a displacement of equilibrium in the carbonic acid and/or bicarbonate ion concentration due to an addition of CO$_2$ and pH variations could explain the duller change in the solubility slope observed in their work for the CO$_2$ gas-to-liquid phase change. This valid point would need careful pH and chemical considerations to answer. However, no such study, quantitative or even qualitative was found in the work of Gao et al. (1997) and
CHAPTER 2. PHASE DIAGRAMS AND LITERATURE REVIEW

this makes their data difficult to justify theoretically. Moreover in their work, the solubility data for (CH₄, N₂, CO₂) in sodium bicarbonate brines are fitted using the same solubility theory (the modified Patel-Teja equation of state). It seems non-intuitive that CO₂, which is active toward bicarbonate ions (as it shifts equilibrium concentration of carbonate acid and bicarbonate ions during aqueous dissolution) presents a similar solubility pattern than the more inert CH₄ and N₂.

(a) Comparison between solubility of CO₂ in pure water and in NaHCO₃ at T = 323.15 K. — solubility of CO₂ in water (from SP solubility model), ■ Gao et al. (1997) 2% mass NaHCO₃, ■ Gao et al. (1997) 7% mass NaHCO₃.

(b) Comparison between solubility of CO₂ in pure water and in NaHCO₃ at T = 373.15 K. — solubility of CO₂ in water (from SP solubility model), ■ Gao et al. (1997) 2% mass NaHCO₃, ■ Gao et al. (1997) 7% mass NaHCO₃.

Figure 2.6: CO₂ mole fraction in NaHCO₃ aqueous solution at T = (323.15 and 373.15) K. Comparison between the work from Gao et al. (1997) at two NaHCO₃ concentrations (2 and 7) m% and the calculated CO₂ mole fraction in pure water resulting from the SP solubility model.

From this analysis, it seems that the data from Gao et al. (1997) should be used with caution until more HPHT measurements are published for this system. Aside from the cited work, the (CO₂+H₂O+NaHCO₃) system remains barren of any phase behaviour measurements in the range of pressures and temperatures of interest in this thesis. This in itself justifies the need for reliable high-pressure and high-temperature phase equilibria data for this pseudo-binary.
2.3 Literature Review of Phase Equilibria of the (N2+H2O) system

2.3.1 Available Data for (N2+H2O) system

Reviews have already been published for the (N2+H2O) system (Folas et al. (2007), Chapoy et al. (2004), Tabasinejad et al. (2011), Mohammadi et al. (2004), Mao & Duan (2006), Goodman & Krase (1931), Webster (1953)), but most of them focus on the dew point. In fact, it appears that for transportation matters (for example, pipeline transportation), this point is critical. These reviews range from the simple acknowledgement of previous studies (Chapoy et al. (2004), Tabasinejad et al. (2011), Mohammadi et al. (2004)) to their systematic evaluation (Folas et al. (2007)). However, reviews of the solubility data of N2 in water are scarcer (Mao & Duan (2006)) or old, and therefore potentially outdated (Goodman & Krase (1931)).

Bubble Point

The most recent review available is that of Mao & Duan (2006). Using their work and combining it with cross references from other works (Alvarez & Fernandez-Prini (1991), Chapoy et al. (2004), Fenghour & Wakeham (1993), Goodman & Krase (1931), Kennan & Pollack (1990), Saddlington & Krase (1934), Sun et al. (2001)), the following section will present an extended review of the available data for the solubility of N2 in water.

Figure 2.7 shows the distribution of the bubble point measurements in the literature for the (N2+H2O) system under reservoir conditions. It appears that at low temperatures ($T < 293$ K), data are not available because of the stability of N2-hydrates in this region (Mao & Duan (2006)). At higher temperatures ($T > 400$ K), very few data are present. Measurements for N2 solubility in water is rather homogeneous, as shown by Figure 2.7 and stated in Mao & Duan (2006). Analyses of the available data are made in the following section.

Dew Point

Water content of N2 at high pressure and temperature has been studied by numerous authors as summarised in Table 2.3. As shown by Figure 2.8, the data are well distributed, except for temperatures between (373 - 423) K. As stated by Folas et al. (2007), data are
scarce at low temperatures and high pressures due to the phase equilibrium of hydrates under these conditions.

2.3.2 Discussion and Evaluation of the Data

Bubble Point Data Evaluation

From Table 2.4, one can notice the absence of recent data. This could be interpreted as a proof of the high quality of the published work. In other words, no more recent work have been published for this system as they present too few discrepancies with older studies. As shown by Figure A.2, available data for the bubble point agree well with each other, other than the work of Goodman & Krase (1931). As stated by Mao & Duan (2006) and by Chapoy et al. (2004), data from Goodman & Krase (1931) deviate from that of others by over 10%. This is highlighted by Figure 2.9a and Figure 2.9b, where all data present similar trends with the exception of Goodman & Krase (1931).

In their work, Frolich (1931) only present their data in a graph from which systematic reading errors might be introduced. This issue is illustrated by Figure 2.9a, where the data from Frolich (1931) are found to deviate slightly from the trend found in the literature. Therefore, this set of data might not represent the most accurate values for N₂ solubility in water at $T = 298.15$ K. The work of Liu et al. (2012) fits well with the array of data shown by
Figure 2.8: Distribution in pressure and temperature of the water content in N\textog in the literature. Data extracted from Table 2.3. The work of Blanco et al. (1999) and Blanco & Velasco (2002) are not plotted due to their lack of agreement with the rest of the literature.

Table 2.3: Bubble point data for the (N\textog +H\textog) system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>T range /K</th>
<th>p range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanco et al. (1999)</td>
<td>250 - 284</td>
<td>0.1 - 10.9</td>
</tr>
<tr>
<td>Blanco &amp; Velasco (2002)</td>
<td>263 - 283</td>
<td>0.5 - 10</td>
</tr>
<tr>
<td>Saddlington &amp; Krase (1934)</td>
<td>323 - 438</td>
<td>10 - 30</td>
</tr>
<tr>
<td>Tabasinejad et al. (2011)</td>
<td>422 - 483</td>
<td>3.6 - 134</td>
</tr>
<tr>
<td>Fenghour &amp; Wakeham (1993)</td>
<td>410 - 595</td>
<td>7.8 - 23.5</td>
</tr>
<tr>
<td>Folas et al. (2007)</td>
<td>258 - 293</td>
<td>0.5 - 20</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1980)</td>
<td>310 - 588</td>
<td>0.3 - 13.8</td>
</tr>
<tr>
<td>Maslennikova et al. (1971)</td>
<td>298 - 623</td>
<td>5.0 - 50.7</td>
</tr>
<tr>
<td>Mohammadi et al. (2005)</td>
<td>282 - 363</td>
<td>0.4 - 5.0</td>
</tr>
<tr>
<td>Rigby &amp; Prausnitz (1968)</td>
<td>298 - 373</td>
<td>2.0 - 10.0</td>
</tr>
<tr>
<td>Sidorov et al. (1952)</td>
<td>373</td>
<td>5.1 - 40.5</td>
</tr>
<tr>
<td>Ugrozov (1996)</td>
<td>311 - 366</td>
<td>0.3 - 13.8</td>
</tr>
<tr>
<td>Althaus (1999)</td>
<td>273 - 293</td>
<td>0.5 - 10</td>
</tr>
<tr>
<td>Namiot &amp; Bondareva (1959)</td>
<td>311 - 366</td>
<td>0.3 - 3.8</td>
</tr>
</tbody>
</table>
Table 2.4: Bubble point data for the (N\textsubscript{2}+H\textsubscript{2}O) system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$T$ range /K</th>
<th>$p$ range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapoy et al. (2004)</td>
<td>274 - 363</td>
<td>1 - 7.6</td>
</tr>
<tr>
<td>Goodman &amp; Krase (1931)</td>
<td>273 - 442</td>
<td>10 - 30</td>
</tr>
<tr>
<td>Saddington &amp; Krase (1934)</td>
<td>338 - 513</td>
<td>10 - 30</td>
</tr>
<tr>
<td>Wiebe et al. (1932)</td>
<td>298</td>
<td>2.5 - 101.3</td>
</tr>
<tr>
<td>Wiebe et al. (1933)</td>
<td>298 - 373</td>
<td>2.5 - 101.3</td>
</tr>
<tr>
<td>Alvarez &amp; Fernandez-Prini (1991)</td>
<td>318 - 636</td>
<td>0.7 - 28.4</td>
</tr>
<tr>
<td>Kennan &amp; Pollack (1990)</td>
<td>298</td>
<td>4.4 - 11.5</td>
</tr>
<tr>
<td>Sullivan &amp; Smith (1969)</td>
<td>323 - 398</td>
<td>10.1 - 60.8</td>
</tr>
<tr>
<td>Smith &amp; Kelemen (1962)</td>
<td>303</td>
<td>1-5.8</td>
</tr>
<tr>
<td>Li et al. (2004)</td>
<td>375 - 398</td>
<td>10 - 61</td>
</tr>
<tr>
<td>Liu et al. (2012)</td>
<td>308 - 318</td>
<td>8 - 16</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1980)</td>
<td>310 - 478</td>
<td>0.3 - 13.8</td>
</tr>
<tr>
<td>Maslennikova et al. (1971)</td>
<td>473 - 623</td>
<td>10.5 - 46.1</td>
</tr>
<tr>
<td>Prolich (1931)</td>
<td>298</td>
<td>2 - 19</td>
</tr>
</tbody>
</table>

Figure 2.9, but the given uncertainty of their data is quite high compared to the rest of the literature. Moreover, due to the difficulty of measuring H\textsubscript{2}O in the gas phase, they assumed that for their ternary system (N\textsubscript{2}+CO\textsubscript{2}+H\textsubscript{2}O), no water vapour was present in the gas phase. This could introduce a systematic error with the values they published, and one should bear this in mind for future use of these data set.

Once the work of Goodman & Krase (1931) is put aside, small gaps in the solubility data distribution are introduced. As shown by Figure 2.7, more measurements would be beneficial at high temperatures, and generally at high pressures, to complete the study of the bubble point for (N\textsubscript{2}+H\textsubscript{2}O) system.

It is to be stated that due to the numerous citations through the different studies in the literature, the work of Wiebe et al. (1933) is of outstanding reliability. Adding to the previous statement, considering the large range of temperatures and the very large range of pressures studied by Wiebe et al. (1933), it can be admitted that their work could be considered as a reference in (N\textsubscript{2}+H\textsubscript{2}O) bubble point matter. High quality data are also provided by Sullivan & Smith (1969), Smith & Kelemen (1962), Alvarez & Fernandez-Prini (1991) and Saddington & Krase (1934). Some more recent measurements are also in agreement with the previous
references (Chapoy et al. (2004), Li & Nghiem (1986)).

As a conclusion, other than that of Goodman & Krase (1931) and Frolich (1931), all studies presented in Table 2.4 can be considered as reliable and can be used as a modelling reference for the bubble point of the (N₂+H₂O) system at HPHT.

Dew Point Data Evaluation

To evaluate the data gathered from the literature, graphs are plotted at different temperatures. Figure 2.10a presents strong agreements between the different literature sources. From this graph, the following conclusion can be drawn: due to their close agreement, the work of Folas et al. (2007), Mohammadi et al. (2005), Rigby & Prausnitz (1968), Althaus (1999) and Maslennikova et al. (1971) can be considered as reliable.

However, as shown by Figure 2.10b, data coming from Ugrov (1996) show poor agreement with the rest of the literature. In fact, when the water solubility from Ugrov (1996) are compared to that of Gillespie & Wilson (1980), the difference is found not in their value but the order of magnitude of the solubility. This puzzling statement could originate from some data processing mistakes from DEHEMA (2004). Moreover, when the data from Gillespie & Wilson (1980) are compared to that of Namiot & Bondareva (1959), the deviation between
CHAPTER 2. PHASE DIAGRAMS AND LITERATURE REVIEW

(a) Water content of $N_2$ for $T = 298$ K. □ Maslennikova et al. (1976), □ Mohammadi et al. (2005), □ Rigby & Prausnitz (1968), □ Althaus (1999), □ Folas et al. (2007).


Figure 2.10: Water content of $N_2$. Literature data for two isotherms: $T = (298, 365)$ K.

their values is found to be nil. This is illustrated by Figure 2.10b where the data sets from Gillespie & Wilson (1980) and from Namiot & Bondareva (1959) are superimposed. The fact that none of the three papers in question were accessible (obtained by means of DECHEMA (2004)) lead to the sole consideration of Namiot & Bondareva (1959) in future reference (as it is the oldest published research of the three). Furthermore, the fact that both Ugrozov (1996) and Gillespie & Wilson (1980) are cited by few references (Mohammadi et al. (2004), Tabasinejad et al. (2011)), and used by even fewer (Tabasinejad et al. (2011)), cements this conclusion.

2.4 Literature Review of Phase Equilibria of the ($O_2+H_2O$) system

2.4.1 Available Data for ($O_2+H_2O$)

Similarly to Section 2.3, only data of interest for this research have been taken into account (same range of pressure and temperature). For the ($O_2+H_2O$) system, such restriction had an important impact on the review.
CHAPTER 2. PHASE DIAGRAMS AND LITERATURE REVIEW

Figure 2.11: Distribution in pressure and temperature of the bubble point measurements for the \((O_2+H_2O)\) system. The gap for high pressure and high temperature measurements identified by Japas & Franck (1985) is clearly visible above 20 MPa.

Bubble Point

A large number of authors published measurements of \(O_2\) solubility in water focusing on the dependence with temperature and salinity. However these work mostly pertain to low pressures (Battino et al. (1983)) - under or equal to atmospheric pressure. Moreover, finding solubility data along isotherms while varying the pressure was difficult, and only very few data could be gathered. As mentioned in Japas & Franck (1985), due to the scarcity of solubility data for this system, measurements are required to fill the gaps in the literature.

Among the few authors who provide adequate data are Pray et al. (1952) and Frolich (1931). Pray et al. (1952) offer solubility of \(O_2\) in water for several isotherms from which only one \((T = 298.15\, \text{K})\) is in our range of study. They also provide solubility values for pressures \((0.7 - 2.1)\, \text{MPa}\). Pray et al. (1952) cites the work of Frolich (1931) in addition to their own measurements. Another paper which provides HPHT data is Japas & Franck (1985). However, the lowest temperature used in his system exceeds the upper limit of our temperature range. These data are, therefore, not useful in this study.

In addition to Pray et al. (1952) and Frolich (1931), the work of Zoss (1952) is one of the few found in the literature on VLE for the \((O_2+H_2O)\) system. Their data is published for temperatures \((273.15 - 545.93)\, \text{K}\) and pressures \((3.4 - 13.8)\, \text{MPa}\). In the same range
of pressures and temperatures are the measurements from Stephan et al. (1956). Their measurements are obtained for temperatures (373.15 - 560.15) K and pressures (2.2 - 20.5) MPa.

Dew Point

Dew point measurements were even scarcer than bubble point data. The only values from the literature were obtained from the work of Zoss (1952). Their data points were measured by means of three isobars (6.89, 10.34 and 13.79) MPa through a range of temperatures (304.26 - 547.59) K. Due to the absence of other measurements, it is difficult to judge the quality of these data. Other dew point measurements were done by Japas & Franck (1985), but their range of temperatures and pressures does not intersect ours.

2.4.2 Discussion and Evaluation of the Data

In the publication of Frolich (1931), one could only find Henry's law, which models the solubility of O$_2$ in water as function of the pressure. No experimental data were provided except for Henry's constant. Thus, the data found in Pray et al. (1952) and attributed to Frolich (1931) are likely resulting from some calculations. Since deviations between predictions and experiments are likely to be found (no value for deviation are given in the work of Frolich (1931)), data from Frolich (1931) should not be considered as reference.

Moreover, from the Figure A.7 it seems clear that the data from Frolich (1931) and Pray et al. (1952) (in red and green respectively) do not belong to the main array of measurements. In fact, compared to other data, which present satisfactory agreement, values from both workers seems to be too low. This judgement is only qualitative, as there is not enough data to provide a detailed comparison for given isotherms. The majority of the data for

<table>
<thead>
<tr>
<th>Authors</th>
<th>$T$ range /K</th>
<th>$p$ range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pray et al. (1952)</td>
<td>436 - 616</td>
<td>6.9 - 20.7</td>
</tr>
<tr>
<td>Frolich (1931)</td>
<td>298</td>
<td>9.7 - 25.5</td>
</tr>
<tr>
<td>Zoss (1952)</td>
<td>273 - 546</td>
<td>3.4 - 13.8</td>
</tr>
<tr>
<td>Stephan et al. (1956)</td>
<td>298</td>
<td>2.5 - 101.3</td>
</tr>
<tr>
<td>McKee (1953)</td>
<td>273</td>
<td>3.4 - 20.7</td>
</tr>
</tbody>
</table>
this system are coming from one source (Stephan et al. (1956)). This fact, along with the
difficulty to compare the available data with each other, make the literature data evaluation
hard to establish. To conclude, for reliable modelling to be developed, additional data must
be obtained for both the bubble point and the dew point in this system in all the ranges of
temperature and pressure, and more specifically for $p > 20$ MPa.

2.5 Literature Review of Phase Equilibria of ($H_2 + H_2O$) systems

2.5.1 Available Data for ($H_2+H_2O$)

($H_2+H_2O$) system bubble point

As shown by Figure 2.12, bubble point measurements for the ($H_2+H_2O$) system present
obvious gaps when $p > 20$ MPa. The only bubble point measurements for pressure above 20
MPa are that of Wiebe & Gaddy (1934). They studied five isotherms $T = (273.15$ to $373.15)$
K and pressures up to 101 MPa, and mention that $H_2$ solubility in water observes a minimum
at high pressures. Kling & Kaiserslautern (1991) offer some data for $H_2$ solubility in water
for pressures up to 12 MPa and temperatures up to 423.15 K. Also, they provide a study of
Henry’s constant. However, the only cross reference given for the ($H_2+H_2O$) is Wilhelm et al.

![Figure 2.12: Distribution in pressure and temperature of the bubble point measurements for the $H_2$-Water system. Gaps in the data are clearly visible for $p > 20$ MPa.](image)
(1977) which, due to the low pressure data set, cannot be used in our study. Dohrn & Brunner (1986) only compare their data with calculated values from a chosen equation of state, while Japas & Franck (1985) only provide data for isotherms well above the temperature range of this study.

Thus, from a direct web search and cross referencing, very few studies with the temperature and pressure of interest were found. Most of the sources obtained were provided by DECHEMA (2004). The various protagonists of the field are presented in Table 2.6 and their data are plotted in Figure A.4.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$T$ range /K</th>
<th>$p$ range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zoss (1952)</td>
<td>273 - 545</td>
<td>3.4 - 13.8</td>
</tr>
<tr>
<td>De Vaney &amp; Eakin (1976)</td>
<td>366 - 477</td>
<td>2.8 - 11.0</td>
</tr>
<tr>
<td>DeVaney et al. (1978)</td>
<td>368 - 589</td>
<td>1.4 - 11</td>
</tr>
<tr>
<td>Ipat'ev &amp; Teodorovich (1934)</td>
<td>373 - 498</td>
<td>3.1 - 10.2</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1980)</td>
<td>310 - 477</td>
<td>0.34 - 13.8</td>
</tr>
<tr>
<td>Wiebe &amp; Gaddy (1934)</td>
<td>273 - 373</td>
<td>2.5 - 10.1</td>
</tr>
<tr>
<td>Kling &amp; Kaiserslautern (1991)</td>
<td>323 - 423</td>
<td>3.2 - 15.4</td>
</tr>
</tbody>
</table>

Dew Point

As shown by Figure 2.13, the distribution of data for dew point measurements for the (H$_2$+H$_2$O) system is quite poor. It appears that there is a lack of data at high pressures (more exactly for $p > 30$ MPa). In addition, there are few data at each isotherm, making the comparison between different data sets difficult to carry out. A significant gap is present for temperatures between (350 - 415) K for both high and low pressures. Similarly, data are scarce for $T < 310$ K. Once again, available solubility measurements are insufficient for a thorough understanding of the dew point behaviour for this system. All of our data have been extracted from one source (DECHEMA (2004)) due to the absence of results when using the classical research motors (Google Scholar (2012) and Thomson Reuters (2012)).
CHAPTER 2. PHASE DIAGRAMS AND LITERATURE REVIEW

Figure 2.13: Distribution in pressure and temperature of the dew point measurements for the \((H_2+H_2O)\) system. No measurements were made for \(p > 30\) MPa.

Table 2.7: Dew point data for the \((H_2+H_2O)\) system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>(T) range /K</th>
<th>(p) range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zoss (1952)</td>
<td>341 - 606</td>
<td>6.9 - 20.7</td>
</tr>
<tr>
<td>De Vaney &amp; Eakin (1976)</td>
<td>366 - 478</td>
<td>2.8 - 11.0</td>
</tr>
<tr>
<td>DeVaney et al. (1978)</td>
<td>366 - 589</td>
<td>1.38 - 11</td>
</tr>
<tr>
<td>Maslennikova et al. (1976)</td>
<td>323 - 573</td>
<td>5 - 30</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1980)</td>
<td>311 - 478</td>
<td>0.3 - 13.8</td>
</tr>
<tr>
<td>Ugrozov (1996)</td>
<td>311 - 366</td>
<td>1.4 - 10.3</td>
</tr>
</tbody>
</table>

(a) \(H_2\) mole fraction in water for \(T = 373\) K. Ipat’ev & Teodorovich (1934), Wiebe & Gaddy (1934), Kling & Kaiserslautern (1991).

(b) \(H_2\) mole fraction in water for \(T = 423\) K. Ipat’ev & Teodorovich (1934), Wiebe & Gaddy (1934), Kling & Kaiserslautern (1991).

Figure 2.14: \(H_2\) solubility in water. Literature data for two isotherms: \(T = (373.15, 473.15)\) K.
2.5.2 Discussion and Evaluation of the Data

Bubble Point

Figure A.4 represents the bubble point data extracted from Table 2.6. All measurements, with the exception of that of Zoss (1952) at 273.15 K, agree well and show similar global trends. In fact, the measured solubility slope from Zoss (1952) at 273.15 K is abnormally high. Additionally, values extracted from this author are very different from that of Wiebe & Gaddy (1934), which is accepted as a good reference according to Kling & Kaiserslautern (1991). This is illustrated in Figure 2.14a, where one can see the consistency between the data of Kling & Kaiserslautern (1991) and Wiebe & Gaddy (1934). Data from Ipat'ev & Teodorovich (1934) are also in good agreement with the aforementioned authors.

Figure 2.14a shows that for temperatures around 423 K, the measurements reported by different authors are consistent. Therefore, for this system, all data can be considered as reliable (other that data from Zoss (1952) at $T = 273.15$ K).

Dew Point

From Figure 2.15, agreement between data is conclusive for DeVaney et al. (1978) and Gillespie & Wilson (1982), but as previously observed, the data from Ugrozov (1996) seems to be too low. The first two authors provide data in strong agreement and can likely be trusted for this system.
2.6 Literature Review of Phase Equilibria of the (H$_2$S+H$_2$O) system

2.6.1 Available Data for (H$_2$S+H$_2$O)

Among the different binaries listed in this review, the (H$_2$S+H$_2$O) phase equilibria data were expected to be scarce. As a matter of fact, H$_2$S is a very corrosive species and attacks even the best grades of stainless steel. Moreover, at HPHT this phenomena is enhanced. However, after review, at low to medium pressures, the literature does in fact contain a satisfactory number of data sets.

Bubble Point

Figure 2.16 gives the distribution of the available H$_2$S solubility data in water. The system is well studied at low pressures. However, due to the corrosive aspect of H$_2$S, very few high-pressure data are available (Selleck (1952)). No data are shown at low temperatures and pressures as it is the stability domain of hydrates (Chapoy et al. (2005)). It is worth noting that H$_2$S behaviour is very close to that of CO$_2$. In fact, a Vapor-Liquid-Liquid (VLL) curve and a three phase system (even four if one takes into account the gas hydrates) is to be expected in our range of temperatures and pressures. Details of phase presences are well-populated under the hydrate domain (Chapoy et al. (2005)), but only the work of Selleck (1952) provides Liquid-Liquid (LL) equilibrium information. Thus, the highest pressures and temperatures available stop when the LL curve is reached. For this reason, the domain above $p > 20$ MPa contains little data and will require a more extensive study for a clearer understanding of the bubble point property.

Dew Point

From Figure 2.17, one can see that for pressures above 25 MPa, measurements are yet to be made. The dew point is studied by a similar number of authors as for the bubble point (see Table 2.8). Measuring the water content of the gaseous phase appears to be more complex than measuring the bubble point (Lee & Mather (1977)). This could explain the narrower range of pressures and temperatures studied for this property compared to the bubble point.
Figure 2.16: Distribution in pressure and temperature for the bubble point measurements for the (H$_2$S+H$_2$O) system. Gaps in the literature are clearly visible for $p > 20$ MPa.

Table 2.8: Bubble point data for the (H$_2$S+H$_2$O) system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$T$ range /K</th>
<th>$p$ range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selleck (1952)</td>
<td>310 - 444</td>
<td>0.5 - 35</td>
</tr>
<tr>
<td>Kozintseva (1965)</td>
<td>433 - 603</td>
<td>&lt; 13</td>
</tr>
<tr>
<td>Burgess &amp; Germann (1969)</td>
<td>303 - 443</td>
<td>1.7 - 2.4</td>
</tr>
<tr>
<td>Koschel et al. (2007)</td>
<td>323 - 393</td>
<td>&lt; 31</td>
</tr>
<tr>
<td>Lee &amp; Mather (1977)</td>
<td>283 - 453</td>
<td>0.1 - 6.7</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1980)</td>
<td>310 - 590</td>
<td>0.1 - 13</td>
</tr>
<tr>
<td>Drummond (1981)</td>
<td>273 - 373</td>
<td>0.1 - 20</td>
</tr>
<tr>
<td>Carroll &amp; Mather (1989b)</td>
<td>313 - 378</td>
<td>0.1 - 10</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1982)</td>
<td>310 - 589</td>
<td>0.1 - 21</td>
</tr>
<tr>
<td>Suleimenov &amp; Krupp (1994a)</td>
<td>298 - 593</td>
<td>0 - 14</td>
</tr>
<tr>
<td>Chapoy et al. (2005)</td>
<td>298 - 338</td>
<td>0.4 - 4</td>
</tr>
</tbody>
</table>
CHAPTER 2. PHASE DIAGRAMS AND LITERATURE REVIEW

Figure 2.17: Distribution in pressure and temperature for the dew point measurements for the (H$_2$S+H$_2$O) system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$T$ range /K</th>
<th>$p$ range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selleck (1952)</td>
<td>310 - 444</td>
<td>0.5 35</td>
</tr>
<tr>
<td>Kozintseva (1965)</td>
<td>433 - 603</td>
<td>&lt; 13</td>
</tr>
<tr>
<td>Burgess &amp; Germann (1969)</td>
<td>303 - 443</td>
<td>1.7 - 2.4</td>
</tr>
<tr>
<td>Lee &amp; Mather (1977)</td>
<td>283 - 453</td>
<td>0.1 - 3.4</td>
</tr>
<tr>
<td>Carroll &amp; Mather (1989b)</td>
<td>313 - 378</td>
<td>2.8 - 9</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1980)</td>
<td>310 - 590</td>
<td>0.1 - 10</td>
</tr>
<tr>
<td>Drummond (1981)</td>
<td>273 - 373</td>
<td>0.1 - 20</td>
</tr>
<tr>
<td>Gillespie &amp; Wilson (1982)</td>
<td>310 - 589</td>
<td>4 - 20</td>
</tr>
<tr>
<td>Suleimenov &amp; Krupp (1994b)</td>
<td>298 - 593</td>
<td>0 - 14</td>
</tr>
<tr>
<td>Chapoy et al. (2005)</td>
<td>298 - 338</td>
<td>0.4 - 2.5</td>
</tr>
</tbody>
</table>
2.6.2 Discussion and Evaluation of the Data

**Bubble Point**

Data evaluation for the bubble point for the \((\text{H}_2\text{S} + \text{H}_2\text{O})\) system is a challenging task. As a matter of fact, \(\text{H}_2\text{S}\) undergoes a phase change to supercritical for \(T = 373.15\) K and \(p = 8.9\) MPa. Unfortunately, after review, only a few authors provide sets of measurements with pressures high enough to witness the apparition of supercritical \(\text{H}_2\text{S}\). According to Koschel et al. (2007), this change of phase implicates a sharp change in the solubility profile in such a manner that the \(\text{H}_2\text{S}\) solubility slope in water increases with pressure when in the supercritical state. This discontinuity in solubility is well-illustrated by all graphs from Figures 2.18a, 2.18b, 2.18c and 2.18d.

When \(\text{H}_2\text{S}\) is under gas form, solubility measurements throughout the literature seem to be in very strong agreement with each other. Selleck (1952), cited as the most reliable set of data by numerous authors, uses smoothed values. Such an operation made Koschel et al. (2007) point out that one should use their data with care. Moreover, Chapoy et al. (2005) calculated the deviation between the values from the literature and the computed values from their work. The work from Selleck (1952) presented the largest deviation: around 15\% while the relative uncertainties given by Chapoy et al. (2005) were \(\pm 5\%\). Aside from this analysis, Figure 2.18a and Figure 2.18c show that the measurements of Selleck (1952) are consistent with other data sets from the literature.

Fernandez-Prini (2003) discarded the works from Suleimenov & Krupp (1994a), Kozintseva (1965) and from Drummond (1981). They pointed out a lower solubility value, likely due to the formation of iron sulfide and hydrogen from the corrosion of the stainless steel set up. Therefore, these data sets should not be considered as highly reliable.

Solubility data for \(\text{H}_2\text{S}\) in water for temperatures and pressures above the critical point of the hydrogen sulphide are much less in agreement with each others. The only two authors providing such information are Koschel et al. (2007) and Gillespie and Wilson (1982). Koschel et al. (2007), the most recent of the two, highlights the differences between their work and that of Gillespie and Wilson (1982), which appears to be systematically higher. The \(\text{H}_2\text{S}\) Henry’s constant from Gillespie and Wilson (1982) proves to be lower than the computed value from Fernandez-Prini (2003). According to Koschel et al. (2007), this could imply a
CHAPTER 2. PHASE DIAGRAMS AND LITERATURE REVIEW

(a) \( \text{H}_2\text{S} \) mole fraction in water for \( T = 310.15 \) K. Chapoy et al. (2004) (\( T = 308.15 \) K), Gillespie & Wilson (1982), Selleck (1952), Lee & Mather (1977) (\( T = 313.15 \) K).

(b) \( \text{H}_2\text{S} \) mole fraction in water for \( T = 323.15 \) K. Chapoy et al. (2004), Burgess & Germann (1969), Selleck (1952), Koschel et al. (2007).

(c) \( \text{H}_2\text{S} \) mole fraction in water for \( T = 344.15 \) K. Selleck (1952), Burgess & Germann (1969), Lee & Mather (1977), Gillespie & Wilson (1982), Drummond (1981).

(d) \( \text{H}_2\text{S} \) mole fraction in water for \( T = 393.15 \) K. Selleck (1952), Burgess & Germann (1969), Drummond (1981), Koschel et al. (2007).

Figure 2.18: \( \text{H}_2\text{S} \) solubility in water. Literature data for four isotherms: \( T = (310, 323, 344 \text{ and } 393) \) K.
systematic error, but too few data are available to confirm this conjecture. More data should be obtained to shine a light on the LL behaviour of this system.

Dew Point

Data provided by Lee & Mather (1977) and by Carroll & Mather (1989a) present the highest deviations when compared to the calculated values from the correlation of Chapoy et al. (2005). In their work, both authors state that measurements of water content in the gas phase were inaccurate due to difficulties to establish the reproducibility of their experiments. Thus, data from Lee & Mather (1977) and from Carroll & Mather (1989a) are not be considered as highly reliable.

Figure 2.19 highlights the differences in solubility measurements from the three authors. From previous statements, Carroll & Mather (1989a) experiments likely underwent systematic deviations, which disqualifies their data. It is not clear which data set, between that of Gillespie and Wilson (1982) and that of Selleck (1952), represents the true dew line for this system. Both works are often used for model calculations. However, the data from Burgess & Germann (1969) and the data from Selleck (1952) present strong agreement in Figure A.5 (respectively the orange and red points). Likewise, at low pressure, solubility measurements from Chapoy et al. (2005) are in agreement with Selleck (1952). These two instances set the dew point measurements from Selleck (1952) as reliable for this system.
2.7 Literature Review of Phase Equilibria of the (SO$_2$+H$_2$O) system

Of all the systems, the phase behaviour data for sulphur dioxide and water is the least investigated. In most cases, the concentration of SO$_2$ is relatively low compared to saturation concentration. Some authors justify this low concentration interest to the real case scenario of flue gases generated in fossil-fired power plants (Siddiqi et al. (1996)). Moreover, a large majority of these data are at low pressure to ambient pressure. In fact, all pressures are below the saturation pressure of SO$_2$. In the vicinity of the saturation pressure a second aqueous phase forms below the gaseous phase (Shaw et al. (2011), Berkum & Diepen (1979))

2.7.1 Available Data for (SO$_2$+H$_2$O)

Bubble Point

From the available literature, the most comprehensive work on SO$_2$ solubility in water is that of Rumpf & Maurer (1992). In their work, the temperature range is (298.15 - 398.15) K and the pressure range (0.035 - 2.5) MPa. Moreover, their work is among the few to publish saturated concentrations of SO$_2$ in water. Other authors publishing saturated measurements are presented in Table 2.10. Another author to have published data at high pressure (p to 15 MPa) is Sayegh & Najman (1987), who studied SO$_2$ solubility in water at $T = 323$ K. It is stated that the solubility of SO$_2$ in water is greater than the solubility of CO$_2$ at the same pressure and temperature. Moreover, an unusual trend for solubility is described: the solubility measurements provided do not change with pressure. SO$_2$ solubility in water reaches a plateau at 7% in mole fraction. Berkum & Diepen (1979) give solubility of SO$_2$ in water up to 39% in mole fraction. They provide phase diagrams for temperatures up to 400 K and pressures up to 400 MPa. However, their study focuses on gas hydrates formation, and thus offers few points in the temperature and pressure range of interest here.

Dew Point

To this day, only one set of data on the water content in SO$_2$ has been found (Sayegh & Najman (1987)). However, this work is more than 50 years old and present an unlikely trend in their measurements. Therefore, it seems likely that the dew point of this system has been
Table 2.10: Bubble point data for the (SO$_2$+H$_2$O) system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$T$ range /K</th>
<th>$p$ range /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maass &amp; Maass (1928)</td>
<td>283 - 300</td>
<td>0.03 - 0.3</td>
</tr>
<tr>
<td>Hudson (1925)</td>
<td>283 - 363</td>
<td>0.1 - 0.13</td>
</tr>
<tr>
<td>Campbell &amp; Maass (1930)</td>
<td>298 - 383</td>
<td>0.01 - 0.45</td>
</tr>
<tr>
<td>Sayegh &amp; Najman (1987)</td>
<td>323</td>
<td>0.1 - 15</td>
</tr>
<tr>
<td>Rumpf &amp; Maurer (1992)</td>
<td>298 - 378</td>
<td>0.03 - 2.5</td>
</tr>
<tr>
<td>Berkum &amp; Diepen (1979)</td>
<td>272 - 400</td>
<td>0 - 400</td>
</tr>
</tbody>
</table>

poorly studied.

2.7.2 Discussion and Evaluation of the Data

Bubble Point

As stated previously, the only work providing solubility measurements at high pressures is that of Berkum & Diepen (1979), with the other data uniquely focused on low pressures. Solubility behaviour for this system is mostly unknown, as the whole range of pressure and temperature of interest is yet to be measured. The data of Berkum & Diepen (1979) should be used as a landmark when possible.

Dew Point

The single data set available provides measurements whose behaviour with $p$ seems non-intuitive. Solubility of water in SO$_2$ turns out to be very quickly constant (around 20% in mole fraction for $p$ above 0.6 MPa) and does not present changes with pressure. This trend remains difficult to assess without other data to compare them with. Again, for this system, all HPHT data will be novel and much needed data for thermodynamic purposes.
2.8 Conclusions of the Literature Gap Analysis

In this chapter, clear gaps in the literature were identified for the phase-behaviour of the binaries of interest under the pressure and temperature range at stake in this work. The conclusions of the available data sets analysis can be summarised as follow:

• The (CO$_2$+H$_2$O) binary contains little potential for new measurements in the pressure and temperature range of interest in this study- $p = (0.1 - 60)$ MPa and $T = (303.15 - 473.15)$ K.

• The (CO$_2$+H$_2$O+NaCl) system, although not as thoroughly explored as the (CO$_2$+H$_2$O) binary, has been extensively measured at $p = (0.1 - 60)$ MPa and $T = (303.15 - 473.15)$ K. Some areas of the $pT$ data distribution graph could be explored more extensively (fewer data sets at pressure higher than 20 MPa), but little mystery lies within them as no phase transition happens in their vicinity. HPHT VLE experimental efforts should be invested in other CO$_2$ pseudo-binaries.

• The (CO$_2$+H$_2$O+NaHCO$_3$) pseudo-binary remains un-studied at $p = (0.1 - 60)$ MPa and $T = (303.15 - 473.15)$ K. Experiments for this salt-species are both needed and valuable, as this compound can be highly concentrated in water formations at depths in the Atlantic, Gulf Coastal Plains and South China Sea. The only HPHT solubility data set available in the literature for this system presented peculiar trends and more HPHT measurements must be published for this system.

• The (H$_2$+H$_2$O) system is poorly studied. Bubble point measurements for this system present obvious gaps when $p > 20$ MPa and $T = (303.15 - 473.15)$ K. The distribution of measurements for the dew point is poor. There is a lack of data for $p > 30$ MPa and few data for each studied isotherms.

• The number of available data in the literature for the (O$_2$+H$_2$O) system is scarce in the range of pressure and temperature $p = (0.1 - 60)$ MPa and $T = (303.15 - 473.15)$ K. There is no measurements for the bubble point at $p > 20$ MPa and even under this threshold pressure data are few. The dew point is even less studied as only one author published in the range of temperature and pressure of interest in this thesis.

• The phase equilibria data for (H$_2$S+H$_2$O) are in satisfactory number at low to medium pressures ($p < 20$ MPa for all isotherms such that $T = (313.15 - 473.15)$) but the domain
above $p > 20$ MPa contains hardly any measurements for both the bubble and the dew point.

- Of all the systems, the phase behaviour data of the $(SO_2S+H_2O)$ system is the least investigated. All found studies maintained their pressure range below the saturation pressure of $SO_2$. The most comprehensive work on $SO_2$ solubility in water offers a temperature and pressure range of $(298.15 - 398.15) K$ and $(0.035 - 2.5) MPa$ respectively. The dew point is mostly unstudied under the conditions of interest in this work.
Chapter 3

Thermodynamic Properties Modelling

Thermodynamic properties are measurable quantities defined to describe the state of a system, usually at equilibrium. The quality of the answers to chemical engineering problems is often related to the quality of the data available. Due to the almost infinite variation of temperature, pressure and composition of study, it is not practical to rely solely on discrete experimental data for thermodynamic properties of a system. Instead, models must be developed and link these data in a continuous manner. This process is achieved by expressing the thermodynamic properties of interest as functions of the condition of the system: the pressure, the temperature and also its composition. Although the end goal of any thermodynamicist, finding such a formulation can be a cumbersome task. In this research, the properties of interest are the solubility limits of one species in another, function of temperature and pressure. The mutual solubility of two fluids is obtained by characterising the composition of all phases at stake under thermodynamic equilibrium (Liquid-Vapour, Liquid-Liquid or Liquid-Liquid-Vapour). These values are usually expressed in a normalised, standard format that is the mole fraction. To predict the value of the solubility of species $i$ in the gas phase, conventionally written $y_i$, or in the liquid phase, written $x_i$, one must embark on a journey where ideality is the first stop. This concept of ideality, however, must be abandoned at an early stage in order to gain a better understanding of the behaviour of the real fluids. Core thermodynamic concepts, such as chemical potential, fugacity and activity, must be introduced to accompany the reader in this journey.
3.1 Thermodynamic Equilibrium

3.1.1 Introductory Concepts

Understanding the thermodynamics of a system generally comes down to quantifying the infinitesimal changes of the energy of a system. Thermodynamic studies, in majority, focus on settled thermodynamic equilibrium, away from any transient state. This translates to a constant temperature and pressure. However, matter can still be transformed, for example via a chemical reaction or interfacial mass transfer. At equilibrium, the internal energy \( U \) of a system of \( N \) species is function of the temperature \( T \), pressure \( p \), chemical potential \( \mu_i \) and the independent variables the volume \( V \), entropy \( S \), and composition, in amount of substance \( n_i \), with \( i \) subscript for each species. The literal relationship that links the infinitesimal change of \( U \) from equilibrium (\( p \) and \( T \) constant) with all its variables is as follow:

\[
dU = TdS - pdV + \sum_{i}^{N} \mu_i dn_i
\]  
(3.1)

Equation 3.1 is a part of the second law of thermodynamics. It embodies the reversible and irreversible changes in entropy, volume and matter for an open or closed system at constant temperature and pressure. From the definition of the derivative of a function, one can write:

\[
dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial p} \right)_S dp + \sum_{i}^{N} \left( \frac{\partial U}{\partial n_i} \right)_{S,V,p_j} d\ln n_i
\]  
(3.2)

And therefore, by identification from Equation 3.1, for a species \( i \) in a system of \( N \) components:

\[
\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,p_j}
\]  
(3.3)

with \( j \neq i \) and \( \{i,j\} \in [1;N] \)

It is usually more practical to use the Gibbs energy, \( G(p,T,n_1, \ldots ,n_N) \), another thermodynamic potential. This is because it is typically difficult to keep \( S \) and \( V \) constant while changing \( n_i \). The Gibbs energy is defined as:
$G = U + pV - TS$ \hspace{1cm} (3.4)

which yields

$$dG = Vdp - SdT + \sum_{i} N_{i}d\mu_{i}$$ \hspace{1cm} (3.5)

and therefore

$$\mu_{i} = \left(\frac{\partial G}{\partial n_{i}}\right)_{T,p,n_{j}}$$ \hspace{1cm} (3.6)

At this point, it is useful to introduce the concept of a phase. A phase is a macroscopic volume of matter, throughout which all intensive functions (for example pressure, temperature, composition and density) are homogeneous once thermodynamic equilibrium is attained. Classic examples are the gas, the liquid and the solid phases. Let us then consider a system composed of $N$ components separated in two phases: a vapour phase and a liquid phase. For thermodynamic equilibrium to be met in this system, three conditions are met (Bett et al. (1975)):

- The temperature of the liquid and the vapour must be equal for thermal equilibrium to be satisfied.
- The pressure of the liquid and the vapour must be equal for mechanical equilibrium to be satisfied.
- The Gibbs energy must be at a minimum in regard to any component exchange between both vapour and liquid phases.

This last condition can be re-written literally as:

$$\delta G = [\mu_{i}(\text{gas}) - \mu_{i}(\text{liquid})] \delta n_{i} = 0$$ \hspace{1cm} (3.7)

In other words, satisfying a thermodynamic state where the chemical potential of each phases for each species are equals necessarily leads to thermodynamic equilibrium:

$$\mu_{i}^{g} = \mu_{i}^{l},$$ \hspace{1cm} (3.8)

where the superscripts $l$ and $g$ are used for the liquid and the gas respectively. Providing a quantitative analysis of the thermodynamic equilibrium of a system starts by solving Equation
3.8. However, this equation has no value without a literal expression between the chemical potential and the system variables: pressure, temperature and composition. The Gibbs-Duhem equation provides the first insight on such a relationship. The derivation of this equation is straightforward (Prausnitz et al. (1998)) and can be expressed as follows:

\[ s_i dT - v_i dp + \sum_{i} n_i d\mu_i = 0, \quad (3.9) \]

where \( s_i \) and \( v_i \) are the molar entropy and partial molar volume of species \( i \). From Equation 3.9, the change in chemical potential for a species \( i \) is the result of a combination of temperature and pressure change at constant entropy, volume and concentration. For a pure fluid, one can establish, equating the expression of the derivative of the chemical potential with \( T \) and \( p \) as variables, with Equation 3.9 that:

\[ \left( \frac{\partial \mu_i}{\partial p} \right)_T = v_i \quad (3.10) \]

Considering the simple case of an ideal gas (described in subsection 3.2.1) and integrating the two members of Equation 3.10 from \( p^0 \), (an arbitrary pressure chosen as reference), to the equilibrium pressure \( p_i \), one can write as follow:

\[ \mu_i = \mu_i^0 + RT \ln \frac{p_i}{p^0} \quad (3.11) \]

Equation 3.11 is only valid for ideal gases. Once the intermolecular potential cease to negligible (increase in density or pressure), the validity of such equation is terminated. This departure from the ideal case was accounted for by Lewis, who defined the fugacity function as:

\[ \mu_i = \mu_i^0 + RT \ln \frac{f_i}{f^0} \quad (3.12) \]

such that

\[ \lim_{p \to 0} \frac{f_i}{y_i p} = 1 \quad (3.13) \]
3.1.2 Quantifying the Thermodynamic Equilibrium in an Ideal System

The fugacity can be seen as a "corrected pressure". It creates a bridge between the behaviour of an ideal mixture, which is based purely on thermodynamics, to that of a real fluid, for which intermolecular forces need to be taken into consideration. For a pure, ideal gas, \( f = p_i \), and for a species \( i \) in a mixture of ideal gases, \( f_i = p_i = y_i p \). Equation 3.12 describes the chemical potential as a function of fugacity along an isotherm. The relationship remains valid for any component in any phase, solid, liquid or gas, pure or mixed, ideal or not. Such a statement is rare and explains why it has led to many usages in thermodynamics as well as in chemistry (for example with Nernst's law). One can re-write Equation 3.8 using Equation 3.12 as an equivalent thermodynamic equilibrium condition:

\[
 f_i^g = f_i^l 
\]  

For ideal gases Henry's law states that, at infinitely dilute concentration, the concentration of a species \( i \) in a liquid solute \( j \) is proportional to its partial pressure \( p_i \) in the gas phase: \( p_i = H_{ij} x_i \) (Mackay & Shiu (2009)). \( H_{ij} \) is Henry's constant for the component \( i \) in component \( j \), and is only a function of the temperature. Therefore, for a mixture of ideal gases in equilibrium with a condensed phase (granted that such equilibrium exists at low pressures), one can write the following:

By definition \( f_i^g = y_i p \) \hspace{1cm} (3.15)

From Henry's Law \( f_i^l = H_{ij} x_i \) \hspace{1cm} (3.16)

From Equation 3.14 \( y_i p = H_{ij} x_i \) \hspace{1cm} (3.17)

Equation 3.17 provides a direct way to obtain the solubility of any component \( i \) in any phase, provided that the system studied is ideal, infinite dilution conditions are respected, and pressure is low. Such a relationship in itself is fully justified theoretically and proves to be reliable when applicable. On the other hand, its range of applicability is narrow and when studying more common real systems, one needs to obtain more accurate predictions for the Vapour-Liquid-Equilibrium (VLE). Instead of building another theory from scratch, thermodynamicists built on the ideal fluid theory and developed new notions to fit it when
solubility and/or pressure and/or density and/or associativity and/or asymmetry are low.

3.1.3 Quantifying the Thermodynamic Equilibrium in a Real Mixture

To take into account that Equation 3.17 deviates from measured solubility values for real systems, the activity $a_i$ of a species $i$ in a fluid (gas or liquid) is defined as such:

$$a_i(T, p, x_1, x_2, \ldots, x_N) = \frac{f_i(T, p, x_1, x_2, \ldots, x_N)}{f^0_i(T)}$$

(3.18)

The activity is a function that describes how "active" a component is in relation to its pure standard state. This definition brings a new expression for Equation 3.12 such that:

$$\mu_i - \mu^0_i = RT \ln a_i$$

(3.19)

Therefore, the value of the activity $a_i$ of a substance $i$ in a mixture is proportional to the difference between the chemical potential of the substance and the value of its reference chemical potential at the studied temperature. The activity $a_i$ of a species in a real liquid can also be linked to its mole fraction $x_i$ with:

$$a_i = \gamma_i x_i,$$

(3.20)

with $\gamma_i$ being the activity coefficient of the substance $i$ in the liquid. $\gamma_i$ translates the non-ideality of the substance, with $\gamma_i = 1$ when the component is under the conditions of ideality. One then finds that, for an infinitely dilute solution, at low pressures:

$$a_i = x_i = \frac{f_i}{f^0_i}$$

(3.21)

Equation 3.20 leads to the expression of the fugacity of a substance $i$ in a real liquid, at low to moderate pressures (inferior to 5 MPa):

$$f^i_i = \gamma_i x_i f^0_i$$

(3.22)

When taking into consideration the effect of pressure on the activity, one has to introduce
a corrective factor known as the Poynting factor, $\tilde{F}_i$, which is defined as follows:

$$\tilde{F}_i = \exp \left[ \int_{P_i^{\text{sat}}}^{P} \left( \frac{v_i}{RT} \right) \, dp \right], \quad (3.23)$$

where $v_i$ is the partial molar volume of the substance $i$. A succinct justification for the expression of this factor can be felt when looking at Equations 3.10 and 3.13. The full derivation of its origin can be found in thermodynamic and fluid-phase equilibria books (Prausnitz, Lichtenthaler & de Azevedo (1999)). Finally, the expression for the corrected fugacity of a species $i$ in a real liquid at any pressure is:

$$f_i^l = \gamma_i \, x_i \, f_i^0 \tilde{F}_i \quad (3.24)$$

Following the same consideration for departure from ideality, the fugacity coefficient of a gas $i$ in a mixture, $\phi_i$, is defined as:

$$\phi_i = \frac{f_i}{y_i \, p} \quad (3.25)$$

with $y_i$ being the gaseous mole fraction of substance $i$ in the mixture, and $p$ the total pressure of the system. $\phi_i$ represents how different $f_i$ is from $p_i$, with the bridge with ideality assured by $\phi_i = 1$ when the gas considered is ideal. In turn, Equation 3.25 yields the general expression of the fugacity of a real gas in a mixture:

$$f_i^g = \phi_i \, y_i \, p \quad (3.26)$$

Using Equation 3.14 and replacing the fugacity expressions with Equations 3.24 and 3.26, one can write the conditions for thermodynamic equilibrium for a VLE of a real system as:

$$\phi_i \, y_i \, p = \gamma_i \, x_i \, f_i^0 \tilde{F}_i \quad (3.27)$$

This equation is the starting point of most HPHT VLE problems. For temperatures under the critical point of the fluid, the chosen state for $f_i^0$ is that of the saturated pure substance at the given temperature. This is a useful reference, as then: $f_i^0 = \phi_i^{\text{stat}} \, P_i^{\text{stat}}$. The saturation fugacity coefficient of a pure substance at a set temperature can be measured using an Equation of State (EoS): see Equation 3.30. Also, the saturation pressure of a pure
substance at a set temperature can either be measured or calculated through a polynomial function of \((1/T)\) (one of the simplest forms being Antoine’s equation).

In this study, only binary systems are of interest, therefore one component is considered as the solvent (usually the less volatile, in this case it is water) and the other as the solute (the gas). Usually, one is interested in obtaining the solubility of the gas in the liquid-rich phase \((x_{\text{gas}})\) and the solubility of the solvent in the gas \((y_w)\). To finally obtain either of these solubilities, one has to first obtain a relation for both, the activity coefficient and the fugacity coefficient, following a procedure known as \(\gamma\)-\(\phi\).

Calculating the Activity Coefficient

Numerous activity-coefficient models were developed to accommodate the excess Gibbs energy, \(G^E\) of non-ideal aqueous systems. All such models describe the activity coefficient as a function of temperature and composition at constant pressure. They are not fully theoretical as, in the best case scenario, their parameters are fitted around experimental value of binaries at one set temperature. They do however, provide predictions for a range of pressures and temperatures for systems composed of two or more components.

The oldest of the models still used in its original form is that of Margules (1895), based on partial derivation of the Gibbs-Duhem equation. It gives the logarithm of the activity coefficient by a power series in composition for each component. Its full form is hardly ever used as its "two-term" equation was deemed to be sufficient for satisfactory activity-coefficient calculations. The "truncated" two-terms equation, slightly arranged as per Carlson & Colburn (1942) work, follows as such:

\[
\ln \gamma_1 = (2B - A)x_2^2 + 2(A - B)x_2^3 \tag{3.28}
\]

\[
\ln \gamma_2 = (2A - B)x_1^2 + 2(B - A)x_1^3 \tag{3.29}
\]

Van Laar derived a fully mathematically justified activity-model coefficient from van der Waals EoS and mixing rules. Although it had a sound theory, due to the fact that its parameters are based on empirical values, its predictive features are only limited. A new theory was introduced with Wilson’s model, who for the first time drafted the concept of "local molality." It states that the concentration in the local volume surrounding a molecule is different than that of the bulk. This is explained with the difference in the energy of
interaction between the central molecule and both the like and the non-like molecules. Based on Wilson’s work and to improve the model weaknesses in describing Liquid-Liquid Equilibriums, other activity-coefficient models were developed. The most successful are the Non-Random Two-Liquid model (NRTL) \( (\text{Renon & Prausnitz (1968)}) \), the T-K-Wilson and the Universal Quasi-chemical (UNIQUAC) \( (\text{Abrams (1975)}) \).

The field of modelling activity-coefficients has depths that extend beyond the range of this work, therefore the curious mind is directed toward the literature which offers extensive details about this matter \( (\text{Prausnitz, Lichtenthaler & Azevedo (1999), Assael et al. (1996), Bett et al. (1975)}) \).

Calculating the Vapour Fugacity Coefficient

By injecting the integral of Equation 3.10 (choosing for the reference state a low pressure state, for which \( f_i^0 = y_i P \)) in Equation 3.12, one arrives to:

\[
\ln \phi_i = \ln \left( \frac{f_i}{y_i P} \right) = \frac{1}{RT} \int_0^P \left( \frac{\nu_i - \frac{RT}{P}}{p} \right) dp,
\]

where \( \nu_i = \left( \frac{\partial V}{\partial n_i} \right)_{T, p, \sum_j} \) is the partial molar volume of \( i \). From Equation 3.30, one can see that obtaining the fugacity coefficient starts by obtaining a literal expression for the volume in function of \( T, p \) and the composition. In other words, an EoS is the necessary start for fugacity coefficient calculation. Many such equations have been developed through the years, some fully theoretical (virial equations of state) and others more empirical (Van der Waals and cubic EoS). With the least amount of fitting comes the highest predictive power of an EoS. Therefore, if the virial EoS could provide good prediction for high density fluid, it would be the favourite choice for thermodynamic properties calculations. Unfortunately, due to the high density of the condensed fluids considered in this research, and the high pressures involved, this type of EoS does not provide the satisfactory range of study conditions. Therefore, for the HPHT VLE calculations it is classic to orient oneself to cubic EoS. In the following section, the main cubic equations of state are presented with their applicability and drawbacks, as well as their advantages.
3.2 Cubic Equation of State

3.2.1 Ideal Gas Law

Since 1662, when Boyle first established that at constant mass and fixed temperature, the product of the pressure and volume of a gas was close to a constant, fantastic advancements have been brought to the field of thermodynamic properties modelling. The discovery of the Gay-Lussac’s law, in combination with Boyle’s law, lead to the ideal-gas EoS, expressed in Equation 3.31.

\[ p = nRT/V \] (3.31)

It states that, for an ideal gas or for a real gas behaving like an ideal gas, the product of the pressure \( p \) and the volume \( V \) is directly proportional to the number of mole in the gas \( n \) and its temperature \( T \). The proportionality ratio is the universal gas constant \( R \), equal to 8.314471 J.mol\(^{-1}\).K\(^{-1}\) (Moldover et al. (1988)). Although this law is useful as an introduction to the science of phase equilibria, its applicability is fairly limited. As a matter of fact, an ideal gas is defined as a gas where no intermolecular forces are taken into account. This is the case for most diluted gases where each of the molecules are far enough from each other to be considered as a particle in a black box. However, when temperature decreases or pressure increases, the density of a real gas increases, the average intermolecular distances are reduced and the attraction and repulsion forces between molecules cease to be negligible.

3.2.2 Van der Waals’ Equation of State

The departure from the perfect gas is the problem van der Waals addressed in his dissertation of 1873 "On the continuity of the gas and liquid state" (van der Waals & Rowlinson (1988)). The EoS in Equation 3.32, which bears his name today, provides a better description of real gas behaviour and has been the basis of most modern EoS used by Chemical Engineers around the world.

\[ p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \] (3.32)

Van der Waals EoS differs from the perfect gases EoS as it takes into consideration the average intermolecular attraction, with the addition of parameter \( a \), and the repulsion parameter with the excluded-volume \( b \). At constant pressure and temperature, this equation
is a 3rd order polynomial in molar volume \( V_m \) (rewriting Equation 3.32 as Equation 3.33). This leads the branch of equations of state inspired from van der Waals Equation of State (VdW EoS) to be referred to as "cubic EoS".

\[
V_m^3 - V_m^2 \left( b + \frac{RT}{p} \right) + V_m \frac{a}{p} - \frac{ab}{p} = 0 \tag{3.33}
\]

Equation 3.33 presents three roots for temperatures below the critical point. Amongst these three values of \( V_m \), the smallest one corresponds to the highest density and therefore describes the liquid form of the substance. Likewise, the highest root describes the gas phase. The middle root has no physical significance. For temperatures higher than \( T_c \), the critical temperature, only one real root is found, which is expected from the definition of a critical fluid. Formally, the critical point is defined as follows:

\[
\left( \frac{\partial p}{\partial V} \right)_T = 0 \quad \text{and} \quad \left( \frac{\partial^2 p}{\partial V^2} \right)_T = 0 \tag{3.34}
\]

Using the two conditions in Equation 3.34, one can come to a literal expression for both coefficients, \( a \) and \( b \):

\[
a = \frac{3p^c}{(V_m^c)^2} = \frac{27(RT^c)^2}{64p^c} \quad \text{and} \quad b = \frac{V_m^c}{3} = \frac{RT^c}{8p^c} \tag{3.35}
\]

The simplicity of the results in Equation 3.35 proves to be helpful when working with mixtures. As a matter of fact, when working with a fluid composed of \( N \) components, one can apply the pure-fluid EoS defined in Equation 3.32 to the mixture, with the condition that \( a \) and \( b \) are defined as follows (Assael et al. (1996)):

\[
a = \left( \sum_{i=0}^{n} x_i \sqrt{a_i} \right)^2 \quad \text{and} \quad b = \sum_{i=0}^{n} x_i b_i \tag{3.36}
\]

With the \( a_i \) and \( b_i \) of each species being calculated as if the species were pure fluid. One can then re-use the expressions in Equation 3.35. Such correlation between the pure-fluid and the repulsion and attraction coefficients of the mixture are known as the Van der Waals mixing rules. It is one of the simplest mixing rules as it considers no interaction between the different species molecules.
The several levels of simplifications necessary to establish Van der Waals’ EoS result in limitations in the prediction of Vapour-Liquid equilibria. In fact, when compared with the experimental data, the vapour-liquid coexistence calculations are qualitatively sound, yet quantitatively unsatisfactory. Following VdW EoS’ path, and in order to improve the shortcomings of its predictions, many equation of states were developed based on the same cubic form. They are usually expressed in the following general expression:

\[ p = \frac{RT}{V_m - b} - \frac{a(T)}{(V_m + c_1 b)(V_m + c_2 b)} \]  

(3.37)

with \( c_1 \) and \( c_2 \) being integers. The modifications to VdW EoS are brought on its second term. In fact, it is admitted that, for chemical engineering applications, failure to include the repulsion parameter in the equation has less impact than doing so for the attraction parameter. Therefore, with an eye to bring about improvement, the nature of the parameter \( a \) is changed from a constant to a function of temperature. Usually, this function will still hold the "old" parameter \( a \) as a factor to extend the validity of the equation from pure fluid to mixture via the adequate mixing rule.

### 3.2.3 Cubic Equations of State

**Redlich-Kwong Equation of State**

Redlich-Kwong equation of state was considered as a considerable step toward accurate thermodynamic property predictions. As a matter of fact, it proved that a simple adjustment, (introducing the concept of binary interaction parameters in the attractive term), could significantly improve the prediction of vapor-phase properties. It brought back interest into cubic EoS for engineering calculations, as before its publication in 1949, the favoured tool (the Benedict-Webb-Rubin EoS) was much more costly in computational power.

There appears to be no theoretical basis behind the equation from the author's work. Rather, its improvement lays behind empirical model tunings (Redlich & Kwong (1949)). One can see that the mixing rule used in Equation 3.39 is built on that of VdW (called "classic mixing rule") with the addition of the binary interaction parameters, \( k_{ij} \), which corrects for the deviation of \( a \) from the geometric mean. The interaction parameters are
close to zero for hydrocarbon/hydrocarbon binaries, but their value increases for other type of binaries. Moreover, only cross-binary interaction parameters are non nil ($k_{ij}=0$) (Tsonopoulos & Heidman (1985)). This addition granted RK EoS strong predictive power for some binaries systems, mostly gaseous and away from their critical point. Latter modifications of this equation provided little improvements until the acentric factor was introduced in the mixing rule. This factor accounts for the non-sphericity of the molecules, which yielded significantly improved EoS predictions. The most famous work presenting such results is that of Soave (1972).

Soave Equation of State and Peng-Robinson Equation of State

The equations of state from Soave-Redlich-Kwong (SRK, built on the earlier RK EoS, Soave (1972)) and from Peng-Robinson (PR, Peng & Robinson (1976)) are considered the most accurate equations for phase equilibria prediction for pure fluids and for mixtures. Thanks to the appropriate model tuning resulting from tailored mixing rules, and incorporating the acentric factor, the EoS describes best phase equilibria of mixtures containing light hydrocarbon or small, non-polar molecules.

SRK and PR are very similar in their expressions. In fact, these equations have turned the attraction parameter, $a$, into a function of both the temperature $T$ and the acentric factor $\omega$. This helps both EoS to perform similarly well for VLE predictions, although PR has a slight advantage on predictions of the liquid density (Tsonopoulos & Heidman (1985)). On the other hand, due to an emphasis on the accuracy of predictions for the vapour pressure of the pure fluid, the reliability of liquid properties predictions for these EoS is poor. This deviation is accentuated in asymmetric systems or systems with associative bonds in the fashion of the hydrogen bonding (Soave (1972)). Two parameters EoS (attraction and repulsion parameters)
cannot provide accurate predictions for VLE and liquid density while at the same time yielding reliable vapour density. Such a shortfall to describe liquid phases, amongst many other theories, led to the development of the introduced $\gamma$-$\phi$ method.

In conclusion, in order to obtain reliable predictions of the solubility of gases in aqueous systems and electrolytes at HPHT, it was necessary to develop further research and developments in activity-coefficient modelling for the liquid phase, in excess Gibbs energy calculations for the gaseous phase, and in system-specific mixing rules. This complex route is the one followed by many authors (Duan et al. (1992), Duan & Sun (2003), Duan et al. (2007), Spycher et al. (2003), Spycher & Pruess (2005, 2010)) and it is the route taken in this work. The theory for these incremental improvements of cubic equation of states is presented in subsection 6.3.3.
Chapter 4

Presentation of the Existing Apparatus in the Thermophysics Laboratories

To obtain HPHT solubility of a solute in a solvent, one usually uses a synthetic or an analytical method. Both options present advantages and drawbacks, and selection of the technique depends on the system and the conditions of study.

The analytical method is based on direct analysis of a sample from the solution to be measured. This usually leads to repeatable and accurate measurements, as the array of detectors is vast and offers an option for most solubility ranges. On the other hand, due to the conditions at play with HPHT, the number of phases, the nature of the components and the solubility levels, obtaining a reliable measurement via an analytical system can easily turn into a complicated process.

The synthetic method has the advantage of relative simplicity, as no direct measurement of composition is required. The solubility is obtained via calculations from the knowledge of the controlled amount of each component in the system, which is known through the use of Equations of State (EoS). These latter are functions of the conditions of operation such as the volume, the temperature and the pressure. With this method, there is therefore a larger error carried with the measurements than that of the analytical method. Indeed, the solubility resolution can only be as high as the combined resolutions at which the experimental conditions have been measured. On the other hand, because it only relies on visual observation and quantitative assessments of temperature, pressure and volumes, instead of cumbersome phase sampling and analysis, the synthetic method provides a fairly simple way of obtaining satisfactory solubility measurements.
Considering the arguments presented, it was only logical that the experimental work of this research started with a synthetic apparatus.

4.1 The Synthetic Apparatus

The equipment used during this investigation was inherited from previous colleagues (Tong et al. (2013)), who successfully measured the CO₂ solubility limit in water and brines for a large range of temperatures and pressures: \( T = (298.15 \text{ - } 473.15) \) K and \( p = (0.1 \text{ - } 50) \) MPa respectively. The details of the rig and its operation are explained in details in their original paper to which the curious reader is referred. More generally, this equipment offered the option to obtain the phase behaviour at HPHT of binaries composed of non-toxic gases and water or brines. From the list of systems considered, \((\text{C}_3\text{H}_8+\text{brines})\) represented the greatest interest, as solubility data for this system were scarce. Studying this system using the synthetic rig was deemed a wise decision as it was the salting out effect that contained the most valuable data. Indeed, the interaction parameter between the light hydrocarbon and the salt could help thermodynamic modelling for numerous systems composed of low-carbon-number hydrocarbon and brine. Also, at the time, the synthetic apparatus was the only rig capable of handling concentrated brines at HPHT.
CHAPTER 4. PRESENTATION OF THE EXISTING APPARATUS IN THE THERMOPHYSICS LABORATORIES

4.1.1 Description of the Apparatus

The main component of the apparatus was the HC 276 vessel (Sitec-Sieber model 740.2225). It had a back-lit view window and was sitting in an air oven (Memmert, model UFP 400). The temperature was measured via a Pt100 sensor, located in the thermowell in the body of the cell. The pressure was measured using a flow-through pressure transducer (DJ Instruments, model DF2) with titanium wetted parts and rated for 50 MPa. The pressure of the system was controlled via the brine injection or withdrawal using a high pressure syringe pump (Teledyne Isco, model 100DM). The pump was thermostated by a water-cooling jacket at $T = 291.15 \, \text{K}$ and its temperature monitored via a K-type thermosensor on its surface.

The cell had a volume of 25 cm$^3$. On top of having two window elements the cell had four high pressure 1/4" ports. The first two ports were used as inlet and outlet for the fluids, the third was connected to a safety head holding a rupture disc and the fourth port was plugged. Both fluids, the gas and the water/brine were injected using the same inlet line. This latter was connected to the vessel via a 1/4" to 1/16" reducing union. The inlet line as well as the outlet line were made of 0.5 mm i.d. 1/16" HC 276 tubing, which helped minimise the dead-volume they introduced.

4.1.2 Operating Procedure

To obtain the bubble point for the binaries of interest, the following procedure was adopted:

1. Introduce the gas to study in the previously evacuated cell.
2. Calculate the amount of gas in the cell with an EoS.
3. Inject solvent and significantly over-pressurise the system above estimated bubble pressure and wait for equilibrium (12 hours).
4. Slowly withdraw the solvent, monitor the pump volume, visually check bubble presence and wait for equilibrium.
5. Isolate the bubble pressure, and calculate the solubility of the gas in solvent.
4.1.3 Volume Calibrations and Calculations

Obtaining the Masses of Gas and Water Available to Dissolution

From Step 1 of the SOP, obtaining the effective mass of gas injected in the system (taking into account the dead volumes) is the first step of the calculations. Reusing the notations from Tong et al. (2013) one can write that:

\[ m_g = \rho_g(T_0, p_i)V_0 + \rho_g(T_{3i}, p_i)V_3 - \rho_g(T_0, p_i)V_1 \]  (4.1)

Where 0, 1, 2, 3 and 4 refer to the optical cell, the internal dead volume, the pump cylinder, the inlet line and the outlet line, respectively. Additionally, subscripts ‘i’, ‘f’, ‘g’, ‘s’, ‘w’ and ‘salt’ are respectively for initial, final, gas/solute, solvent (brine), pure water and pure salt. Therefore, to obtain the amount of gas available for dissolution in the solvent, or in other words, the effective gas content in the cell, one had to accurately quantify the volume of the cell, \( V_0 \) and the dead-volumes, \( V_1 \).

Similarly, one can calculate the mass of solvent in contact with the solute as follows:

\[ m_s = [\rho_s(T_{2i}, p_i)V_{2i} - \rho_s(T_{2f}, p_i)V_{2f}] - [\rho_s(T_{3i}, p_i)V_3 + \rho_s(T_{4i}, p_i)V_4] \]  (4.2)

Equation 4.2 states that the effective mass of water is obtained by subtracting the mass of water in the inlet and outlet lines (sum of \( V_3 \) and \( V_4 \)) from the mass of water injected (difference between the initial and final volume in the syringe pump, multiplied by the density at the temperature of the pump).

Obtaining the Volume of the Cell \( V_0 \)

From Equation 4.1, it appears that the effective volume of the cell, \( V_0 \), for the temperature of interest must be known. To obtain this volume, one needs a reference fluid with a well-known density evolution throughout the range of pressure and temperature of study. Water is, as it often is for these conditions, the chosen substance for such process. Pure water was injected multiple times at a controlled oven temperature of \( T_{\text{ref}} = 323.15 \text{ K} \) and set pressure of \( p_{\text{ref}} = 1 \text{ MPa} \). This was done using the thermostated syringe pump, injecting into a fully-evacuated and dry system. The associated change in the volume of the cylinder of the pump was reported as the full volume of the system. The effective volume of the cell is derived from this value by
subtracting the volumes from the inlet and outlet line. One writes this as follows:

\[ V_{\text{ref}} = \left\{ \left[ \rho_{w}(T_2, p_i)V_{2,f} - \rho_{w}(T_2, p_f)V_{2,w} \right] - \left[ \rho_{w}(T_3, p_i)V_3 + \rho_{w}(T_4, p_i)V_4 \right] \right\} / \rho_{w}(T_{\text{ref}}, p_i) \]  \hfill (4.3)

Where \( V_{\text{ref}} \) is the effective volume for the cell at the oven reference temperature \( T_{\text{ref}} \). The volumes \( V_3 \) and \( V_4 \) of the inlet and outlet line were measured: \( V_3 = 0.30 \text{ cm}^3 \) and \( V_4 = 0.23 \text{ cm}^3 \).

Once outside this temperature, one must take into consideration the thermal expansion resulting from heating the vessel. The effect can be described as follows:

\[ V_0(T, p) = V_{\text{ref}}[1 + \alpha_v(T - T_{\text{ref}})] \]  \hfill (4.4)

Where \( \alpha_v \) is the mean volumetric expansivity, taken as \( 36.10^{-6} \), three times the linear thermal expansion coefficient of HC 276 (Hoyt (1956)) as taken from Tong et al. (2013). The calibration yielded a reference for the volume of the cell of 26.53 mL (standard deviation \( 4.92.10^{-4} \)) at \( T_{\text{ref}} = 303.15 \text{ K} \).

4.1.4 Dead-Volumes Discussion

As visible in Step 2 from the Operating Procedure, a quality monitoring of the operative conditions such as temperatures and pressures was quintessential in obtaining a reliable estimation of the injected amount of each component in the system. Similarly, non-accounted for dead-volumes can be very detrimental to synthetic measurements, especially as pressure
CHAPTER 4. PRESENTATION OF THE EXISTING APPARATUS IN THE THERMOPHYSICS LABORATORIES

Figure 4.2: Synthetic Apparatus View Cell, Front and Side View.

External Dead-Volumes: The Channels Connecting the Bulk to the HP Ports

From Figures 4.2a and 4.2b, one can see that between the well-agitated bulk of the cell and each of the four ports resides a connecting channel, where the solvent remains still as soon as the vessel is full. Thus, a question that came to mind was, should these channels be considered as part of the inlet and outlet lines (external dead-volume) or part of the volume of the vessel. To bring an element of answer, one had to quantify to which extent the volume of these capillaries contained gas. It was agreed that, if the gas concentration in the solvent, \( C \), in these spaces was, on average, superior to 63% of the saturation concentration at the chosen pressure and temperature, the volumes were part of that of the cell.

The problem was one of diffusion, as in a solute slowly diffusing from a saturated liquid phase into a cylinder of fresh solvent. Simplifications to the formulation of the problem were introduced as the walls of the cylinder were considered not to influence the diffusion (this simplification actually undermines the diffusion rate of the gas into the solution). Therefore, the only dimension to impact the profile of the concentration was the depth, \( z \). The other variable to take into consideration was the time of equilibration, \( t \). Essentially, the equation
to solve this issue was Fick’s 2\textsuperscript{nd} Law of diffusion, which can be expressed as follows:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2},
\]

where D is the diffusion coefficient of the gas in the solvent. This differential equation of the second order has the famous error-function as solution. One can therefore write the mole fraction of the solute in the solvent as:

\[
x(z, t) = x_0 \left[ \frac{2}{\sqrt{\pi}} \int_{0}^{z/\sqrt{4Dt}} \exp(-t^2) \, dt \right]
\]

Equation 4.6 was numerically solved for the slowest diffusion conditions which is the lowest isotherm in the range of study. Indeed, the diffusion coefficient increases with temperature and pressure effect on diffusion is deemed negligible according to Cadogan et al. (2014). The length of the capillaries, L, is approximately 11 mm.

The case of CO\textsubscript{2} was used to solve Equation 4.6 \((D = 2.5 \times 10^{-9} \, \text{m}^2\text{s}^{-1} \text{ (Cadogan et al. (2014))})\) and the results are plotted in Figure 4.3. From these results, it appears that allowing 10 hours to pass after co-injection of the gas and the water yields an average concentration of CO\textsubscript{2} in the capillary of 63%. This lead to the 12 hours equilibration period in Step 3 of the
CHAPTER 4. PRESENTATION OF THE EXISTING APPARATUS IN THE THERMOPHYSICS LABORATORIES

Figure 4.4: Cross-sectional view of the window assembly: 1, internal trapped volume; 2, seal recess, filled by PTFE O-ring; 3, retaining ring; 4, sapphire disc; 5, window support (sealed to component 4 by means of a proprietary bond); 6, cell body; 7, threaded gland. From Tong et al. (2013)

Operating Procedure. The conclusion of these calculations is that, in the case of CO₂ and gases with similar diffusion behaviour in water, if allowed to rest over 10 hours, the water in the capillaries will contain enough gas for these volumes to be considered part of the volume of the cell.

Internal Dead-Volumes: The Dead-Volumes Associated with the Window Assembly

It was established in previous work that 0.2 mL of dead-volume within the cell (internal dead-volume) was to be accounted for. Located in the window assembly, this volume was filled with water during the calibration, and solely with solute during operations. From the drawings of the window assembly in Figure 4.4, one can see that behind the threaded ring resides an annular void in which the volume was measured to be 0.1 mL. During operation, the initial gas filling would push the solute through the clearance between the outer diameter (o.d.) of the threaded ring and the internal diameter (i.d.) of the cell and fill the void. This would have not been an issue if the solvent could have also filled the space, but the capillary entry pressure generated by the tight fit between the ring and the cell acted as a stopper. One can prove, using the Young-Laplace equation for parallel plates, that this capillary entry pressure is higher than the hydrostatic head introduced by the water/brine in the cell.

These two small volumes (one per window) had to be taken into account, as its content in solute raised with pressure. Therefore, in Equation 4.1, \( V_1 \) is taken as twice 0.1 mL (0.2 mL) at the cell conditions at the measured bubble point.
CHAPTER 4. PRESENTATION OF THE EXISTING APPARATUS IN THE THERMOPHYSICS LABORATORIES

(a) Bubble pressure graphic estimation. The sharp change of pressure from solvent injection represents the phase change representative of the bubble point. Under these conditions, $p_b = 3.45$ MPa.

(b) Bubble pressure visual estimation. The image is a shot from the camera facing the view window of the pressure cell. The fluid is CO$_2$-saturated water. The apparition of CO$_2$ bubbles, specks on the image, happens when crossing the bubble curve. Here, $p_b = 3.5$ MPa.

Figure 4.5: (CO$_2$+H$_2$O) bubble point measurement at 1.05 MPa initial filling pressure and 373.15 K. Two methods used: graphic method and visual method. The two value for the bubble pressure are in agreement with each other.

4.1.5 Validation using the (CO$_2$+H$_2$O) System

The rig in question was moved to another lab before the start of operations. This created an opportunity to become familiar with the experimental procedure and to validate the re-installed set up. The system chosen to do so was that previously studied with the same set-up: the (CO$_2$+H$_2$O) system. For operative simplicity, the temperature of the oven was set to 373.15 K. It was expected that the determination of the bubble point would be easier at pressures belonging to the low bracket of our pressure range. To maximise the return on the time spent in the lab, the bubble pressure chosen for validation was to be under 40 bar.

To measure the sought-after bubble pressure, the equipment offered two methods:

- A graphic method which relies on the sharp slope change in the pressure with the injection or withdrawal of solvent. This slope change is representative of the change of compressibility coefficient of the mixture in the vessel, with the number of phases increasing or reducing from one liquid phase to a liquid and a gas phase or vice-versa. Figure 4.5a illustrates the implementation of the method.

- A visual method which is based on identifying, via the camera mounted on the rig, the
pressure at which microscopic bubbles appear in the system. These micro-bubbles materialise when the solute concentration in the solvent becomes superior to the saturation limit which, in turn decreases when pressure decreases. Figure 4.5b is an example of such a scenario.

From the validation run, the bubble pressure at 373.15 K with an initial CO\(_2\) filling pressure of 1.05 MPa was found to be (using two different methods) \(p_b = 3.54\) MPa. The resulting CO\(_2\) mole fraction was \(6.22 \times 10^{-3}\), which is in very strong agreement with the value from Duan & Sun (2003). Indeed, their work gave a mole fraction of \(6.14 \times 10^{-3}\), equivalent to an absolute deviation of 1.3% from our measurement. Such a positive conclusion regarding the measurement which was obtained via two different methods, signified that the rig was validated and ready for HPHT solubility measurements of gases in water. The \((\text{C}_3\text{H}_8 + \text{H}_2\text{O})\) system presented gaps in the range of pressures and temperatures offered by the synthetic rig, and therefore was chosen for the next measurement campaign.

4.1.6 Attempts on the \((\text{C}_3\text{H}_8 + \text{H}_2\text{O})\) System

Due to the highly combustible character of Propane, a nitrogen gas line was added and connected to the system. This safety feature was introduced in order to flood the heated oven and push air out of it. Indeed, in case of propane leakage the oxygen in the air presented a risk of fire ignition if the concentration of propane reached a value between the Lower Explosive Limit and Upper Explosive Limit (2.1 to 9.5 %v).

The isotherm chosen to start the measurements was \(T = 398.15\) K. Three gas filling pressures were measured: \(P = (0.17, 0.23\) and 0.32) MPa. The results are presented in Table 4.2. Unfortunately results were not satisfactory for this system. The calculated mole fraction based on the used amount of water and propane diverged greatly from the literature value (as high as 133% difference). This is likely due to the combined effect of the sparingly-soluble character of propane in water and the presence of the internal dead-volume behind each window-assembly. In fact, under the high operative pressures, the internal volume turns itself into a great reservoir for the molecules of gas which are driven into the additional space until filling it. Under high bubble pressures, this volume of high-density compressed propane can represent as much as 80% of the original amount of gas injected. Having such a major proportion of the gas isolated and not taking part of the dissolution is a convincing argument
CHAPTER 4. PRESENTATION OF THE EXISTING APPARATUS IN THE THERMOPHYSICS LABORATORIES

Table 4.2: Result of measurements for \((C_3H_8+H_2O)\) at \(T_{\text{ref}} = 398.15\) K.

<table>
<thead>
<tr>
<th>(p_{g,i}/\text{MPa})</th>
<th>(p_{\text{pump,f}}/\text{MPa})</th>
<th>(x_p^{*}10^4)</th>
<th>(x_p^{L}10^4)</th>
<th>(\delta x/x/%)</th>
<th>(\rho_{\text{mix}}/(\text{kg/m}^3))</th>
<th>(\rho_w/(\text{kg/m}^3))</th>
<th>(\delta \rho/\rho/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>6.85</td>
<td>2.14</td>
<td>3.87</td>
<td>44.7</td>
<td>950.7</td>
<td>961.49</td>
<td>1.12</td>
</tr>
<tr>
<td>0.23</td>
<td>6.48</td>
<td>5.90</td>
<td>3.82</td>
<td>-54.5</td>
<td>941.9</td>
<td>961.28</td>
<td>2.02</td>
</tr>
<tr>
<td>0.32</td>
<td>7.90</td>
<td>9.42</td>
<td>4.04</td>
<td>-133.2</td>
<td>945.7</td>
<td>961.97</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Figure 4.6: Deviation introduced by 0.1 mL internal dead-volume on the theoretical bubble pressure. Calculations resulting from Krichevsky-Kasarnovsky equation.

- \(CO_2\), \(T = 313\) K,
- \(CO_2\), \(T = 353\) K,
- \(N_2\), \(T = 313\) K,
- \(N_2\), \(T = 353\) K and
- \(C_3H_8\), \(T = 298.15\) K.

to sustain that, this set up, albeit providing good results for \(CO_2\) in water/brines, is not adapted to measure the HPHT phase behaviour of the \((C_3H_8+H_2O)\) system.

4.1.7 Synthetic Apparatus - Conclusions

The synthetic apparatus presented consequent advantages: a capacity to measure high pressure and high temperature phase behaviour of versatile systems, from systems containing strongly corrosive components (highly concentrated brine) to systems containing explosive compounds (propane). It produced reliable data for \(CO_2\) in aqueous solutions (our validation provided a solubility that agreed as well as 1.3% with the literature data) during the validation phase. However, the set-up struggled with the \((C_3H_8+H_2O)\) system. As detailed earlier, this is certainly explained by both the 0.1 mL internal-dead volume introduced by each window-assembly in the cell, and the fact that propane is sparingly soluble in water under
CHAPTER 4. PRESENTATION OF THE EXISTING APPARATUS IN THE THERMOPHYSICS LABORATORIES

(a) Densities of fluids with pressures at $T = 303.15 \text{ K}$. $N_2$, $C_3H_8$ and $CO_2$.

(b) Henry’s constant function of the temperature for six gases of interest.

Figure 4.7: Example of density profiles with pressure and Henry’s constant evolution with temperature for the gases of interest in this research. $N_2$, $H_2$, $O_2$, $C_3H_8$, $CO_2$ and $H_2S$.

these conditions.

A valid question to raise at this point is: would the rig behave similarly in regards to other binaries in our array of systems to study? An element of the answer is found by looking at both the density of the compound in question, as well as its Henry’s constant (or solubility limit if available). As shown by Figures 4.7a and 4.7b, the two properties will either compete or join forces in regards to separating the gas from the bulk of the cell. Indeed, a high density will potentially hold a large amount of solute in the internal dead-volume, but the capacity of the gas to dissolve in the solvent will counter or add to this effect as the bubble pressure will be lowered or increased in response. Using the Krichevsky-Kasarnovsky EoS, the bubble pressure of the $(N_2+H_2O)$, $(CO_2+H_2O)$ and $(C_3H_8+H_2O)$ were estimated for $T$ under 373.15 K as recommended by Carroll & Mather (1992). The impact of the introduction of 0.1 mL in a system of 25 mL on the theoretical bubble pressure is shown in Figure 4.6. One can clearly see that the case of propane presents the worst deviations, with a shift in the bubble pressure as high as 27%. If one considers the two windows in the synthetic system, this means that the measured $p_b$ could carry an error as high as 54%, which is unacceptable. This confirms the conclusions drawn for this system. Similarly, the $(N_2+H_2O)$ presents high deviations, which in the worst case scenario is a biased bubble pressure of 38%. This could lead one to think that this system is not to be measured with the synthetic rig. However, at low temperature
and past 20 MPa, the errors carried with the nitrogen are somewhat similar to that of the CO\textsubscript{2}. This might mean that for a narrower range of pressures and temperatures, the binary (N\textsubscript{2}+H\textsubscript{2}O) could be measured accurately with the synthetic method in the Thermophysic Lab. However, the range and the accuracy of the measurements resulting from the analytical rig in the Lab were expected to be higher. It was, therefore, decided to switch to the analytical equipment to carry the future inert gases measurement campaigns.

4.2 The Analytical Apparatus

The analytical rig offered the possibility to extend the content analysis to systems of gases sparingly soluble in water and brines, a feature that the synthetic apparatus proved not to offer. This higher concentration threshold was provided by the nature of the analysis offered by the rig, which relied on gas chromatography and its sensitive detectors. This section details the findings and conclusions resulting from the work with this apparatus.

4.2.1 Description of the Apparatus

The system is a circulation-type analytical apparatus (Hou et al. (2013\textsuperscript{b,a})). Figure 4.8 shows the various elements composing the system, including a circulation loop for homogenisation (P4), the different pumps (P1, P2 and P3), a high pressure view-cell (R), the different transducers (Ps), the sampling valves (V10 and V11) and a Gas Chromatograph (GC).

The 95 mL high-pressure reactor is built with 3 sapphire windows to allow visual check during experimentation. It is made from Hastelloy C276 and built by SITEC to sustain pressures up to 50 MPa and temperatures up to 473.15 K. However, other elements introduced a pressure limitation and, therefore, the system was only used up to 18 MPa. To avoid an accidental over-pressurisation, a safety head with a bursting disc was connected to one of the vessel ports. The fluid phases were actively homogenised in a double-loop by a magnetic pump controlled by micro-switches. The vapour phase was continuously pumped in the first part of the loop and re-injected at the top of the vessel. The second half of the circulating loop was connected at the inlet to a rotating elbow probe. This allowed the operator to choose which fluid to circulate in case of a multiphase system. The unidirectional flow in the loop was insured by gravity-operated check valves on each side of the loop. Both sides of the circulation
loop were connected to ROLSI sampling valves. These are electro-mechanical valves activated by a magnetic spring. By setting parameters such as the time or the frequency of retraction of the spring, one had control on the opening and the separation time between each sampling. The polymer tip of the ROLSI (either PPS or polyamide, for water based and hydrocarbon based systems, respectively) valves were isolating the high pressure system from the heated transfer line, leading to the GC via a carrier gas (helium in most cases). The sampling valves were heated above 473 K to ensure vaporisation of the samples reaching the capillary column in the GC. It is these elements that limited the maximal operating pressure to 20 MPa,\(^1\) and it is thought that their wide-spread usage amongst the experimental scientific community is the reason behind the 20 MPa cap in solubility data of water-based binaries found in the literature (see Chapter 2).

The vessel, the circulating pump and the tip of the ROLSI valves were placed in a MEMMERT oven (model UFP 600), ensuring the system temperature to be constant within \(\pm 0.03\) K. The temperature in the vessel was monitored by means of a platinum resistance thermometer (PT100, Sensing Devices Ltd) located in a thermowell bored into the wall of the reactor. The pressure in the system was measured by a pressure transducer connected by a dead-end to the vapour part of the circulating loop. The pressure transducer (Honeywell, model Super TJE) had a 50 MPa range. Both the thermometer and the pressure transducer were connected to a data acquisition/switch unit (Agilent technologies, model 34970A). This device allowed for monitoring of the pressure and temperature on a computer screen and controlling the air flux to the circulation pump and the inlet pneumatic valve (Vindum Engineering, model CV-420). This valve was isolating the system from the injection components when necessary. Fluids injection was completed by three syringe pumps (Quizix pump, model Q5310-HC-A-GH-S, Vindum Engineering) connected in parallel to the line. Each pump was filled with a different fluid, but all had Hastelloy C276 and ceramic wetted parts. Moreover, all the wetted seals were made of UHMWP (Ultra high molecular weight polyethylene), which made them suitable for the use of CO\(_2\).

\(^1\)During the discussion of the PhD Viva, it came to light that a new version of the ROLSI valve, commercialised in 2016 several years after the time when these experiments were carried out, does offer the option to work with pressures largely superior to 20 MPa thanks to a new metallic seal. The aforementioned improvement is acknowledged with this note.
Figure 4.8: P&ID Analytical Apparatus in Thermophysics Lab
4.2.2 Operating Procedure

1. Firstly, the system is evacuated using the vacuum pump while the needle valve (V8) and the Vindum valve (V5) are opened. The system is then flushed with the solute and evacuated again to remove any traces of impurities. The needle valve (V8) is then shut.

2. A selected amount of the solvent is first charged into the cell using Quizix pump (P2) until the vessel is slightly more than half-full. This is to account for the liquid compression brought about when introducing the solute. The objective is to have the interface of the phases located in the centre of the windows. The other compound is charged into the equilibrium cell until the set pressure to be measured is reached. Stirring is then activated, and the pressure controlled via the solute pump (P1). The time evolution of the volume of the cylinder of the pump is representative of the state of equilibration. In fact, the gas dissolving in the solvent will reduce the pressure of the system. The pump will thus compensate by injecting more matter (solvent in this case) until no more gas can be dissolved and the pressure is stabilised. At this point, the variation of the volume of the pump cylinder will reach a minimum. This point indicates that the thermodynamic equilibrium of the system is established.

3. The magnetic pump, which is operated using a pneumatic control system, is activated to circulate both the vapour and liquid phases and fill the respective recirculation-lines with representative mixtures. The transfer lines are heated to thermal equilibrium.

4. Small amounts of either liquid or vapour phase are sampled out from the pressurised system by opening the ROLSI samplers (V11 for the liquid phase, V10 for the gaseous phase) for a set period (usually microseconds for the dense liquid phase and milliseconds for the gaseous phase). The compounds are then analysed using the appropriate method (temperature of the oven and the detectors, split-ratio, dean-switch and column selection) for the GC.

5. In case of brine usage, the deposited crust of salt trapped in the transfer lines are subsequently washed out with a metered quantity of water (using the syringe pump P3).

6. To discharge the system, the needle valve (V8) is opened, and the mixture is evacuated to the waste bottle connected to the apparatus.
CHAPTER 4. PRESENTATION OF THE EXISTING APPARATUS IN THE THERMOPHYSICS LABORATORIES

4.2.3 The (O₂+H₂O) System

Calibration

The evolution of the Thermal Conductivity Detector (TCD) response with increasing amount of O₂ was to be quantified precisely in order to obtain reliable measurements. To do so, a variable known-amount of oxygen was exposed to the TCD, and the response was recorded. The function linking the electric response to the quantity of matter is the result of the calibration. It is the transcription key between raw data from the detector and the sample composition.

The oxygen was purchased from BOC Ltd (99.998% purity). It was injected from a 4-port 2-position Internal Sample Injector (VICI ED2CI4UWE1) with an internal sampling loop of 1 µL. The temperature of the valve was monitored using a type K thermocouple, and the pressure in the line that ends with the valve V6 was also measured. Through the usage of the EoS from Schmidt & Wagner (1985), the amount of oxygen introduced was estimated and the measured response of the detector was associated with this quantity. The result of the calibration is shown in Figure 4.9a. A very linear response can be seen and the extracted calibration coefficient was \( \alpha_{O_2} = 1.33 \times 10^{-2} \text{ mol.s/µV}. \)

Figure 4.9: Calibration of the TCD on the Analytical rig for O₂ and H₂O.
The water calibration was less fruitful, as the principle was to use a diluted solution of various water concentrations to vary the injected amount of water. The issue came from the solvent used for dilution, Tetrahydrofuran (THF), non-freshly purchased, which contained a non-negligible amount of water. While a new batch of solvent was ordered and delivered, a temporary solution was implemented: the water calibration coefficient taken was that of Hou et al. (2013a,b) with $\alpha_{\text{H}_2\text{O}} = 1.12 \times 10^{-2} \text{ mol.s/\muV}$. Measurements with oxygen and water were started, and before an appropriate water calibration run was made, conclusions were reached with this system.

**Measurements, Discussions and Conclusions**

Prior to any introduction of pressurised and heated pure oxygen in a system, an in-depth material compatibility analysis had to be done. Exhaustive lists were made of the components as well as the risks of ignition to consider while filling them with pure pressurised oxygen. The guidelines from Gregory (1996) on safe oxygen handling were followed and the risk assessed and reduced appropriately. The nature of the ignition mechanisms associated with oxygen-exposure for each component, as well as their likeliness are presented, in Appendix B.

Two isotherms were measured: $T = (308.15 \text{ and } 348.15) \text{ K}$ and up to 17.95 MPa. The measurements themselves proved to be of a low quality, with a high average deviation and low repeatability. The ROLSI capillaries repeatedly became stuck or partially blocked from particulates in the system. This was a cause of the lack of repeatability. Another principal reason behind the poor quality of the measurements was the signal-to-noise ratio (S/N). In fact, in the worst conditions ($T = 308.15 \text{ K and low pressure}$) the TCD response to the oxygen content was not significantly different from the noise, with oxygen peak height around 0.5 $\mu\text{V/s}$ when the water peak height was around 1000 $\mu\text{V/s}$.

The solubility of oxygen in water is low compared to, for example CO$_2$ (Figure 4.7b). The mole fraction of oxygen in water varies depending on the conditions between $10^{-4}$ and $5 \times 10^{-3}$ (Zoss (1952)), while the CO$_2$ concentration in the same solute can go as high as 3% (Duan et al. (2006)). This spare solubility, combined with the small volume (1 $\mu\text{L}$) sampling loop, the diluting split/splitless unit at the GC inlet and the sensitivity of the detector used (Thermal Conductivity Detector, TCD) generated challenges for measuring the phase equilibria of the (O$_2$+H$_2$O) system. The oxygen concentration remaining in the sample post
column-elution was close to the sensitivity of the TCD (around 50 ppm), which introduced residual uncertainties to the measurements. Therefore, to increase the S/N ratio, and increase the precision of the oxygen data, a larger amount of sample was introduced for the detector to analyse.

A point to keep in mind when working with chromatographic analysis is the matter of the size of the sample sent to the detector. In fact, the maximal value that can be introduced in the detector has to be within the range of calibration, which in this case was up to 1176 µV/mol.s for oxygen and up to 3571 µV/mol.s for water. This is to insure that the linear relationship established during the calibration, linking the area under the peak to the number of mole, stays valid during the experiments. If the upper calibration value happens to be exceeded, the amounts of substance extracted from the electrical signal will be the result of an extrapolation which carries by definition high uncertainty. Beyond the calibration range, the response of the TCD could diverge from linearity (see Figure 4.9b for illustration of such divergences). Because of such unknowns, extrapolation is not accepted as good practise for obvious data reliability reasons. Therefore, the size of the sample to be sent to the detector was bound by:

- An amount that must be large enough for the oxygen peaks to be clearly defined and the S/N ratio to be lowered.
- An amount that must be sufficiently small enough for the water peaks to respect the boundaries established by the water calibration range.

The issue in this study stemmed from the fact that the amount of water measured by the detector is four orders of magnitude higher than that of the oxygen. Therefore a dead-end was encountered when the only way to increase the S/N ratio for oxygen was to introduce larger samples, because these latter, in turn, introduced more water than the upper limit of the TCD water calibration.

One solution to this problem could have been to extend the calibration range, but no adequate hardware (4-port 2-position External Sample Injector with an external sampling loop of at least 10 µL) was directly available at the time to do so. Instead of investing in the additional equipments, it was decided to try to utilise what was available, and therefore the decision was made to move to a system where these issues should not be encountered: the (C3H8+H2O) system.
CHAPTER 4. PRESENTATION OF THE EXISTING APPARATUS IN THE THERMOPHYSICS LABORATORIES

(a) Dean-Switch working principle.

(b) Typical use of the Dean-Switch. The first peak (in this case propane) is sent to the FID while the second larger peak (in this case water) is sent to the TCD.

Figure 4.10: Deans Switching System from Agilent Technologies.

4.2.4 The (\(\text{C}_3\text{H}_8+\text{H}_2\text{O}\)) System

Preliminary Work

The (\(\text{C}_3\text{H}_8+\text{H}_2\text{O}\)) was advantageous compared to the (\(\text{O}_2+\text{H}_2\text{O}\)) system as the TCD sensitivity issue toward the spare component was no longer handicapping. In fact, the propane was not to be measured with the TCD, but rather with the second detector fitted on the GC: the Flame Ionised Detector (FID). This device presented a significantly higher sensitivity to hydrocarbon-based compounds (order of magnitude of the ppm). The two detectors could also work in parallel, which granted the option to send each component, the water or the propane, to their respective detector of predilection for an optimised analysis.

As explained in Subsection 4.1.6, safe handling of HPHT propane was only fulfilled by placing the pressurised system in a oxygen depleted environment. The analytical rig was enclosed in an oven, to which a \(\text{N}_2\) inlet was connected in order to flood the volume and push
oxygen out of the system through side-bored holes. This was an absolutely key feature for safe operations, and an absence of N₂ flow would mean immediate interruption of experimentations.

The Agilent GC did not offer the option to connect both the TCD and the FID in series. Instead, a proprietary device to Agilent Technologies, called Deans Switching System (DSS), was installed to provide pairing of the detectors. This device was the equivalent to a very fine T-piece with laser cut channels that hard cut the main to one or the other output. A diagram showing its main features is presented in Figure 4.10a. The DSS would activate a Solenoid valve connected to a Pressure Control Module (PCM) in one way or the other, and (similar to a track-switch in train track junction) send the effluent of the primary column to the primary detector (TCD) or to the secondary detector (FID). In theory, the Dean-Switch is most useful for highly similar chemical compounds, which overlap at the end of the primary column. A secondary column, with different affinity properties, would then force the components to elute distinctly. For this system, the only two components would already have well separated peaks when eluting from the primary column. Therefore, there was no need for a secondary column. Instead, an inert silica tubing was installed between the primary column and both the TCD and the FID.

Calibration

For better time management, it was decided to start with phase behaviour measurements, after which the detector calibration would be carried out. Meanwhile, a modified peak-area-ratio method was temporarily implemented in order to translate the raw electrical signal given by the detectors into a concentration.

The method resides on the assumption that the responses of the detectors at stake are linear. In other words, one can formulate it as follows:

\[ n_i = \alpha_i A_i, \] (4.7)

where \( n \), \( \alpha \) and \( A \) are, respectively, the amount substance in the sample, the response factor and the area measured in the chromatogram for the component \( i \). From Equation 4.7 one
obtains:

\[ x_i = \frac{\alpha_i A_i}{\sum_j \alpha_j A_j} \]  

(4.8)

Which for a binary system can be re-written as \( x_p = \frac{\alpha_p A_p}{(\alpha_p A_p + \alpha_w A_w)} \), where \( \alpha_i \) and \( A_i \) are, respectively, the calibration sensitivity coefficient and the area under the curve in the chromatogram for component \( i \). Defining \( r_w = \frac{\alpha_p}{\alpha_w} \) one then writes:

\[ x_p = \frac{A_p}{A_p + r_w A_w} \]  

(4.9)

And hence

\[ r_w = \frac{A_p x_w}{A_w x_p} \]  

(4.10)

To obtain a temporary estimation of \( r_w \), the literature was used to obtain the mole fraction at one chosen pressure and temperature. From the work of Kobayashi et al. (1953), the mole fraction of propane in water at \( T = 308.15 \text{ K} \) and \( p = 10 \text{ MPa} \) is \( x_p = 2.20 \times 10^{-4} \). This yields:

\[ r_w = 1.7210^{-2} \]  

(4.11)

With the value of \( r_w \) in Equation 4.11, one needs only to inject the area under the measured peaks to obtain a representative estimate of the measured \( x_p \). This temporary calibration allowed the measurement campaign to be started.

Measurements

The isotherm \( T = 308.15 \text{ K} \) was investigated up to 17 MPa. The results of the measurements are plotted in Figure 4.11 and carry an average standard deviation of 1.44%. One can see that the agreement with the literature is very satisfactory and that the data are highly reproducible. Also, the three-phase equilibrium pressure was identified at \( p = 1.3 \text{ MPa} \). An attempt to measure the liquid propane-rich phase produced a much lower repeatability than the other data in the set. This was probably due to inhomogeneous phase entrainment. Limited efforts were invested in obtaining better measurement at this pressure as obtaining data for other conditions was a higher priority.

Measurements for isotherm \( T = 308.15 \text{ K} \) were initiated, and the resulting values seemed to follow the literature well. Unfortunately, these results were limited as a key safety feature
Table 4.4: Result of measurements for \((C_3H_8+H_2O)\) at \(T = 308.15\) K.

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>(x_p \times 10^4)</th>
<th>StD, (\sigma /%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.13</td>
<td>2.55</td>
</tr>
<tr>
<td>1</td>
<td>1.92</td>
<td>2.49</td>
</tr>
<tr>
<td>2</td>
<td>2.02</td>
<td>0.92</td>
</tr>
<tr>
<td>4</td>
<td>2.04</td>
<td>1.41</td>
</tr>
<tr>
<td>7</td>
<td>2.13</td>
<td>1.60</td>
</tr>
<tr>
<td>10</td>
<td>2.20(^a)</td>
<td>1.76</td>
</tr>
<tr>
<td>12</td>
<td>2.16</td>
<td>0.58</td>
</tr>
<tr>
<td>14</td>
<td>2.23</td>
<td>1.04</td>
</tr>
<tr>
<td>17</td>
<td>2.28</td>
<td>0.64</td>
</tr>
</tbody>
</table>

\(^a\): Conditions used for the modified peak-area-ratio calibration.

Table 4.5: Result of measurements for \((C_3H_8+H_2O)\) at \(T = 348.15\) K.

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>(x_p \times 10^4)</th>
<th>StD, (\sigma /%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.64</td>
<td>4.42</td>
</tr>
<tr>
<td>1.3</td>
<td>1.19</td>
<td>1.58</td>
</tr>
<tr>
<td>2.1</td>
<td>1.65</td>
<td>1.24</td>
</tr>
<tr>
<td>2.8</td>
<td>2.11</td>
<td>1.60</td>
</tr>
</tbody>
</table>

broke down mid-experiment, and only pressures up to 2.8 MPa were measured. Results are presented in Table 4.5.

The nitrogen generator, which flooded the oven, broke-down and with it the analysis of the \((C_3H_8+H_2O)\) system was brought to an end, as replacements for a nitrogen source fell short. This was a setback for the measurement campaign as encouraging results were being obtained for this system. It was felt that, considering the state of the analytical equipment at the time, no other water-based binary could be studied with this rig. Therefore, all efforts were switched to the design of a new, more versatile apparatus, with a wider range of pressure, fit for highly concentrated brine measurements and with a more adapted design to HPHT toxic gases handling. The product of this work is presented in the following chapters.
Figure 4.11: $C_3H_8$ mole fraction in pure water at $T = (308.15$ and $348.15) \text{ K}$ in function of pressure. • This work $T = 308.15 \text{ K}$, ▲ This work $T = 348.15 \text{ K}$, ♦ Kobayashi et al. (1953) $T = 310.92 \text{ K}$. ♦ Kobayashi et al. (1953) $T \approx 349.18 \text{ K}$. 
Chapter 5

The New Semi-Analytical Apparatus - Presentation

When attempting to study the solubility of sparingly soluble gases in brines, the advantages that the synthetic and the analytical equipments had provided in previous studies (Hou et al. (2013a), Hou et al. (2013b) and Tong et al. (2013)) were overpowered by limitations inherent to these rigs. In fact, the inner dead volumes in the synthetic equipment were not causing major experimental issues with gas solubility in water/brine in the order of magnitude of 10,000 ppm. However, when using gases with a solubility level of 100 ppm, these pockets of dead volume introduced a much larger deviation: undissolved gases accumulated in the dead-space and unreliably shifted the synthetic calculations.

On the other hand, even though limited in its range of measurements (to pressures under 20 MPa and for the solvent phase, only to pure water), the analytical apparatus could have yielded meaningful data for sparingly soluble hydrocarbon gases in water (see Figure 4.11). Unfortunately, a vital safety feature of the rig broke down while experimentations were ongoing and no resource was available to replace it. Therefore, measurements for these particular systems had to be stopped with no further results obtainable from this rig (see 4.2.4).

The list of potentially interesting binary systems for our research shrank consequently after the aforementioned dead-ends were encountered. Looking forward, only one type of binary system of interest was left with a large absence of data in the literature: the sulphuric gases and aqueous solvents binaries. However, due to the high risk pertaining from working with
such materials (see Appendix D), an adequately ventilated, fully enclosed setup, remotely operated, fitted with the appropriate detectors in a dedicated laboratory was required. At the time these conclusions were reached, no present equipment was up to the safety standards for toxic gases work.

A new apparatus in a dedicated sulphur gas lab were to be developed to allow the safe measurements of such systems.

5.1 Working Principle

This apparatus was described as semi-analytical as its working principle was based on analytical sampling methods (use of sampling valves, column and gas chromatography) but it exclusively focused on the solvent-rich phase. This was because the experiences of the previous chapters with Vapor-Liquid Equilibrium (VLE) and Liquid-Liquid Equilibrium (LLE) showed that it might be simpler to obtain HPHT solubility measurements for this phase.

The semi-analytical equipment offered the possibility to measure the composition of the solvent rich phase for a wide range of temperatures and pressures with $T = (273.15 - 473.15)$ K and $p = (0.1 - 70)$ MPa. The main components of the equipment are presented in Figure 5.1. The pumps were used to inject the components in the main vessel R (described at length in Subsection 5.2.4), which was located in a thermostated oil bath (Lauda Proline RP 3530C). The pressure was monitored by a pressure transducer (Keller PA-33X), rated for pressures from 0.1 to 70 MPa. Located on the gas line (see Figure 5.2) it was situated away from the heated bath, as this device is vulnerable to high temperatures. The pressure transducer is connected via a RS485 to USB interface adapter to the control computer. Additionally, a visual display, EV-06, also from Keller, was connected to the device for direct pressure monitoring of the equipment. All wetted parts in the system were made of Titanium Grade 2 and 4, thus providing adequate corrosion resistance to the high pressures heated mixture composed of highly concentrated brines saturated in acid and/or sour gases.

The main reactor contained the pressurised mixture which equilibrates via a double convective process: a local convection with a magnetic stirrer and a global convection with the recirculation flow generated by the circulation pump (CP in Figure 5.1). The stirring happens via a magnetic plate which sat under the base of the reactor R, spinning via a gear system,
Figure 5.1: Simplified P&ID for the semi-analytical equipment.
Figure 5.2: Full P&ID for the Semi-Analytical Apparatus.
driven by a vertical shaft with its end connected to a duo single phase induction motor (Panasonic M61X6GV4GGA) and gear box (Panasonic MX6G3BA). The speed of rotation of the shaft was set by an analogue controller MGSDB2, with its power switch connected to the control computer. The circulation pump is described in Subsection 5.2.2 and provided a continuous recirculating stream at a flow rate of up to 0.3 mL/min. This movement streamed fluid from the bulk of the solvent-rich phase through the 10 µL Liquid Sampling Loop (LSL).

The mixture was cooled prior to contact with the High Pressure Liquid Chromatography (HPLC) sampling valve and heated before being flushed back into the heated reactor (see Subsection 5.2.1 for more background on this process). The sampling valve was a 2 position, 6 port valve (C72H-1676EH VICI Cheminert), electrically actuated and rated for pressure up to 70 MPa and temperature up to 323.15 K (which was why the temperature of the heated mixture must be brought down before encountering the valve). Insurance that this temperature change will not change the phase composition was based on the principle that solubility of gases usually (but not always) increases with temperature decrease. Therefore, when cooling the liquid phase, the saturation limit would increase and maintain the solute in it. The mixture would then have the same composition, even with the temperature difference.

Once re-circulating and stirring have started, the pressure was controlled and monitored by the gas pump. There were two syringe pumps, both Quizix pumps (5000 series, rated for 140 MPa and (273.15 to 323.15) K with all wetted parts made of Hastelloy), one for the solute (called "gas" without consideration for the nature of the phase of the molecule), the other for the solvent (water or brine). The gas pump was used in a pressure-control mode, which allowed its cylinder to be used as an indicator of the system equilibrium. When first introduced, the gas dissolved in the water and the pressure drops. The pump, in order to maintain the set pressure, injected more solute to counter balance this pressure-drop. The injection flow-rate could then be plotted with time. When the average of the latter was oscillating close to the injection-rate 0.0 mL/min, thermodynamic equilibrium was deemed to be achieved.

Thanks to the re-circulation flow, the composition of both the mixture in equilibrium in the vessel, at the set conditions of operation, and the mixture in the circulating line/LSL were the same. Therefore, sampling the content of the LSL was equivalent to sampling directly from the cell, thus equivalent to measuring the water/brine composition of the rich phase at
any desired pressure and temperature of interest.

The sampling line was made of 2 m long, electrically heated, 1/16" SS thin walls (1 mm i.d.) tubing. An ON/OFF solenoid valve (Burkert 134071) in series with a hand throttle valve (Hamlet H300U) allowed He to flow through the line in a controlled fashion up to the filling pressure of 0.6 MPa. The He was a CP grade gas purchased from BOC Ltd. The pressure in the line was monitored by a flow-through pressure transducer (DJ Instruments, model DF2) with an internal volume of just 12 µL and a full-scale pressure of 1.7 MPa. The sampling line was connected to a 2 position 3 port selector (VICI model EDC3UW) which introduced either fresh DI water to wash the transfer line (using a Nexus 3000 CHEMYX syringe pump) or He to transport the samples. The selector outlet then passed through the LSV and lead to the flash vessel F inside the heated valve box of the gas chromatography, where it sat horizontally. During a sample analysis, the mixture transported by the He carrier gas, vaporised fully in F until pressure equilibrium was reached by filling with more He. The design of the flash vessel is described in Subsection 5.2.5 and the time evolution of the pressure is explained in Subsection 5.2.6. The gases in F were continuously mixed via a magnetic stirrer designed in-house and optimised for convective gas mixing. Once the pressure reached the He bottle pressure, the content of F was sent passing through a 25 µm i.d. 5cm length silica restriction tube open to the atmosphere. The pressure drop introduced by the capillary helped control the depletion rate of flash vessel (flow through the capillary at constant pressure was 1-2 mL/min). Between this capillary and F, in the heated valve box, sat a 0.5 mL GSL which would get filled with the bleeding gas mixture. The content of the GSL was then sent to the gas chromatography (SRI model 8610c) for analysis. The GC was fitted with two detectors in series to offer a better range of systems available to study: a TCD and an FID. More details regarding the architecture of the GC system are provided in subsection 5.2.3.

5.2 Design

The new apparatus had to offer in situ analysis of the phase compositions. Our previous experience with the synthetic method helped foresee possible issues incumbent to the combination of sparingly soluble mixtures and dead volume. The choice of the analysis protocol for the new rig went to the analytical method. As seen in Section 4.2, this technology presented
very promising results as long as the appropriate safety features were enforced. However, the previous analytical apparatus presented a pressure range that was limited at 20 MPa. As shown in Chapter 2, 20 MPa is the threshold under which most of the literature is published for our binaries, therefore that range of pressure has little potential for new data.

The experience gained on the analytical apparatus available, helped us understand that the pressure limiting piece of equipment was the ROLSI sampling Valves. Therefore, developing another sampling technology to unlock a new, wider, pressure range was the first challenge for the design of this new apparatus.

5.2.1 Unlocking Previous Pressure Limitations

The VICI UHPLC Valve

Although the design was being worked away from the ROLSI technology, the need to sample the pressurised mixture to an analyser in order to obtain its composition still remained. The VICI Microbores UHPLC (Ultra High Pressure Liquid Chromatography) valve, often used in the lab, helped start working on a sampling protocol around the need of a ROLSI valve. The pressure range targeted lead to the choice of the Chenminert valve C72H-1676EH. The product was a 2-position, 6-port valve, electrically actuated, and rated for pressure up to 70 MPa. Its sealing technology revolved around two components: one static (the stator) and one rotating (the rotor), as shown in Figure 5.3. The seal was provided by the rotor, compressed by the stator, screwed in place by 2 fasteners through the body of the valve. The rotor was made of Valcon E3 (an engineered polyaryletherketone) and had a recess with 3 channels in its surface. The stator was made of a stainless steel specially coated with a hardened surface for better material compatibility and score resistance VICI (n.d.b). It also had 6 ports for inlets that accommodated proprietary 1/16" VICI fittings. These ports were drilled through the stator with a very fine diameter bore: 0.15 mm - thus the name "Microbores UHPLC". The ports were very precisely situated over the channels of the rotor and the latter was tightly sealed against the mirror-finish surface of the stator. This allowed fluid to flow between two selected ports without leaking into other ports.

This design provided sampling operations at pressure up to 60 MPa but it had an impact on the temperature rating of the valve. As a matter of fact, when the rotor and stator were
exposed to high temperatures, they swelled. This in itself was not a problem when parts were static. However when the rotor switched from position A to B or vice-versa, the hardened orifices behaved like blades to the soft rotor. Each rotation then dug deeper and deeper channels into the rotor until the purposeful channels and the newly made channels formed only one full circle. This was not a desirable scenario as connecting all the ports, pressurised ports with sampling ports, would results in an uncontrollable leakage, the nemesis of high pressure equilibrium analysis. To avoid this handicapping situation, the valve had been rated to temperatures up to only 323.15 K. Limiting the temperature insured that the expansions generated were not harmful to the sealing technology.

The Heat Exchangers

The temperature rating for the valve presented many challenges which the design step revealed. However, respecting this temperature constrain, while at the same time offering a solubility temperature range that overcame the literature limitations (studying temperatures as high as 473.15 K), was the main issue to solve at the time of the design. An efficient way to drop the temperature from the heated bulk of the mixture to the LSL was to add a counter-current heat exchanger between the two. Another heat exchanger was also added in order to re-heat the solution before sending it to the mixture at equilibrium with the analysis conditions. The first heat exchanger needed to bring the temperature of the mixture down to under 323.15 K. The 1/16" Ti tube containing the hot mixture flowing upwards, passed through a 1/4" tube filled with cold water circulating in the opposite direction, for a length of $L = 1$ m. This classic problem of heat exchangers yields an exit temperature for the mixture, $T(z=L)$,
CHAPTER 5. THE NEW SEMI-ANALYTICAL APPARATUS - PRESENTATION

(a) Cooling Counter-Current Heat Exchanger: bringing the temperature of the heated mixture under the LSV temperature rating. The length taken was \( L = 1 \text{m} \).

Figure 5.4: The heat exchangers design: pre-LSL cooling and post-LSL/before entering equilibrium vessel heating.

(b) Temperature profile of the cool mixture when going through the coiled tube in the heated silicon oil, in function of the length, \( l \). Computations resulting from Equation.

expressed as follows (Spakovszky (2007)):

\[
T(z = L) = \frac{\dot{m}_c c_p}{\dot{m}_m c_p^m} \eta (T_{cl} - T(z = 0)) + T(z = 0),
\]

with \( \dot{m}_c \) and \( c_p^c \) representing the massic flow rate and the heat capacity at constant pressure for the cold fluid, with the subscript c, and for the mixture, the subscript m. \( T_{cl} \) and \( T_{cl} \) are the temperature of the cooling fluid at the entrance of the Heat Exchanger (HEX) and at the exit, respectively. \( T(z=0) \) is the temperature of the mixture at the entrance of the HEX. \( \eta \) is the efficiency of the HEX and can be defined as follow:

\[
\eta = \frac{W_c}{W_m} \frac{1 - \exp \left( \frac{-h_0 \pi D L}{W_c} \left( \frac{1}{W_c} - \frac{1}{W_m} \right) \right)}{1 - \frac{W_c}{W_m} \exp \left( \frac{-h_0 \pi D L}{W_c} \left( \frac{1}{W_c} - \frac{1}{W_m} \right) \right)},
\]

where \( W_i = \dot{m}_i c_p^i \), \( h_0 \) is the overall heat transfer coefficient of the assembly, \( D \) is the diameter.
of the inner tubing and L the length of the HEX.

The fluids at stake being water for the cooling fluid and at least 95% under any conditions for the mixture, it was admitted that the $C_p$ are the same for both fluids, and equal to the heat capacity at constant pressure for water, $C_p^w$: $C_p^f = C_p^m = C_p^w$. One had then to consider the mass flow rate for both fluids. The circulation pump described in the following sections provides, at best, a circulation flow of $\dot{m}_m = 1 \text{ g/min}$. In comparison, the circulating industrial pump of the Huber minichiller used to flow cooling water provided a mass flow rate of $\dot{m}_c = 1 \text{ kg/min}$. Therefore, it was legitimate to write:

$$\dot{m}_c \gg \dot{m}_m \quad (5.3)$$

Which yields:

$$W_c \gg W_m \quad (5.4)$$

From Equation 5.4, one can obtain, using Equation 5.2 to prove that $\eta$ tends to $W_m/W_c$, that Equation 5.1 can be re-written as:

$$T(z = L) = T_{cl} \quad (5.5)$$

Equation 5.5 shows that, in theory, with the configuration mentioned, virtually no length of heat exchanger was necessary to cool the mixture. In practise, it was made sure no experimental upset would impact the cooling so the length of the pre-sampling HEX was set to $L = 1 \text{ m}$. The temperature $T_{cl}$ was also set to 285.15 K, well under the LSL temperature rating of 323.15 K. These conditions were proven to work very efficiently in practice.

The heating HEX, downstream of the LSV, was straightforward in the calculations as it was a coiled tube in a heated oil bath of constant temperature. In this simplified case of counter-current HEX, the outlet temperature can be expressed as:

$$T(z = 1) = T_{hot}(1 - \exp\left(-\frac{L}{\delta}\right)) - T(z = 0) \exp\left(-\frac{L}{\delta}\right), \quad (5.6)$$
CHAPTER 5. THE NEW SEMI-ANALYTICAL APPARATUS - PRESENTATION

with \( T_{hot} \) representing the temperature of the silicon oil and \( \delta \) defined as:

\[
\delta = \frac{1}{\dot{m}C_p} \cdot \frac{1}{\log\left(\frac{r_{out}}{r_{in}}\right)} \cdot \frac{1}{2\pi k_w} - \frac{1}{h2\pi r_{in}},
\]

(5.7)

with \( \dot{m}, C_p, k_m \) being the mixture's mass flow rate, constant pressure heat capacity and heat transfer coefficient. \( r_{in} \) and \( r_{out} \) are, respectively, the 1/16" Ti tube's internal diameter and outer diameter. \( h \) is the convective heat transfer coefficient, extracted from the Nu number. Computation lead to the temperature profile plotted in Figure 5.4b. Therefore, to ensure that the temperature of the recirculating fluid was equal to the bath temperature before re-entering the thermally equilibrated vessel, the length of coiled tube, \( l \), was chosen to be 1m. Similar to the cooling HEX, the operation of the heating HEX turned out to be fully satisfactory, with no disturbance in equilibrium conditions noticed during operations.

5.2.2 The Circulation Pump

As explained in Section 5.1, flowing the mixture in the circulation line, through the LSL was an important part of the operating procedure. To generate this necessary movement, a pump was to be added to the line. Its function was to draw fluid from the bottom of the heated water rich phase, pump it through the heat exchanger (for cooling), pass the mixture through the LSL and send it back via a heat exchanger (for heating to operating temperature) before arriving at the top of the solvent rich phase. The pump was composed of the following main components:

- An annular magnet (Sintered Samarium 2:17 disc SMDC01427 - 12.5 d x 3.5 mm).
- A 1/4" Titanium grade 5 nipple. Gundrilled and honed to a mirror finish with i.d. = 3mm ±0.01mm.
- A magnetic piston (i.d.=2.935, SS 431) sitting in the nipple, and in the centre of the field generated by the magnetic wheel.
- 2 custom T-piece/check valves (See Figure 5.6).
- A block, connected to the magnetic wheel and moving up and down on 2 rods from the back plate. Frictionless movement up and down these rods was insured by well
lubricated ball bearings.

- A pneumatic piston, sitting on the back plate and driving the block back and forth (SMC Pneumatics CJP2L10-40D).

- 2 microactuators located on a tray on the back plate. They were connected to an electronic valve and acted as a stop for the block driving the magnetic wheel.

The working principle of the circulation pump was based on a lateral pneumatic movement equating to a lateral magnetic translation which drove the fluid vertically. In more detail the process went as follows:

1. Pressurised air inlet is turned ON.

2. The pneumatic piston pushed the shaft, which was connected to the block, putting it in motion. The block, itself, linked by an horizontal rod to the magnetic wheel, also set the latter in movement (see Figure 5.5a).

3. The piston, providing a tight seal with the walls of the nipple, magnetically followed
the wheel. It was in contact with the pressurised mixture, and therefore displaced the fluid when it travelled.

4. On one end of the nipple, the left end, the fluid was pushed towards the check valve/T-pipe piece. The latter only allowed liquid to flow upwards or, in other words, downstream the circulation pump (see later for more details on the working principle of the valves). No flow was coming from downstream on this end of the pump during the "push" part of the motion.

5. On the other end of the nipple, the right end, the displacement of the piston created a sharp pressure drop. It was instantly filled by more fluid flowing from downstream the pump. No flow was coming from upstream on this end of the pump during the "push" part of the motion.

6. The block then hit the microactuator at the end of the tray, sending an electric signal to the pneumatic valve, which inverted the direction of the pressurised air feeding the pneumatic piston. The latter, in return, switched from a pushing motion to a pulling motion.

7. The process described from step 2 to step 5 was then inverted: instead of having fluid pushed downstream the circulation pump on the left end, and drawn from upstream on the right, the fluid was now pulled from the left and pushed on the right.

8. The block then hit the microactuator at the end of the tray, sending an electric signal to the pneumatic valve, which inverted the direction of the pressurised air feeding the pneumatic piston. The latter, in return, switched from a pulling motion to a pushing motion.


The fluid in the vessel, upstream of the circulation device, was continuously "pulled and pushed" downstream the pump through these steps. This process insured the constant circulation of the fluid, vital part of our analytical protocol.

The proper functioning of the re-circulation pump was heavily reliant on the accurate functioning of the custom check-valve/T-pieces. As a matter of fact, in order for circulation to take place, the fluid had to be "pulled up and pushed up". If, instead, it was "pulled up and pushed down", a plug of fluid would have been moving one direction for one pump stroke.
and moving back the other direction while the pump reciprocated, overall resulting in a nil movement.

The role of the check-valve was, therefore, to ensure that:

- While the pump was pulling fluid in the depressurised side of the nipple, only upstream fluid can flow in that space.
- The fluid that the pump was pushing out of the nipple can only flow downstream of the pump.

Failure for the check-valve to fulfil these conditions would result in a weakened or absent recirculation flow.

The chosen design for the check valve/T-piece was a gravity-operated ball seal. As shown in Figure 5.6c, on each end of the T-junction, a 2mm ruby ball (then switched for Ti grade 5) resided in a volume sandwiched by:

- On one end, a conical seat. When the ball rested on it due to gravity, the fluid from atop was stopped from flowing downstream.
5.2.3 The Gas Chromatograph

The GC offered 3 main compartments:

- The Valve Box
- The Column Oven, fitted with a 3m 1/8" Hayesep D Packed Column
- The Detector Boxes

On the other end, a 3mm o.d. perforated screen, 1 mm thick. The screen was perforated to allow fluid to pass through it and, at the same time, contained the ball in its residing pocket.

This directional seal was what confers to the T-piece its check-valve property. No cracking pressure was needed to operate the check-valve, as no spring was used to maintain the ball on the sealing seat. However the T-pieces could only be used vertically, as they sealed thanks to the pulling force of gravity. Also, it is worth mentioning that it was only the combined correct orientation of both T-pieces at the same time that allowed continuous re-circulation of the fluid.
The GC was an SRI 8610C, fitted with a TCD (and a disabled FID). This brand of gas chromatography had interesting features as the embedded technologies were well documented and fairly accessible for users to customise or modify them appropriately. The first considerations regarding the GC were the detectors. The essence behind the new design was to offer an adapted system to measure the sulphurous binaries. Therefore, the detectors at stake should obviously offer a high sensitivity not only to H$_2$S and SO$_2$ but should also detect water well. The combination of their Thermal Conductivity Detector (TCD) in series with their Flame Ionised Detector (FID) offered a positive solution to the needs of this thesis. As a matter of fact, SRI rated their TCD with a sensitivity as good as 100 - 300 ppm and their FID with a sensitivity as low as 1ppm. The TCD in itself fulfilled the needs to measure H$_2$S and SO$_2$ in H$_2$O, as their solubilities were expected to be similar to that of CO$_2$ (see Chapter 2) as well as the thorough sensitivity analysis given in Subsection 5.2.6). The FID was thought to be added to offer greater sensitivity to hydrocarbons which are sparingly soluble in water. More specifically, the ambition was to offer a mean to measure C$_3$H$_8$ in water, as it used to be possible with the Analytical equipment (see Section 4.2).

The valve box only contained one VICI, 2-position, 10-port Gas Sampling Valve with a 1 mL external sampling loop connected to two of its port. For our purpose (see Figure 5.7c), another selector (4 ports selector from VICI, part number EDC3UW) had to be fitted inside the valve box with an electric heater and appropriate insulation. The GC was then sent back to have the detector fitted, a new hole drilled to the body of the valve box and an additional valve heater block connected to the electric heating board of the GC.

Once the GC returned, it underwent numerous customisations, (the results of which are shown in Figure 5.8a and 5.8b) some of which are listed here:

- The whole valve box was elevated by 5mm, to accommodate the 3" standoff for the selector.
- The high temperature selector valve was fitted in the valve box and the appropriate plumbing was done.
- Four new ports were drilled to the front face of the valve box, fitted with a VICI chromatography bulkhead union to accommodate the new plumbing.
- The flash vessel was horizontally connected to the back of the left side of the valve box. A heater and thermocouple were added to the surface of the reactor for additional
control of its temperature.

- Aligned with the position of the flash vessel F, on the red steel cover of the GC, a small rotating motor was fitted. A plate with two button magnets, one for each magnetic poles, was connected perpendicularly at the end of the shaft of the rotor. The magnets were 1mm away from the side wall of the valve box to insure tight magnetic connection with the stirrer inside the flash vessel.

The column oven did not need modification as the column was thought to be optimal for the needs of the experiment (VICI (n.d.a)). The detectors were not supposed to require any work before usage, but the FID was not responding to any input and showed an unnaturally flat signal. After examinations, it turned out that the electronic board linked to the detectors was missing the power components feeding the FID (see Figure 5.9a and 5.9b). After attempting
to manually solder each component to the board, a new board was delivered from the factory. Post-installation, the FID signal showed good response when excited, allowing operations to begin.

### 5.2.4 Material Compatibility and Reactor Design

The aim of the new design was to unlock the limitations found in the literature regarding pressures and temperature for solubility measurements for the sulphuric gases in aqueous solutions. To achieve this objective, the new rig should allow measurements up to 70 MPa in pressure and 473 K in temperature. Taking into consideration the conditions of operations, corrosion prevention was a key feature of the design. As a matter of fact, the phases to work with could contain pure sulphuric gases and/or highly concentrated brines at high pressures and high temperatures. The combination of these substances generates a powerful corrosion potential which will attack the best grades of austenitic stainless steel (Craig
Therefore, all the wetted parts in the rig were made out of Titanium, a material with established corrosion resistance properties for wet, salt rich, high temperature environments, and with a high compatibility with sour gases (Boyer et al. (1994), p.192, also Craig et al. (1995), p.54). The grade mostly available in the UK at the time of the design was Ti Grade 4 and Grade 2 (both commercially pure solid grades of the Ti element), which were used for the bulk of the reactors and the tubing, respectively.

To reduce risks in case of catastrophic leakage of the pressurised fluids, the total volume was kept to a minimum and the whole rig had to fit fully in an extracted enclosure providing 120 air changes per hour, from CleanAir Ltd (see Figure 5.10). This insured that air would flow from outward into the extraction system, therefore limiting risks of leakage outside the extracted enclosure.

The 3" Titanium Grade 4 rod used (supplier NeoNickel Ltd) had an Ultimate Tensile Stress of $\sigma_u = 365$ MPa and Yield Stress of $\sigma_y = 255$ MPa at the maximum operating temperature (Titanium (2000)). Sound Engineering Practise design was followed to come up with the three-piece reactor with a base cylinder, a plug closure and a screw cap. Taking into account a shear stress safety factor $M = 4$, and operating pressures at 2/3 of the material yield pressure, the calculated dimensions generated the drawing of the 3 components shown in Figure 5.11a and 5.11b (additional drawings are available in Appendix E). The fully-assembled vessel is a compact cylindrical piece. Some elements of geometry are presented in the following list:

- **Cylindrical Base:**
  - 76.2 mm Outer diameter
  - 25.4 mm Wall thickness
  - Cylindrical well drilled and honed to mirror finish. Diameter = 25.4 mm. Depth = 95 mm.
  - Neck thread to accommodate the screw cap: M60x6.
  - 2x1/4" SITEC holes in its body: one in the middle of its side (for solvent injection and/or recirculation) and the second at the bottom (for system evacuation and/or recirculation)

---

1The reader is reminded that, although its corrosion resistance is attractive, Titanium can be the vector of catalysis of many reactions, some involving the very sulphuric gases which this thesis was deemed to work with. For example, in the Claus process, an environment rich in SO$_2$ and H$_2$S will see these two compounds transformed into elementary sulphur, and Titanium is a well known catalyst of such reaction. It is therefore important to remember that Titanium can sometimes lose its inert character and take a more undesirable role in regard to composition analysis.
Figure 5.10: Rendering of the Semi-Analytical rig sitting outside the extracted enclosure. All parts were designed and assembled on Solidworks prior to any actual construction. This gave full insurance that the rig would fit through the doors of the enclosure.
• Plug:
  – Shoulder Diameter = 49.50 mm
  – Shoulder Thickness = 15 mm
  – Neck diameter = 25.32 mm, providing a snug fit with the base well.
  – Height = 85 mm
  – 2 Recesses to accommodate 2 high pressure, high temperature seals. The lower seal in contact with the fluids, the second seal as a backup seal.
  – 1x1/16" NPT port for gas injection.

• Screw Cap:
  – 76.2 mm Outer diameter.
  – Internal diameter = 25.4 mm
  – Thread dimensions: Height = 28 mm, diameter = 60 mm and coarseness = 6 mm.

The technology chosen to seal high pressures (70 MPa), high temperatures (473.15 K), wet, sour fluids was a T-seal from Greene-Tweed (Part number 126-21000-799-0450). The wetted sealing material used originally was Fluoraz, a proprietary name for tetrafluoroethylene-propylene elastomer, which is compatible with our conditions of operation (G-T Rings - 11,000 series \ Product data (2008)). This material was later on changed to FKM due to modifications of the system of interest. The o-ring is a multi-components polymer seal, which is resilient to heavy duty operations, and to pressure and temperature loading. The originality in the product is the two outer hard polymer rings: they do not provide any seal but are strategically added to provide an additional mechanical support against pressure-generated polymer extrusion. For our conditions of operation, these rings are made of Polyetheretherketone.

5.2.5 The Flash Vessel

Prior to sending the liquid mixture to the detectors of the gas chromatograph, the fluid had to be vaporised. This was achieved by heating the mixture to a temperature higher than the highest boiling point of the components to be analysed. In our case of aqueous binaries, the highest boiling point was always that of water, therefore it was important that the heat generated provided a temperature well above 373.15 K. In fact, considering the slight pressure
(a) Drawing of the main vessel R, with its 3 parts, the base, the plug and the cap assembled for operating conditions. Inner mixing volume is 25 mL. It has 3 ports: 1x1/16" NPT at the top for the gas inlet and 2 x 1/4" SITEC -1 in the middle of its side and one close to the bottom, for the solvent injection and mixture circulation.

(b) Main Reactor, exploded view. Rendering via Solidworks. Visible are, the Cap, the Plug and the Base, top to bottom.

Figure 5.11: The main vessel R.
CHAPTER 5. THE NEW SEMI-ANALYTICAL APPARATUS - PRESENTATION

(a) Transverse cut of a T-seal. The grey o-ring, with the rounded "T" shape is made of Fluoraz and is the part that provides the seal. The 2 outer rings, represented in green, are the anti-extrusion rings, made of Polyetheretherketone.

(b) Piston seal configuration. The recesses dimensions for the plug piece were inspired from these specifications.

Figure 5.12: T-seal from Greene-Tweed. The technology reduces the polymer o-ring’s extrusion during pressure cycling (courtesy of Greene Tweed)

which the GC worked under (0.3 - 1 MPa), the heating temperature were to be selected above 383.15 K.

The vaporising fluid expanded significantly, and to make sure the pressure inside the sampling line did not cross the Liquid-Vapor (LV) equilibrium line, the volume of the line was increased by adding a buffer volume to the line: the flash vessel. Originally, the vessel had another key purpose: to be the first heated point in the line. This was to ensure that any salt deposition from the vaporising brine would occur in the large diameter of the flash vessel, which would substantially lower the risk of line clogging from salt accumulation.

The Flash Vessel was made of Ti Grade 4 for the same material compatibility reasons as those presented earlier. Its working temperature were taken to be 473.15 K, and its operating pressure 30 MPa. The simple, two-piece design with a blind cylinder, a plate closure and a face seal was chosen. Working with a shear stress safety factor of $M = 4$, and operating within the Sound Engineering Practise, the final drawings for the flash vessel F are presented in Figure 5.13b. It had an internal volume of about 6.5 mL (vessel had to be large enough to be the scene of all the liquid vaporisation, but not excessively large as it would over-dilute the samples before analysis), 2x1/16" SITEC connectors on its closure plate for connections
and 6xM4 screw sockets for pressure containment. On the face of the cylinder, a visible recess accommodated the pressure-sealing o-ring. The sour-gas compatible FKM (Viton) o-ring was ordered in a batch from Polymax Ltd under the part number BS020V75.

5.2.6 Volume Considerations

The determining criteria for sizing the various volumes involved in the apparatus was the sensitivity limit of the detectors of the gas chromatograph. The GC manufacturer provided the bracket 100 - 300 ppm for their TCD and 1 ppm for their FID. Therefore, the volumes involved in the sampling protocol had to verify that samples sent to the detectors would have a concentration higher than the detector sensitivities.

Another good practice is to have the volume of the sampling loop far smaller than the total reactive volume, as illustrated in Equation 5.8.

$$V_{LSL} \leq 10^{-3}V_R$$  \hspace{1cm} (5.8)

The previous equation set an upper value for the volume of the LSL. However, to adequately size the LSL, the flash vessel and the GSL, one had to go through an argument presented in the following lines. For the sake of the demonstration, the particular case of CO$_2$ in water was chosen. It covered well the question of the sensitivity of the TCD. The same process could be followed using for example C$_3$H$_8$ to establish the relations obtained for the FID.
The worst scenario in terms of solute solubility was considered here. In other words the lowest pressure in the analysis range: \( p_{LSL} = 5 \text{ MPa} \). The temperature could not vary, as it was fixed and equal to the room temperature \( T_{LSL} = 303.15 \text{ K} \). Therefore, a first relationship can be written as follow:

\[
\frac{n_{LSL}}{V_{w}} = \frac{V_{LSL}}{V_{w}} \tag{5.9}
\]

With \( n_{LSL} \) as the number of moles in the LSL, \( V_{LSL} \) as the volume of the LSL and \( V_{w} \) as the molar volume of water at the LSV conditions. One could also link the amount of water and \( \text{CO}_2 \) sent to the sampling line, \( n_{LSL}^{w} \) and \( n_{LSL}^{\text{CO}_2} \) respectively:

\[
\begin{align*}
    n_{LSL}^{w} &= (1 - x)n_{LSL} \tag{5.10} \\
    n_{LSL}^{\text{CO}_2} &= x n_{LSL} \tag{5.11}
\end{align*}
\]

with \( x \) being the mole fraction of \( \text{CO}_2 \) at the LSL conditions: \( x(p_{LSL}, T_{LSL}) = 1.08 \text{ mol/kg} \) (Duan et al. (1992)). Once sent to the sampling line of volume \( V_{S} \), the mixture from the LSL was diluted in the He carrier gas. The next step was to quantify this dilution and, therefore, obtain the solute concentration before it was sent to the detector.

The pressurised liquid water and dissolved \( \text{CO}_2 \) vapourised when in contact with the heated walls of the flash vessel, \( T_{S} = 453.15 \text{ K} \). This step raised the pressure in the sampling line until all the mixture was vapourised. He was then introduced until the pressure in the sampling line was at equilibrium with the pressure in the He bottle, \( p_{He} = 0.6 \text{ MPa} \). This step generated the dilution of the solute. Therefore, ability to quantify the amount of He injected until pressure equilibration was key to our argument. From the ideal gas law one has:

\[
\begin{align*}
    p_{w} &= \frac{n_{LSL}^{w} RT_{S}}{V_{S}} \\
    &= \frac{(1 - x)V_{LSL}}{V_{w}} \cdot \frac{n_{LSL} RT_{S}}{V_{S}} , \tag{5.13}
\end{align*}
\]

With \( p_{w} \) being the equilibrium vapour pressure once all the \( n_{LSL}^{w} \) had vapourised. \( R \) is the gas constant in J.mol\(^{-1}\).K\(^{-1}\).
The same logic could be applied to obtain the CO\textsubscript{2} vapour pressure, \( p_{\text{CO}_2} \):

\[
p_{\text{CO}_2} = \frac{n_{\text{LSL}}^{\text{CO}_2} R T_{\text{S}}}{V_{\text{S}}} \quad \text{(5.14)}
\]

\[
= \frac{x V_{\text{LSL}} n_{\text{LSL}}^{\text{CO}_2} R T_{\text{S}}}{V_{w} V_{\text{S}}} \quad \text{(5.15)}
\]

The pressure in the sampling line, prior to filling with the carrier gas, was equal to the sum of the water vapour pressure \( p_w \) and the CO\textsubscript{2} vapour pressure \( p_{\text{CO}_2} \), lower than the pressure in the He bottle. Therefore, when the carrier gas was introduced to the sampling line, the pressure in the line increased to match the He pressure. One can then calculate the number of moles of He introduced, \( n_{\text{He}} \) via Equation 5.17:

\[
n_{\text{He}} = \frac{\Delta p V_{\text{S}}}{R T_{\text{S}}} \quad \text{(5.16)}
\]

\[
= \frac{(p_{\text{He}} - (p_w + p_{\text{CO}_2})) V_{\text{S}}}{R T_{\text{S}}} \quad \text{(5.17)}
\]

Finally, the concentration of the solute in this mixture of He, water vapour and gasified solute was obtained by Equation 5.18:

\[
y^{S} = n_{\text{LSL}}^{\text{CO}_2} \cdot \frac{1}{1 + \frac{n_{\text{He}}}{n_{\text{LSL}}^{\text{CO}_2}}} \quad \text{(5.18)}
\]

The decision making was done when comparing \( y^{S} \) to 100 - 300 ppm (the previous range being the TCD lower sensitivity limit) with the final relationship 5.19:

\[
y^{S} \geq 100\text{-}300\text{ppm} \quad \text{(5.19)}
\]

Volume values of \( V_{\text{LSL}} = 10 \) µL and \( V_{\text{S}} = 6.5 \) mL yielded a \( y^{S} = 2000 \) ppm, which fulfils requirements of Equations 5.9 and 5.19.
Figure 5.14: Control Panel for the Semi-Analytical Apparatus. The software used is the Visual Engineering Environment, VEE, from Agilent. The top left graph plots the volume, in mL, of the Quizix pump. The bottom left graph provides a pressure reading for the reactor R, with the temperature of the gas line before entering R. The top right graph is dedicated to the various temperatures in the rig: TcirP is the reading from the thermocouple situated at the exit of the cooling HEX, and TmLine is from one part of the transfer line, whereas TtrsfL is for the other part, and Tvess is the temperature of the flash vessel F. Finally, the bottom right section activates the switches to set the valves and the motors to their desired positions.

5.3 Standard Operating Procedure

All procedures are remotely operated as per initial design. The Visual Engineering Environment (VEE) used to send digital instructions from the control unit to the devices on the rig is VEE from Agilent (see Figure 5.14). The following section goes into the details of each procedure, always referring to the nomenclature from the full Process and Instrumentation Diagram (P&ID) from Figure 5.2.
5.3.1 Filling R

Filling the reactor R is the first step from vacuum to measurements. From the valve set up detailed in Table 5.8, and after making sure that the solvent has been properly degassed (see Subsection 5.3.11) and reopened to atmosphere (see Subsection 5.3.12), switch the valves to the configuration presented in Table 5.1. At this point, pressure in the reactor is close to vacuum and the valve of the solvent Quizix pump, V14, has been opened to the reactor. Inject the full 10 mL of water/brine in the reservoir. When the first drop of water is in contact with the hot walls of the heated system, it will start to evaporate, raising the pressure by couple hundredth of MPa. Repeat the water/brine injection until the reservoir pressure reaches 1 MPa (total volume to inject is 30 mL). This is usually a good time to check that the circulation pump is correctly primed and functioning by switching it ON. The temperature shown by the thermocouple at the end of the cooling heat exchanger (HEX) will show a sharp change (the direction of the change depends on the operating conditions: the temperatures of the heated bath, of the cooler and of the room) if the pump is circulating the fluid properly. The gas to dissolve in the solvent is now to be introduced. Close the valve of the solvent Quizix pump OFF and open the valve of the Gas Quizix pump ON. Control the injection until the desired pressure is reached and maintain this latter. Start the magnetic stirrer and monitor the gas cylinder volume change. Equilibrium is reached when the variations of the volume of the pump reach a minimum (as explained in Subsection 4.2.2).

Table 5.1: Filling R, valves set up.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>ON&amp;OFF</td>
<td>OFF&amp;ON</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>OFF</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
</tr>
</tbody>
</table>

5.3.2 Filling F

Filling F is an important step for a correct sample analysis. Prior to setting the valves to the configuration detailed in Table 5.2, make sure the sampling line is under vacuum, as detailed in Subsection 5.3.7. It is also key to check that the heated sampling lines are showing an appropriate temperature (usually close to 447.15 K). Introduce He by switching V00 to the open position until the pressure reaches around 0.2 MPa. Switch back V00 to "closed" position, and then send V18 to position 2 to introduce the pressurised mixture in the sampling line. The full detail of the pressure change is presented in Subsection 5.2.6.
5.3.3 Bleeding F

Once the sample is fully vaporised and equilibrium is established, analysis can start. To do so, the GSL on V07 in Figure 5.2 needs to be filled with the mixture in F. A capillary, installed downstream of the loop, allows the pressurised gas mixture to slowly flow, from F through the GSL and to the vent. This process fills the loop without instantly depleting the content of the flash vessel. In fact, this operation only dilutes the concentration of the solute in the vessel proportionally to the bleeding time. With the dimensions of the capillary installed (smooth silica tube of length 5 cm and i.d. 5 \( \mu m \)), the bleeding flow rate was assessed to be around 1.5 mL/min. Therefore, from the valve configuration presented in Table 5.2, switch the selector valve V06 from position 4 to position 2. The gas mixture is now flowing through the restriction tube downstream to the 0.5 mL GSL, slowly filling the latter. Now, the content of the GSL should be sent to the GC for analysis, as explained in Subsection 5.3.4.

Table 5.3: Bleeding F, valves set up.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>ON</td>
<td>OFF</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>OFF</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>OFF</td>
<td>OFF</td>
<td>ON</td>
</tr>
</tbody>
</table>

5.3.4 GC Sampling

To send the content of the 0.5 mL GSL on the 10 ports valve V07 to the GC for analysis, switch the valves configuration from the one in Table 5.3 to the one in Table 5.4. This will connect the GSL to the carrier gas He, which will transport the gas mixture to the detectors. After all the elements have eluted from the column and been shown on the chromatogram, return the valves to the configuration shown in Table 5.2. You might have to repeat the bleeding and sampling several times to obtain a representative analysis of the composition of the mixture in F.

Table 5.4: GC Sampling, valves set up.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>ON</td>
<td>OFF</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>OFF</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>OFF</td>
<td>OFF</td>
<td>ON</td>
</tr>
</tbody>
</table>
5.3.5 R Content to Waste

This is step one of two, along with the cleaning of the flash vessel (Subsection 5.3.9), that require a physical operation on the rig. As a matter of fact, the waste valve V16, is a hand-operated micrometer throttle valve from SITEC, and has no electronic equivalent to help with remote operation. A flexible arm for remote physical operation has been designed and purchased specifically for this purpose, but it never reached the stage of installation. Therefore, to send the content of the main reactor R to waste, first, put V17 to position 1 and then carefully control the opening throttle of the waste valve V16. It is good practise to allow a flow through the waste valve no higher than 5 min/100 bar dropped. Failure to follow this advice will shorten the life span of the o-rings, as a sudden drop in pressure results in adsorbed gas to violently come out of the seals and shatter their structures.

Table 5.5: R content to waste, valves set up.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>OFF</td>
<td>OFF</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>OFF</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>OFF</td>
<td>OFF</td>
<td>ON</td>
</tr>
</tbody>
</table>

5.3.6 F Content to Waste

This is a straight forward step: to send the content of the flash vessel F to waste, just go from any of the valve configurations presented in Tables 5.2 and 5.3 to the configuration showed in Table 5.6. The positions of V01 and V00 are not vital but it is recommended to use the driving force of the He carrier gas to flush all components out of the sampling line before evacuation - Subsection 5.3.7.

Table 5.6: R content to waste, valves set up.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>OFF</td>
<td>OFF</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>OFF</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>OFF</td>
<td>OFF</td>
<td>ON</td>
</tr>
</tbody>
</table>
5.3.7 Evacuate F

Before sending anything into the sampling line, it is important to start from a near to vacuum stage, so as not to corrupt the next analysis. To do so, after having sent the content of the flash vessel to waste (Subsection 5.3.6), set the selector valve V06 to position 3. It is recommended to start with He flowing through the line during this step, making sure any residuals are pushed out of the line and, after a couple of minutes, turning V00 OFF, to get as close to vacuum as possible.

Table 5.7: F to vacuum, valves set up.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>ON</td>
<td>OFF</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>OFF</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>ON</td>
<td>OFF</td>
<td>ON&amp;OFF</td>
</tr>
</tbody>
</table>

5.3.8 Evacuate R

Evacuating R is a straightforward step, as it is simply a switch for V17 from position 1 (R to waste, see Subsection 5.3.5) to position 2 (R to vacuum). The pressure in the reactor might never reach relative vacuum pressure as some water droplets might be retained in the unheated circulation line. If the next filling is different in composition from the previous one, it is then important to go through the cleaning step (Subsection 5.3.9) beforehand.

Table 5.8: R to vacuum, valves set up.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>ON</td>
<td>OFF</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>ON</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
</tr>
</tbody>
</table>

5.3.9 Cleaning F

Cleaning F is only necessary when working with brines. To do so, connect the sampling line to the water syringe pump by switching V01 to position 1. Start injecting water, making sure the throttle valve for the He flow is fully open. When the pressure inside the sampling valve reaches 1 MPa (volume of sampling line full with incompressible liquid water), the syringe pump will jam due to its operating limitation. The volume to inject before jamming should be 3.3 mL, when all the elements in the sampling line are appropriately heated. Any lower value could mean that a blockage in the line is stopping the water from flowing. In this case, blow the line counter-flowingly with pressurised He. Reinject water and repeat the operation.
until the injected volume of water, from an empty line, is 3.3 mL. Then, open the selector from a plug position (Table 5.9) to waste (Table 5.6) to allow the now salty water to escape to waste. Repeat the cleaning up to three times, depending on how advanced the crust deposit is. In case of operations with highly concentrated brines, it is recommended to clean the sampling line once every day. Analysing the case of NaCl, highly soluble salt in water, we explain the cleaning frequency.

The solubility of NaCl in H₂O at 393.15 K and atmospheric pressure is s(NaCl) = 359 g/L. Therefore, the LSL with a 10 µL volume contains 3.59 mg of salt at this temperature (the pressure change is neglected as liquid compressibility is neglected). When the content is sent to the sampling line, the water and gas vaporise, while 3.59mg of salt (With ρ(NaCl) = 2.165 g/cm⁻³, this mass represents volume Vₛ = 1.6µL) is deposited on the wall of the tubing, as shown in Figure 5.15. The crust of salt has a length l (taken to be l = 3cm) and with each vaporisation, the thickness of the salt layer increases (each time volume of the crust increases by Vₛ). This continues so forth until the annular crust grows to a disc and blocks the flow of the vapour phases. This stage is usually to be avoided. The critical volume of the crust to
be avoided, $V_c$, is taken to be 70% of the volume of the cylinder of length $l$ and diameter $d$, where the i.d. of the 1/16" SS tube used for the transfer line ($d = 1$ mm). Therefore:

$$V_c = 0.7 \frac{\pi d^2}{4} l$$  \hspace{1cm} (5.20)

$$= 16 \mu L$$  \hspace{1cm} (5.21)

Which leads to a critical number of injections $N$, of:

$$N = \frac{V_c}{V_s}$$  \hspace{1cm} (5.22)

$$= 16/1.6$$  \hspace{1cm} (5.23)

$$= 10$$  \hspace{1cm} (5.24)

In practice a prolific day of work will yield 10 samplings. Therefore, the recommendation, to avoid any delaying issues, is one cleaning per day.

**Table 5.9: Cleaning the Flash Vessel F, valves set up.**

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>ON</td>
<td>OFF</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>ON</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
</tr>
</tbody>
</table>

### 5.3.10 Cleaning R

Cleaning the reactor R is done by injecting clear water from the valve V14 of the solvent Quizix pump. Set the throttle valve V16 on open (ON) and V17 to Waste (position 1). Refer to the valves set up detailed in Table 5.10. After a full cylinder of water has been injected to the reactor, close the throttle valve and inject water until the system is full. Stir and start the circulation pump. Wait for 15 min and set the valves to the configuration described in Subsection 5.3.5. If the next system is of the same composition, 1 cleaning usually suffices. However, if the next system has a different composition, repeat the cleaning up to three times with the washing liquid being the solvent to be used in the next measurement.

**Table 5.10: Cleaning R, valves set up.**

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>ON</td>
<td>OFF</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>ON</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
</tr>
</tbody>
</table>
5.3.11 Brine Bottle Degasing

Degasing the solvent is an important step to go through prior to any injection in the system. Air is dissolved in the liquid and needs to be removed by vacuuming, so as not to corrupt the analysis. To do so, make sure the pressure transducer of the Quizix pump is connected to the solvent bottle by opening the valve V14 to Fill and closing the Deliver position. The Quizix pump is not connected to the pressurised system. Stir the aqueous solution and close V02. Allow up to 20 min of degasing to happen before switching the bottle back to atmosphere.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>OFF</td>
<td>OFF</td>
<td>1</td>
<td>1</td>
<td>OFF</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>OFF</td>
<td>ON</td>
<td>OFF</td>
</tr>
</tbody>
</table>

5.3.12 Brine Bottle to Atmospheric Pressure

From vacuum, one must open the solvent bottle to atmosphere before being able to suck any fluid back into the Quizix pump. To do so, just switch the stirrer OFF and open V02. The pressure read on the pressure transducer should be 0.0 MPa (absolute pressure) before any pump filling occurs.

<table>
<thead>
<tr>
<th>Valve</th>
<th>V14</th>
<th>V12</th>
<th>V11</th>
<th>V01</th>
<th>V18</th>
<th>V16</th>
<th>V17</th>
<th>V06</th>
<th>V07</th>
<th>V05</th>
<th>V02</th>
<th>V00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>OFF</td>
<td>OFF</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>OFF</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>ON</td>
<td>OFF</td>
<td>OFF</td>
</tr>
</tbody>
</table>

5.4 Calibration Methods

The raw voltage response from the detectors of the gas chromatograph must be translated in a number of mole before interpretation. This capital part of the analytical process, where the response of the detector (identified by the area under the curve of each peak) is associated via a mathematical relationship to an amount of substance, is called the calibration. Usually, depending on the range of operation and on the component studied, the calibration curve of a detector is linear. Under the same conditions used during the measurement campaign, a sample of known amount is sent to the detector. Its response is shown as a peak from which the embedded software extracts a value for the area under the curve. By varying the amount
of matter injected and accordingly recording the response, the linear relationship is obtained, with the sought after calibration coefficient. The amount of substance introduced is obtained by using an EoS where the calibration conditions (temperature and pressure) are entered as input. A number of mole per volume (or density) is then yielded by the EoS. Using the volume of the sample, which, in this case, is the volume of the gas sampling loop, the amount introduced can then be obtained by timing the two values.

Before being sent to the gas chromatograph for analysis, a component must be vaporised. Therefore, components which are gaseous at ambient conditions are easily transported and analysed. However, detector calibration of liquids is a more cumbersome task, which is especially true with water. Full vaporisation of the injected water must occur before entering the column, with no disruption of the carrier gas Flow Rate (FR) during this process. Gathering experience on the appropriate calibration protocol, three different methods were chronologically used to finally come to a satisfactory water and CO₂ calibration:

- **Method 1**: Manual injection to the GC inlet port using a 1 μL liquid chromatography syringe.

- **Method 2**: Automatic injection to the valve box from an unheated sampling valve with a 1 μL internal volume.

- **Method 3**: Automatic injection to the valve box from a syringe pump with vaporisation of the sample prior to filling a 500 μL GSL.

Each one of these methods yielded different results, which led to difficulties when interpreting experimental results. In the following part, the details of the different calibration protocols and their resulting coefficients are presented. Moreover, the reasons behind the difference in these results are described. By the end of the investigations, it becomes clear that variations in the flow rate and the flow path of the carrier gas or in the oven temperature have significant impact on the TCD response.

### 5.4.1 Method 1

As introduced in the previous section, this method simply consisted of injecting the content of a micrometered chromatography syringe into the front inlet of the GC. To calibrate the
water, the syringe used had a volume of 1 µL (Hamilton series 7000) and was fitted on a
digital syringe-holder (Hamilton Digital Syringe) for an improved precision of injections (0.5% error in injected volume). The pure water was degassed and transferred to a glass vial with a
PTFE septum, where it was sampled at ambient conditions by the syringe. For the gas, a
500 µL gas-tight chromatography syringe (VICI Series A-2) was used. The syringe featured a
push button valve to help pressurised fluid to remain in the container until injection. The
gas was sampled from a low permeability gas sampling bag (Thames Restek Multi-layer Foil
Gas Sampling Bag) fitted with a PTFE septum. It was filled to close to atmospheric pressure
and was at ambient temperature. For each volume, a series of 6 injections was made. The
averaged response from the detector was then attributed to the injected volume. For the pure
water, the volumes were 0.25, 0.35 and 0.45 µL. For CO₂, the volumes were 150, 300 and
500 µL. The calibration curves obtained from this method are presented in Figure 5.19a and
5.19b under the label Method 1. An explanatory schematic of the sampling protocol is shown
in Figure 5.16a.
Table 5.13: TCD response in function of column temperature with same size sample.

<table>
<thead>
<tr>
<th>$T_{\text{oven}}$/K</th>
<th>403.15</th>
<th>473.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Area</td>
<td>4223.9</td>
<td>5352.1</td>
</tr>
<tr>
<td></td>
<td>4206.9</td>
<td>5305.1</td>
</tr>
<tr>
<td></td>
<td>4203.8</td>
<td>5333.9</td>
</tr>
<tr>
<td>Average</td>
<td>4211.5</td>
<td>5330.4</td>
</tr>
</tbody>
</table>

During experiments, the elution time of the components are set optimally to avoid crossing of the peaks. However, for the calibration, the samples are pure components. Therefore, looking to be more time efficient and reduce the retention time, the oven temperature was set to $T_{\text{oven}} = 473.15$ K instead of $T_{\text{oven}} = 403.15$ K. Unfortunately, it was later on found out that this was an operative mistake: the temperature of the column oven does have an important impact on the TCD response. Experimental proof was established by changing the oven temperature and injecting the same size sample. The results are shown in Table 5.13. Therefore, the results of this calibration were discarded in favour of the later ones from Method 3.

5.4.2 Method 2

Learning from Method 1, Method 2 had the same operative conditions as these used during experiments and, especially, the same oven temperature. The sampling method was in itself changed as it seemed that the repeatability of the water peaks from Method 1 could be improved. Instead of using a chromatography syringe to inject to the front inlet of the GC, the samples were injected to the valve box by a 4-port 2-position Internal Sample Injector (VICI ED2CI4UWE1) with an internal sampling loop of 1 µL. As shown in Figure 5.16b the valve was set in series with the injection pump (Quizix syringe pump) and a throttle valve, which, either let fluid flush through or acted as a dead-end. The calibration valve was at room temperature and its temperature was monitored by a Type K thermocouple on its body with an accuracy of ±1 K. The fluid was injected in the calibration line via the pump, filled the internal loop of the injector and reached the throttle valve, the latter being open to atmosphere. Once enough fluid had flushed through the injector valve, the throttle valve was closed and the pressure was controlled with the Quizix pump until stabilisation was reached. Then, the calibration valve would be operated to switch position and send the content of its
internal loop to the heated sampling line \((T = 473.15\ \text{K})\) where He would vaporise it (if liquid sample) and carry it to the detector. The injection protocol differed for water and gas as the way to increase the amount of matter sampled at fixed volume is dependant on the phase density.

To increase the amount of gas injected, increasing the filling pressure is sufficient. However, the compressibility coefficient of liquids being insignificant, the increase of matter from an increase of pressure in a fixed volume is negligible. Various concentration mixtures between water and another solvent were then used. The solvent used was high purity acetone (Sigma Aldrich 99.5% purity) and the water concentrations in the mixtures were, in mole fraction, 0.32, 0.85 and 1. Similarly, the injection pressures for \(\text{CO}_2\) were \(p = (5.1, 4.1, 3.1, 2.1)\ \text{MPa}\). For each condition, the content of the internal loop was injected 6 sequential times. The average of the response of the detector was subsequently attributed to the injected amount of the component under calibration. The results of this calibration are presented in Figure 5.19a and 5.19b under the label Method 2. An explanatory schematic of the sampling protocol is shown in Figure 5.16b.

The results of this calibration were used to reassess the quality of previous experimental data. The newly calculated solute concentrations appeared to be in agreement with literature values, which seemed positive at first. However, after more experience was gained on the rig, the sampling protocol was improved significantly, thanks to a better understanding of the injection process (see Subsection 6.1.1). The new solubilities, obtained using the improved method of sampling (sampling Method B), were systematically lower than the literature, which could only be explained by an error in the calibration parameter. In fact, this could only be resulting from an overestimated water calibration coefficient. Further investigations showed that the TCD response was heavily reliant on the He flow rate, as shown in Figure 5.19b and Figure 5.19a. It was then thought that, due to their flow path differences, with one bypassing the valve box and the other going through it, the flow rate in Method 2 (Figure 5.16b) would be different than the flow rate from experiments. However, looking at the calibration curves from Method 1 to Method 2, the \(\text{CO}_2\) fits present a change of slope of 11 % when the water fits present a change of 98 %. Therefore the nature of the phase might have had a bigger impact on the flow rate than the flow path in Method 2. Building on this
understanding, a final calibration was designed, overcoming the issue that the liquid water sampling represented. The method is explained in Subsection 5.4.3.

5.4.3 Method 3

This method was built on two previous calibrations that turned out to be unsuccessful for the following reasons:

- The oven temperature was different than experimental conditions.
- The He flow path was different than experimental conditions.
- Sampling liquid water had not provided satisfactory calibrations.

Therefore, for this calibration method, the oven temperature and the flow path were the same as for experiments and a steam-generator was added to the sampling line to circumvent the liquid sampling issue. The device was an insulated, electrically heated, 1/4" stainless steel tube, 400 mm length, fitted in series with the injection line (see Figure 5.16c). A K-type thermocouple, housed under the insulation, monitored the temperature of the steam-generator, which was set to 473.15 K. To insure the water was fully turned into steam, a low, continuous flow-rate (maximum of 0.2 mL/min) was injected by the syringe pump, with the other end of the line open to atmosphere to reduce pressure build up. To fully acknowledge the effect
of pressure build up, three samples with different injection flow rates were made. The TCD response was linearly regressed in function of the injection FR and the ordinate to the origin was taken as the response at a pressure of 0.1 MPa. This process yielded one calibration point: the amount of matter contained in the volume of the GSL at a pressure of 0.1 MPa. The number of points measured was directly linked to the number of different volumes available for the GSL. In this case, two volumes, 0.5 and 1 mL GSL, were used, which yielded two measured points and a third virtual thanks to the 0 intercept (see Figure 5.18 where the two intercepts from the two fits generated the calibration line for Method 3 in Figure 5.19b).

The coefficients obtained with this calibration method sat perfectly in-between the coefficient from Method 1 and Method 2 (as can be seen from Figure 5.19b) when the CO$_2$ coefficient remains little different to the coefficients from Method 1 and 2 (Figure 5.19a). Because this method was the final improvement to a series of gradually enhanced methods it was accepted that its outcomes were superior. The following values for the water calibration coefficient, $\alpha_w$, and the CO$_2$ coefficient, $\alpha_c$ were obtained:

$$\alpha_w = 9.0610^{-6} \text{ mol/mV} \tag{5.25}$$

$$\alpha_c = 4.8810^{-6} \text{ mol/mV} \tag{5.26}$$
These values are the ones used to interpret raw voltage data from the TCD to mole fraction, throughout the rest of this thesis.

5.4.4 Uncertainty Analysis

The standard relative uncertainty of the calibration coefficient for component $i$ is found through the square root of the product of the calibration coefficient $\alpha_i$ with the sum of the square of standard relative uncertainty for the quantity of matter introduced and for the area under the response curve of the TCD $u_r(n_i)$ and $u_r(A_i)$ (see Appendix Equation C.11):

$$u_r(\alpha_i) = \sqrt{\alpha_i^2[u_r^2(n_i) + u_r^2(A_i)]} \tag{5.27}$$

To obtain the uncertainty related to the quantity of matter and the area under the curve, the following expressions were used:

$$u_r^2(n_i) = u_r^2(p) + u_r^2(T) + u_r^2(V) + u_r^2(\rho) \tag{5.28}$$

$$u_r(A_i) = s(\overline{A_i})/|\overline{A_i}| \tag{5.29}$$

The quantity of matter sent to the TCD is contained in a sampling loop with a volume uncertainty $u(V) = 1.56 \times 10^{-11}$ m$^3$, filled with fluid of density $\rho$ (known at $u_r(\rho) = 5 \times 10^{-4}$
% at a temperature $T$ given within $u(T) = 1$ K and a pressure $p$ given with a relative uncertainty $u_r(p) = 0.25 \%$. The relative uncertainty related to the area is equal to the standard relative deviation from the mean divided by the absolute value of mean, as it is a type A uncertainty (see JCGM (2008)).

From these relations and values, the standard relative uncertainties for CO$_2$ and water were calculated and are reported in Table 5.14.

<table>
<thead>
<tr>
<th></th>
<th>$u_r(n)$</th>
<th>$u_r(A)$</th>
<th>$u_r(\alpha_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$3.07 \times 10^{-3}$</td>
<td>$4.40 \times 10^{-2}$</td>
<td>$2.15 \times 10^{-10}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$2.17 \times 10^{-3}$</td>
<td>$1.37 \times 10^{-2}$</td>
<td>$1.25 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
Chapter 6

The Semi-Analytical Apparatus - Solubility Measurements

6.1 Validation of the New Semi-Analytical Apparatus: The (CO$_2$+H$_2$O) System

Upon design and assembly completion of the new rig, the equipment was yet to be validated. Validation of an analysis equipment consisted of comparing the data obtained when following the standard operating procedures with the accepted literature values. Therefore, a simple, well-understood system, with little room for uncertainty, was to be the chosen reference. The (CO$_2$+H$_2$O) system fulfilled these conditions, with many literature data sets agreeing with each other for our study range of pressures and temperatures, $p = (0.1 - 70)$ MPa and $T = (298.15 - 473.15)$ K (see Section 2.2). Also, a comparatively positive feature of this system was its solubility inversion point at room temperature, which resided at temperatures and pressures high enough to validate the new apparatus.

The solubility inversion point is a concept defined for the purpose of this thesis. It is the point past which, the solubility of a solvent in a solute, in this case a gas in water/brine, at the reference temperature (in this case, the room temperature) becomes lower than the solubility of the heated system. This situation is to be avoided when using the semi-analytical apparatus as this could mean that while the fluid is being circulated (and therefore cooled to the room temperature), the saturation limit could be crossed and a two-phase flow could be established (which introduces high uncertainties in the sample composition).
Figure 6.1: CO₂ mole fraction in pure water. Evolution with temperature for seven isobars. \( p = 5 \text{ MPa}, \ p = 10 \text{ MPa}, \ p = 20 \text{ MPa}, \ p = 30 \text{ MPa}, \ p = 40 \text{ MPa}, \ p = 50 \text{ MPa} \) and \( p = 60 \text{ MPa} \).

Figure 6.1 presents the evolution of solubility with temperature at various isobars. From the graph, one can see that the lowest conditions at which an iso-solubility line can cross an isobar twice is at \( p = 20 \) MPa and \( T = 360.15 \text{ K} \). These conditions define the solubility inversion point for a reference temperature of \( T_{\text{ref}} = 360.15 \text{ K} \). When the reference temperature is the room temperature, \( T_{\text{ref}} \approx 303.15 \text{ K} \), no iso-solubility line crosses the isobars until \( p = 30 \) MPa. The solubility inversion point is thus located between \( p = (20 - 30) \) MPa and the maximum temperature to be measured is \( T = 448.15 \text{ K} \), at this pressure. The range of temperatures accessible without crossing the solubility inversion point is \( T = (298.15 - 448.15) \text{ K} \). This range narrows down with increased experimental pressure. The temperatures at reach under the solubility inversion points at 60 MPa are \( T = (298.15 - 398.15) \text{ K} \).

It was thought that an important improvement could be brought to the LSL solubility inversion point by cooling the circulation line to \( T_{\text{ref}} \approx 285.15 \text{ K} \). In the case of a LSL temperature at \( T_{\text{ref}} \approx 285.15 \text{ K} \), the highest measurable isotherm was shifted to \( T \approx 423.15 \text{ K} \). The range of pressure and temperature measurable by the semi-analytical rig for the (CO₂+H₂O) system should, therefore, be such that \( T = (303.15 \text{ to } 423.15) \text{ K} \), and \( p = (0.1 \text{ - } 60) \text{ MPa} \). Such a range was sufficiently large to validate the new rig.
6.1.1 Sampling Protocol

Once equilibrium between the two phases had been established, with the circulation pump functioning efficiently and the transfer line properly evacuated, the sampling could begin. This process consisted of sending the content of the LSL to the sampling line by operating the LSV. This action switched the connection of the LSL ports, disconnecting the loop from the high pressure branch and connecting it back to the transfer line. There, He displaced the pressurised, gas-saturated liquid content and sent it to the flash vessel. During this process, various reactions of thermodynamics and fluid mechanics competed, which translated to a complex fluid distribution in the sampling line:

- The high pressure gas dissolved in the water, once exposed to the low pressure inside the sampling line and, therefore, to a much lower CO\textsubscript{2} saturation value, violently came out of solution in gas form. A front of CO\textsubscript{2} was then created.
- The explosiveness of the CO\textsubscript{2} coming out of solution projected liquid water onto the walls of the sampling line. This process was similar to an atomisation, with a mist of water droplets being generated in the vicinity of the LSL. Once in contact with the heated walls of the sampling line, the water turned into steam in less than half a minute and a steam front is then created.
- The displacement of the fronts differed in velocity, which resulted in an inhomogeneous distribution of the species in the sampling line (see Figure 6.2b). The CO\textsubscript{2} front appeared earlier on than the steam front, as it was not the result of a phase change. Due to its early appearance in the sample line, the draft force generated by the He carrier gas was more consequent than later on, when the line pressure was closer to the bottle pressure. Therefore, the CO\textsubscript{2} was transported quicker in the line than in the steam front, which appeared only relatively later.

When the pressure inside the sampling line equated to the pressure from the He bottle, fluids stopped their motion. The distribution of each species in the line was highly non-homogeneous, for reasons explained earlier. It is important to mention that the sampling protocol used before understanding this concept consisted of 4 to 6 successive gas samplings from the filled 0.5 mL GSL. This method, which we will refer to as sampling Method A, yielded systematic overestimations of the gas content in the water-rich phase compared to
accepted literature values (see Figure 6.4b). This could be explained simply by considering the fact that the front of CO$_2$ travelled faster than the steam front, therefore the bulk of the water remained upstream of the GSL in the sampling line. Thus, the first 0.5 mL gas samples from the sampling line would yield a CO$_2$ enriched gas mixture. On the other hand, the water content in the gas samplings would increase with increasing samples. This composition inhomogeneity in the line is illustrated in Figure 6.2b, where, from measurements at 5 MPa and at $T = 348.15$ K, one can see that the CO$_2$ concentration was much higher in the earlier samples, when the release of the water was slightly delayed. More on this phenomenon is illustrated in Figure 6.2a, where the CO$_2$ mole fraction in each of the 0.5 mL gas samples for the (CO$_2$+H$_2$O) at $T = 398.15$ K were monitored, for thirty one 0.1 µL liquid samples. One can see from the graph that the first five samples were systematically highly enriched in CO$_2$ and that the tail of the mole fraction curve was systematically enriched in water. Solely considering the first 5-6 gas sampling would then clearly yield an overestimated CO$_2$ solubility in water. It was only after taking into consideration the increasing water content in the following gas samples that one could approach a representative solubility value.

Throughout this chapter, the sampling method used, which we will refer to as sampling Method B, obtains the global CO$_2$ mole fraction value instead of an average of the local mole fraction. Mathematically, we calculate:

$$x_{CO_2} = \frac{\sum n_{iCO_2}}{\sum n_{iCO_2} + \sum n_{iH_2O}},$$

where $n_{iCO_2}$ and $n_{iH_2O}$ are, respectively, the CO$_2$ and the H$_2$O number of moles measured by the TCD for gas sample $i$. From Equation 6.1, the value of $x_{CO_2}$ is directly linked to the number of gas samples. To find out how many samples had to be operated from the gas mixtures before passing enough CO$_2$ and water to obtain a representative solubility value, one had to consider another crucial factor in the sampling protocol: the displacement flow generated when bleeding the gas mixture through the GSL. In the case of a weak bleeding and with a fixed number of gas samples, N, only a small amount of water would be displaced, yielding an overestimation in the overall $x_{CO_2}$. On the contrary, with the same N, too high of a displacement flow would underestimate the concentration of CO$_2$ by streaming majority of the solute to waste. Therefore, blockages in the transfer lines (for example, salt crust
(a) Evolution of $x_{\text{CO}_2}$ in pure water in function of number of gas sample. Mole fractions are calculated based on measurements at $T = 348.15$ K and pressures up to 60 MPa.

(b) Evolution of water and CO$_2$ number of mole with each gas sample. 
- Profile of water quantity and 
- Profile of CO$_2$ quantity

Figure 6.2: CO$_2$ mole fraction evolution in function of the number of samples.
accumulation or particulates from the pressurised line could generate such blockages) or restrictions of the bleeding capillary had a major impact on the measured CO₂ mole fraction and the measurements, repeatability spread. Monitoring these factors was an important feature of the sampling process. Trial and error proved that the optimal number of samplings, N, working in pair with a 50 mm length 50 µm i.d. bleeding capillary was between 14 and 15 gas samples. Such a combination was used in sampling Method B. It does yield a representative cumulative amount of water and CO₂ through the TCD, as shown by Figures 6.4a and 6.4b. In the next two subsections, we explain how the measurements were developed for the two isotherms studied, and how sampling Method B was established.

### 6.1.2 Measuring isotherm $T = 348.15$ K

From Figure 6.1, working with temperature $T = 348.15$ K no solubility inversion should be encountered, as solubility saturation increases as temperature decreases at this temperature. Therefore, when the hot mixture passed in the cooling heat exchanger and its temperature dropped, the CO₂ solubility limit in water rose and all the solute was kept in the solvent until sampling.

The bleeding capillary was an important part of the sampling protocol as mentioned earlier. Therefore, keeping it in good working condition was central for the good repeatability of the measurements. While studying this isotherm, the capillary used underwent repetitive blockages. Various restriction tubing were switched and tested, but all would systematically become irremediably blocked. One design allowed us to carry experiments at this temperature: a 1/16" Stainless Steel tube 200 mm length, 1 mm i.d. with multiple "crushed-wall" type of flow restriction. This home-made restriction tube would also become blocked. However, because its body was made of metal instead of silica, blowing high pressure gas in reverse flow while thermally expanding its i.d. with a heat-gun proved to work efficiently at unblocking it.

The variation in the number of gas samplings, which can be noticed from Figure 6.2a, was due to the change of bleeding flow-rate due to the creeping partial blockage of the capillary. A cycle would establish itself: from full working state, to partial blockage, to complete blockage, to full working state after unblocking procedure and so on. As blockages seemed to appear at higher pressures (or possibly after longer operation time), isobar $p = 30$ MPa presents a larger deviation than the lower pressures.
While measuring higher pressures, the handicapping issue of the capillary blockages was elucidated: the sealing polymer from the T-seals used during the experiments was a tetrafluoro-ethylene-propylene elastomer, rated for usage with H₂S. However, CO₂ having exceptional affinity with most polymers, this material was not ideal for prolonged usages with high pressure and thermal cyclings; the proper material being FKM. Carbon Dioxide was dissolving at high pressures and high temperatures in the polymer seal, and too-sudden pressure drops (most likely due to an opening to waste), would see the gas burst out of the matrix of the seal, shattering it in the process. As these blockages delayed the measurements significantly, it was decided not to wait for the arrival of the new seals, but rather carry on with business as usual until the isotherm was fully measured. However, less points were measured for pressures higher than \( p = 30 \text{ MPa} \). The isobars \( p = 40 \) and \( 50 \text{ MPa} \) only use two liquid samplings to obtain the reported value, instead of a minimum of 5 used for all other isotherms. This introduced artificially low AAD for isobar \( p = 40 \text{ MPa} \) as the two samplings yielded a very close mole fraction. Despite these two isobars, the set of measurements is in very good agreement with the accepted SP model, with an absolute average deviation of 1.8% and a highest deviation of -4.2% at isobar \( p = 5 \text{ MPa} \). This set of measurements was considered a successful validation for the rig: it yielded very acceptable results even through recurrent blockages which lead to severe sampling issues.

Using this isotherm and the obtention of high-quality results, a previously studied isotherm, \( T = 398.15 \text{ K} \), was re-appraised. As a matter of fact, measurements at this temperature were obtained using the sampling Method A instead of B, thus, systematically overestimated \( x \text{CO}_2 \). It was thought that, because the raw data was of high-quality, further statistical research could bring the most out of this data set. The next subsection explains the details of the statistical re-appraisal.

### 6.1.3 Isotherm \( T = 398.15 \text{ K} \) - Reappraisal

Previous attempts to study isotherm \( T = 398.15 \text{ K} \), using sampling Method A, proved to yield measurements that systematically overestimated literature values for \( x \text{CO}_2 \) (see Figure 6.4b). Since then, the study of isotherm \( T = 348.15 \text{ K} \) yielded an improved sampling protocol (sampling Method B). From this point onwards, the validation was accepted, and therefore the need to go through another measurement campaign for the isotherm \( T = 398.15 \text{ K} \) was
deemed unnecessary. However, a very consequential amount of time was spent measuring the system with the old sampling protocol: at the temperature $T = 398.15$ K, more than 1500 gas samples were made. Although the values obtained from these data sets were deviating from the calculated SP solubility values, some parts of the data sets were repeatable. This was considered to be proof that some of the raw data from these measurements could be useful. Moreover, the mentioned systematic overestimation of the CO$_2$ concentration could be justified when considering the fact that, sampling Method A prematurely calculated the CO$_2$ content in the water rich phase only from the first 5 gas samplings. Furthermore, as demonstrated in Subsection 6.1.1, these first samples were always enriched in CO$_2$. Therefore, if (using the results from isotherm $T = 348.15$ K as a benchmark) a systematic way of calculating the correct mole fraction (Equation 6.1) from the first 3 to 6 samples was found, it could then be applied to the old results from $T = 398.15$ K, resulting in new re-appraised solubility values.

For every liquid sample from $T = 348.15$ K, the first five mole fractions (calculated based on Equation 6.1 for $i$ from 1 to 5) were divided by the final mole fraction (based on 15 gas samples) and a ratio for a number of sampling going from 1 to 5 was obtained. The details of the operations are presented in Table 6.2 and plotted in Figure 6.3, where the mean of each set of ratios was successfully fitted with a mathematical function. The coefficients of the fit, as well as the function itself are given in Tab 6.1. The average relative standard error resulting from the fit was 0.23%. Such a relation meant that, for any mole fraction calculated on the basis of under 6 gas samples, an accurate estimation of the full mole fraction could be obtained. As explained earlier, such a relationship provided a mean to obtain the true solubility data for these conditions based on the earlier "premature" mole fraction measurements for isotherm $T = 398.15$ K. The results of these calculations are plotted in Figure 6.4b. From this plot, the following conclusions regarding the rig operation could be drawn:

- A mathematical correlation between the number of gas samplings and the full value of $x_{\text{CO}_2}$ was established. This proved the validity of the theory behind the complex process of liquid and gas sampling (explained in Subsection 6.1.1) and the minute understanding of the working principle of the set-up.
- The ability of the apparatus to provide reliable data (AAD from the re-appraised data was 3.3%), in good agreement with the literature (average deviation from SP was 2.2%), was established again with this second studied isotherm.
Table 6.1: Mathematical function used to fit the ratio of partial mole fraction over full mole fraction. Fit illustrated in Figure 6.3.

\[ x_{\text{full}} = a + \frac{b + c}{1 + (x/d)^e} \]

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.14</td>
<td>3.11</td>
<td>-1.14</td>
<td>1.44</td>
<td>1.28</td>
</tr>
<tr>
<td>Pressure /MPa</td>
<td>Number of total gas samples</td>
<td>Full xCO₂</td>
<td>Partial xCO₂, based on Equation 6.1</td>
<td>Ratio Partial/Full /%</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------</td>
<td>-----------</td>
<td>-----------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i=1</td>
<td>i=2</td>
<td>i=3</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>1.15 10⁻²</td>
<td>3.13 10⁻²</td>
<td>1.95 10⁻²</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.53 10⁻²</td>
<td>2.15 10⁻²</td>
<td>2.44 10⁻²</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.46 10⁻²</td>
<td>2.31 10⁻²</td>
<td>2.03 10⁻²</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.42 10⁻²</td>
<td>2.72 10⁻²</td>
<td>2.14 10⁻²</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.15 10⁻²</td>
<td>2.54 10⁻²</td>
<td>2.36 10⁻²</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>1.14 10⁻²</td>
<td>2.12 10⁻²</td>
<td>2.06 10⁻²</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.06 10⁻²</td>
<td>2.64 10⁻²</td>
<td>2.03 10⁻²</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.16 10⁻²</td>
<td>2.31 10⁻²</td>
<td>2.11 10⁻²</td>
</tr>
<tr>
<td>10</td>
<td>13</td>
<td>1.64 10⁻²</td>
<td>3.23 10⁻²</td>
<td>2.83 10⁻²</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.52 10⁻²</td>
<td>4.08 10⁻²</td>
<td>3.14 10⁻²</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.59 10⁻²</td>
<td>3.89 10⁻²</td>
<td>3.20 10⁻²</td>
</tr>
<tr>
<td>Pressure /MPa</td>
<td>Number of total gas samples</td>
<td>Full $x_{\text{CO}_2}$</td>
<td>Partial $x_{\text{CO}_2}$, based on Equation 6.1</td>
<td>Ratio Partial/Full /%</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------------------------</td>
<td>-------------------------</td>
<td>-------------------------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$i=1$</td>
<td>$i=2$</td>
<td>$i=3$</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>2.15 $10^{-2}$</td>
<td>4.43 $10^{-2}$</td>
<td>3.87 $10^{-2}$</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>2.33 $10^{-2}$</td>
<td>5.36 $10^{-2}$</td>
<td>4.30 $10^{-2}$</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>2.03 $10^{-2}$</td>
<td>5.41 $10^{-2}$</td>
<td>4.28 $10^{-2}$</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>2.07 $10^{-2}$</td>
<td>5.24 $10^{-2}$</td>
<td>4.10 $10^{-2}$</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>2.12 $10^{-2}$</td>
<td>3.75 $10^{-2}$</td>
<td>3.18 $10^{-2}$</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>2.44 $10^{-2}$</td>
<td>7.05 $10^{-2}$</td>
<td>5.51 $10^{-2}$</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>2.18 $10^{-2}$</td>
<td>5.02 $10^{-2}$</td>
<td>4.52 $10^{-2}$</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>2.44 $10^{-2}$</td>
<td>6.9 $10^{-2}$</td>
<td>5.45 $10^{-2}$</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>2.44 $10^{-2}$</td>
<td>5.39 $10^{-2}$</td>
<td>4.53 $10^{-2}$</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>2.40 $10^{-2}$</td>
<td>6.34 $10^{-2}$</td>
<td>5.13 $10^{-2}$</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>2.11 $10^{-2}$</td>
<td>6.31 $10^{-2}$</td>
<td>4.83 $10^{-2}$</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>2.26 $10^{-2}$</td>
<td>5.72 $10^{-2}$</td>
<td>4.47 $10^{-2}$</td>
</tr>
</tbody>
</table>
Table 6.2 Continued:

<table>
<thead>
<tr>
<th>Pressure /MPa</th>
<th>Number of total gas samples</th>
<th>Full xCO₂</th>
<th>Partial xCO₂, based on Equation 6.1</th>
<th>Ratio Partial/Full /%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>i=1</td>
<td>i=2</td>
<td>i=3</td>
</tr>
<tr>
<td>40</td>
<td>14</td>
<td>2.43 10⁻²</td>
<td>6.79 10⁻²</td>
<td>5.25 10⁻²</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>2.41 10⁻²</td>
<td>6.42 10⁻²</td>
<td>5.30 10⁻²</td>
</tr>
<tr>
<td>50</td>
<td>14</td>
<td>2.79 10⁻²</td>
<td>6.97 10⁻²</td>
<td>5.74 10⁻²</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>2.55 10⁻²</td>
<td>6.32 10⁻²</td>
<td>5.13 10⁻²</td>
</tr>
</tbody>
</table>

Figure 6.3: Mathematical function used to fit the ratio partial mole fraction over full mole fraction presented in Table 6.2. • Average of each sampling set and —Mathematical fit, coefficients from Table 6.1.
(a) CO₂ mole fraction in pure water at $T = 348.15$ K in function of pressure.
- This work, $T = 348.15$ K, Sample Method B and \( \text{SP} \) for CO₂ in pure water.

(b) CO₂ mole fraction in pure water at $T = 398.15$ K in function of pressure.
- This work, $T = 398.15$ K, Sample Method A ● This work, $T = 398.15$ K, Sample Method B and \( \text{SP} \) for CO₂ in pure water.

Figure 6.4: CO₂ concentration in water-rich phase for the two isotherms $T = (348.15; 398.15)$ K.
6.1.4 Uncertainty Analysis

The temperature in the bath is controlled at ±0.2K, and the calibration parameters used for the Pt100 thermo probe (temperature range from 198.15 to 473.15 K) were those provided by the manufacturer. The pressure readings were obtained via the Keller pressure transducer, which offered an accuracy of 0.03% of the pressure scale. Similarly than for the thermo probe, the calibration parameters for this device were those provided by the manufacturer. To obtain the values of $(\partial x_{CO2}/\partial T)$ and $(\partial x_{CO2}/\partial p)$ from Equation C.12 at each isotherm and isobar of interest, the derivative of the SP solubility model of CO$_2$ in pure water was used (obtained using the definition of the derivative of a function at a set point). The resulting values from the uncertainties pertaining to the temperature and pressure readings had a negligible impact on the cumulated uncertainty analysis.

The relative standard uncertainty of the raw measurement, $u_r(A_{CO2})$ is calculated as follows (the measurements are obtained from repeated observations and therefore follow a type A uncertainty):

$$u_r(A_{CO2}) = s(A_{CO2})/\bar{A}_{CO2}, \quad (6.2)$$

where $s(A)$ is the experimental standard deviation of the mean, or "standard error," and $\bar{A}_{CO2}$ is the CO$_2$ peak area average. The uncertainty deriving from the calibration of the detector can be found in subsection 5.4.4. Considering all of the above, the results of the uncertainty evaluation for this system for both isotherms are summarised in Table 6.3.

6.1.5 Discussions and Conclusions

Before obtention of any meaningful data, many hurdles were faced during the (CO$_2$+H$_2$O) measurement campaign. The following subsections attempt to present the knowledge gained from such experiences and the conclusions reached at the stage of the validation of the equipment.

Experimental hurdles, confusions and causes of delays

Obtaining reliable data for the isotherm $T = 398.15$ K was the trickiest part of the measurement campaign as, chronologically, isotherm $T = 348.15$ K was measured subsequently. Some of the hurdles responsible for the difficult experimentations were only consequences of deeper causes which, on many occasions, handicapped the evolution of the research. In Figure
6.5, summaries of the measurements are presented. In each graph, arrows of different colours are shown. These represent explanations for the changing behaviour of the mole fraction of CO₂ with each liquid sampling:

- A full blue arrow indicates a new system fill, with fresh water, newly introduced CO₂, a new equilibrium and an established fluid circulation.
- A striped blue arrow indicates a new fill following a notable change in the design configuration. For example, this could be a valve position change or a change in regard to the circulation pump.
- A grey arrow indicates weak, low or absent circulation flow rate.
- A striped grey arrow indicates a new fill following a change in the operating conditions. For example, this could be using a higher circulation flow rate, or manually unblocking the sampling line.
- A black arrow indicates unrepeatable measurements, likely to be due to partial or advanced blockage of either the transfer line or the narrower valve box tubing.
- A red arrow indicates a leak, from the pressurised branch of the rig to the analysis branch.

Table 6.3: Combined expanded uncertainty, $U(x_{\text{CO}_2})$ for the solubility measurement of CO₂ in water for the (CO₂+H₂O) system at $T = (348.15, 398.15) \text{ K}$, using a coverage factor $k = 2$.

<table>
<thead>
<tr>
<th>$T / \text{K}$</th>
<th>$p / \text{MPa}$</th>
<th>$x_{\text{CO}_2}$</th>
<th>$U(x) = k.u_c(x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>348.15</td>
<td>5</td>
<td>$1.0910^{-2}$</td>
<td>$3.2510^{-3}$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$1.5810^{-2}$</td>
<td>$3.7810^{-3}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$2.1010^{-2}$</td>
<td>$6.7410^{-4}$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$2.2910^{-2}$</td>
<td>$3.5510^{-3}$</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>$2.4610^{-2}$</td>
<td>$5.0810^{-3}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>$2.6710^{-2}$</td>
<td>$3.2310^{-3}$</td>
</tr>
<tr>
<td>398.15</td>
<td>5</td>
<td>$4.9510^{-3}$</td>
<td>$5.0610^{-3}$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$8.9710^{-2}$</td>
<td>$1.4310^{-3}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$1.5210^{-2}$</td>
<td>$7.8110^{-4}$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$1.8010^{-2}$</td>
<td>$1.2610^{-3}$</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>$1.9810^{-2}$</td>
<td>$8.1610^{-4}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>$2.2610^{-2}$</td>
<td>$1.6710^{-3}$</td>
</tr>
</tbody>
</table>
One can clearly see that, for most cases, it is not until the last 5-10 measured points, following the appropriate problem solving, that the correct value was measured. For months, it was thought that the numerous experimental issues encountered were unrelated. The lack of repeatability of the measurements was attributed to the lack of understanding of the important sampling parameters. At the time, black particulates were found repeatedly in the pressurised waste line, and fluidised black matter in the sampling waste line. This was unfortunately confused with Epoxy, used in both parts of the rig: 0.5 mL at each end of the magnetic piston of the circulation pump and 0.2 mL to bond the rod magnet inside the core of the stirrer in the flash vessel. It was thought that due to mechanical movement and friction, the epoxy used would erode and become responsible for the blockage issues encountered. The operations issues undergone during experiments were actually multiple, with the main draw-back being sporadic handicapping leakages from the pressurised side of the system to the sampling side. The separation of the two branches of the system was insured by the HPLC valve. Therefore, the leak could only happen if the valve was not properly isolating the two parts of the system from each other. This would introduce a higher amount of pressurised fluid than the expected volume from the sampling loop, thus biasing the measurement. After investigations, it turned out that the valve had a continuous scratch present on its stator surface. The shape of the latter was perfectly circular, which permanently drew a connection from one of the high pressure ports to the sampling port, resulting in an obsolete high pressure seal. The expensive valve had to be replaced twice, as this scenario occurred four times. The cause of such scratches were attributed to the aforementioned particulates. After many attempts to thoroughly wash and clean the system, no more visible particulates were found in the pressurised waste line and measurements carried on. However, later analysis of the solubility measurements showed that blockages still remained (shown by the black arrows in the graphs in Figure 6.5), and after few weeks of operations cycles, particulates were back in the waste line again.

Re-apparition of the unidentified matter in the waste line forced the investigations away from the epoxy. As a matter of fact, the latter could not be released in the system with such a volume. Therefore, the particulates had to have been discontinuously generated by a large source. The source was found when opening the main reactor R: the primary seal of the plug piece had undergone significant damages, with one of its polymer rings being cracked.
CHAPTER 6. THE SEMIANALYTICAL APPARATUS - SOLUBILITY MEASUREMENTS

Figure 6.5: $\text{CO}_2$ mole fraction evolution with each liquid sample for each isobar studied at $T = 398.15 \text{K}$. 

(a) Isobar $p = 5\text{MPa}$. Final value for the $\text{CO}_2$ mole fraction.

(b) Isobar $p = 10\text{MPa}$. Final value for the $\text{CO}_2$ mole fraction.

(c) Isobar $p = 20\text{MPa}$. Final value for the $\text{CO}_2$ mole fraction.

(d) Isobar $p = 30\text{MPa}$. Final value for the $\text{CO}_2$ mole fraction.

(e) Isobar $p = 40\text{MPa}$. Final value for the $\text{CO}_2$ mole fraction.

(f) Isobar $p = 50\text{MPa}$. Final value for the $\text{CO}_2$ mole fraction.
Table 6.4: Documentation of the actions taken toward the overall improvement of quality and repeatability of the sampling protocol for the new semi-Analytical rig.

<table>
<thead>
<tr>
<th>Pressure /MPa</th>
<th>Sample Number</th>
<th>Arrow style</th>
<th>Nature of Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>21</td>
<td>Striped Grey</td>
<td>Switch from unheated to heated transfer line AND tube i.d. change: from 0.3 to 1 mm</td>
</tr>
<tr>
<td>43</td>
<td>Striped Blue</td>
<td>New piston fitted for circulation pump o.d.: 2.935 mm AND Heaters for transfer line upstream LSV added AND throttle valve replaced restriction tube for He FR</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>Striped Blue</td>
<td>Replacement of leaking LSV with new one.</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>Striped Blue</td>
<td>LSV position change</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Striped Blue</td>
<td>New piston fitted for circulation pump o.d.: 2.935 mm AND Heaters for transfer line upstream LSV added AND throttle valve replaced restriction tube for He FR</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Striped Blue</td>
<td>LSV position change</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Striped Grey</td>
<td>Reduced He FR</td>
<td></td>
</tr>
<tr>
<td>Pressure /MPa</td>
<td>Sample Number</td>
<td>Arrow style</td>
<td>Nature of Change</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
<td>-------------</td>
<td>------------------</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>Striped Blue</td>
<td>New piston fitted for circulation pump o.d.: 2.935 mm AND Heaters for transfer line upstream LSV added AND throttle valve replaced restriction tube for He FR</td>
</tr>
<tr>
<td>8</td>
<td>Striped Blue</td>
<td></td>
<td>New 5µL LSL</td>
</tr>
<tr>
<td>43</td>
<td>Striped Blue</td>
<td></td>
<td>New home-made LSL with 0.3 mm i.d.</td>
</tr>
<tr>
<td>54</td>
<td>Striped Grey</td>
<td></td>
<td>High pressure gas injection unblocking transfer line</td>
</tr>
<tr>
<td>59</td>
<td>Striped Blue</td>
<td></td>
<td>Loop insulation and cooling</td>
</tr>
<tr>
<td>29</td>
<td>Striped Blue</td>
<td></td>
<td>Heaters for transfer line upstream LSV added AND throttle valve replaced restriction tube for He FR</td>
</tr>
<tr>
<td>30</td>
<td>Striped Grey</td>
<td></td>
<td>Throttle Valve replaced restriction tube for He FR</td>
</tr>
<tr>
<td>60</td>
<td>Striped Blue</td>
<td></td>
<td>New piston fitted for circulation pump o.d.: 2.935 mm</td>
</tr>
<tr>
<td>68</td>
<td>Striped Blue</td>
<td></td>
<td>LSV position change</td>
</tr>
<tr>
<td>59</td>
<td>Striped Blue</td>
<td></td>
<td>Loop insulation and cooling</td>
</tr>
</tbody>
</table>
Table 6.4 Continued:

<table>
<thead>
<tr>
<th>Pressure /MPa</th>
<th>Sample Number</th>
<th>Arrow style</th>
<th>Nature of Change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17</td>
<td>Striped Blue</td>
<td>New piston fitted for circulation pump o.d.: 2.935 mm</td>
</tr>
<tr>
<td>40</td>
<td>23</td>
<td>Striped Blue</td>
<td>New home-made LSL with 0.3mm i.d.</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>Striped Blue</td>
<td>LSV position change</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>Striped Grey</td>
<td>Trial and error switching Circulation pump ON/OFF before sampling</td>
</tr>
<tr>
<td></td>
<td>63</td>
<td>Striped Grey</td>
<td>Increase Circulation Flow rate</td>
</tr>
<tr>
<td></td>
<td>67</td>
<td>Striped Blue</td>
<td>Loop insulation and cooling</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>Striped Blue</td>
<td>New 5µL LSL</td>
</tr>
<tr>
<td>50</td>
<td>33</td>
<td>Striped Blue</td>
<td>First attempt at home-made LSL with 0.3 mm i.d.</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>Striped Blue</td>
<td>New home-made LSL with 0.3mm i.d. AND Loop insulation and cooling</td>
</tr>
</tbody>
</table>
Figure 6.6: The particulates from the T-seals and one of the damages it generated on this apparatus - HPLC leakage.

open (see Figure 6.6b). Material compatibility explained this phenomenon. As a matter of fact, at the time of the design, and as explained in subsection 5.2.4, the purpose of the seal was to optimise the system for high pressure and high temperature work with concentrated sulphuric gases. Therefore, the polymer chosen for this usage was Fluoraz, a proprietary name for tetrafluoro-ethylene-propylene elastomer. However, as CO₂ is an excellent solvent for hydrocarbon and has a high affinity with polymers, the best recommended material for HPHT measurements of Carbon Dioxide is Viton/FKM. Not having the right material caused CO₂ to be absorbed into the polymer seal, causing its content to increase with pressure. Rapid pressure drops would then suddenly force the gas out of the polymer matrix, in such a quick manner that the stress induced would rupture its structure. Such pressure drops could be due to, for example, large leaks, quick opening of the waste valve and/or pressure cycles (inherent to the measurement process).

It is likely that the material used by the T-seal company contained metal inserts to increase its mechanical properties. These metallic aggregates were released in the mixture and reached
the LSV. Once in contact with the tight space between the stator and the rotor, their sharp edges and high material strength caused the subsequent scores found on the body of the valve. After changing the sealing polymer for the appropriate Viton/FKM, no further leakages nor blockages were experienced, and measurements were substantially more repeatable, as shown by the results in Sections 6.2 and 6.3.

Another important hurdle to overcome was concerned with the lack of repeatability of data at high pressures for isotherm $T = 398.15$ K. In fact, as can be seen from Figure 6.5, until the last design change was brought to the system, isobars $p = 40$ and $50$ MPa showed a large spread in their data. Due to the position of the sampling valve, which was located in the vicinity of the device-cooling systems of the rig (which release heat by removing it from the apparatus), these measurements were made while the temperature of the thermocouple, located on the LSL, was around $T = 313.15$ K. As shown by Figure 6.1, when compared, at $40$ MPa, the CO$_2$ solubility in water at $313.15$ K is equal to the solubility of CO$_2$ at $398.15$ K. At $50$ MPa, the CO$_2$ saturation in water is even lower at $313.15$ K than it is at $398.15$ K. This change in the solubility relationship signified that the solubility inversion temperature was either reached or passed. In other words, when the hot, pressurised, saturated mixture passes through the cooling HEX, the temperature drop at these pressures was translated as a solubility saturation drop (shown by Figure 6.1). The over-saturated solution saw CO$_2$ come out of the solution. A two-phase region then settled from the point in the circulation line where the temperature of the fluid rose above the solubility inversion temperature of a point somewhere in the heating HEX. It was thought that an easy way to help improve the repeatability of the measurements was to change the position of the LSV. Therefore, the HPLC valve position was switched from downstream of the circulating pump, with fluid being pushed into it (as shown by the P&ID in Figure 5.2), to upstream of the pump, with fluid being sucked from it. Switching the position of the LSV was to improve the situation in two ways:

1. Bringing the LSL closer to the cooling HEX would reduce the heat loss from the fluid thermalisation during re-circulation. This should maintain the CO$_2$ in solution, as the temperature of the latter would remain lower than the solubility inversion temperature.

2. The possibility of gas coming out of solution and accumulating at the highest elevation point of the re-circulation line was non-negligible, especially while the circulation pump
was undergoing flow issues from blockages discussed earlier. Therefore, moving the LSV from its original location (roughly at the highest point in the re-circulation line) to a lower point would help to measure a homogeneous single phase mixture.

This switch of position was followed by severe blockages of the sampling loop, which lead to attempts to fit wider bore loops. Better measurements were obtained with a sampling tube with the same diameter as the small bore Ti tubes used in the rest of the rig (0.3mm i.d.). However, measurements still presented an important lack of repeatability at high pressures. It was, therefore, decided to insulate the sampling loop and cool its walls with a temperature-controlled copper tube wrapped around it. This last change dropped the LSL temperature significantly (around 386.15 ± 4 K) and, as can be seen from the graphs in Figure 6.5, greatly helped the quality of measurements. Such an improvement validated the theory of phase separation from solubility inversion during the circulation process. Table 6.4 describes in detail the various actions taken to improve the data gathered during the \((\text{CO}_2+\text{H}_2\text{O})\) measurement campaign at \(T = 398.15\) K. One can refer to the corresponding graphs from Figure 6.5 to evaluate their effects.

Conclusions from the validation of the apparatus

The results presented in Subsection 6.1.2 and 6.1.3 fully validated the newly developed equipment. The viability of its design was proven by establishing its thermodynamic limitations, pushing their boundaries, developing an optimised sampling protocol and statistically re-appraising old-data sets.

While doing so, complex sampling problems, specifically repeated blockages, were encountered. These issues lead to handicapping leaks, lack of repeatability in the data and other experimental set-backs. The origin of these blockages was identified as being particulates from \(\text{CO}_2\) incompatible polymer seals, originally installed for sulphuric gas HPHT work. Through pressure cycles, these rubber rings underwent irremediable damages and released significant volumes of polymer particulates, which generated the experimental issues encountered. These blockages were not fully solved during this study, but were largely improved by thorough washing of the system and avoiding pressure cycles - the secondary ring provided a pressure seal until full replacement of the rubber seal was possible.

At higher pressures, the solubility inversion concept added to the list of sampling issues as more unreliable data were measured. This problem was solved by bringing the sampling valve
closer to the cooling HEX (upstream the circulation pump), insulating its loop (LSL) and cooling it to under 283.15 K.

These efforts lead to the first reliable data sets obtained with the newly designed and assembled semi-analytical apparatus, thus providing a full pressure range (5 to 50 MPa) validation for this new rig for the isotherm $T = 328.15$ K. Old data sets, thought to be obsolete (as measured via an old sampling protocol), were re-appraised statistically with a second order polynomial. This polynomial linked so-called "pre-matured" mole fraction to full mole fraction, obtained via the new sampling protocol. This re-appraisal systematically yielded satisfactory CO$_2$ solubility. Such conclusions further validated our sampling protocol and our detailed understanding of the sampling principles of the new rig.

In conclusion, the data sets gathered for the (CO$_2$+H$_2$O) system were in good agreement with the literature (1.8% and 2.2% AAD deviation from SP in average for $T= (328.15, 398.15)$ K respectively) and presented low absolute average deviation. Such statements fully validate the novel semi-analytical apparatus for HPHT solubility measurements of soluble gases in pure water. However, more than pure binaries systems, it is the pseudo-binaries systems that contain a high potential for novel measurements and storage applications. Therefore, the next test for the rig was to measure the solubility of gases in highly concentrated brines, and more specifically in this case, NaCl at a concentration of $m = 3$ mol/kg, which is what the next subsection discusses.

### 6.2 The (CO$_2$+H$_2$O+NaCl[3mol/kg])

#### 6.2.1 Measurements at $T = 348.15$ K

The positive outcome from Section 6.1 validated the novel rig for a consequent range of pressure and temperature: $p = (0.1 - 50)$ MPa and $T = (308.15 - 398.15)$ K. The validation was obtained using the (CO$_2$+H$_2$O) binary system, which offered the right level of experimental hurdles to calibrate and evaluate the operative protocols. This achievement meant that systems with similar phase behaviour properties could be studied with the semi-analytical apparatus at pressures and temperatures higher than previously found in the literature. These measurable systems encompass:

- (Gas+Water) type binaries
• Systems with solubility behaviour such that the solubility inversion point will not be crossed at a sampling temperature of 283.15 K. Unfortunately, for an unknown system, this condition can only be answered through measurements.

• Systems with a phase behaviour such that a sampling temperature of 283.15 K will not be in the equilibrium region for hydrates.

This list, however, does not include systems composed of gases in highly concentrated brines, as no salt was present during our previous validation. Most of the mutual solubilities of these systems are untapped and represent the highest potential for understanding injection-related phase behaviour. Therefore, measuring the solubility of a well-studied, pseudo-binary was the final step of the validation of the new equipment. If the solubility of such systems were to agree with the literature, then the apparatus should be able to measure unstudied pseudo-binaries, as long as they respect the conditions cited earlier. Building on the acquired understanding of the (CO₂+H₂O) system, it was decided to use the similar (CO₂+H₂O+NaCl) system for this last step of the validation of the new apparatus.
The NaCl salt used was purchased from Sigma Aldrich with a stated purity greater than 99%. A total weight of 96.66 g was weighted with a Mettler Toledo precision balance (model PR5003 with an accuracy of $10^{-3}$ g) and added to 544.68 g of 294.65 K deionised water, which gave a brine concentration of $m = 2.98 \text{ mol/kg}$. The device used for the water purification was the Millipore Milli-Q system, combining reverse osmosis and infrared irradiation, and yielding an ultrapure water with an electrical resistance of 18 MΩ/cm.

The purpose of this study was to compare the solubility obtained for this system with the accepted literature value. To obtain confirmation that the rig allows measurements with salt solutions, only one isotherm was sufficient, as the results would subscribe to a campaign of measurements which began with the (CO$_2$+H$_2$O) system. The chosen temperature was $T = 348.15 \text{ K}$, which, for the (CO$_2$+H$_2$O) system, turned out to be a good experimental choice as it remained far from both, the supercritical point of CO$_2$ and the solubility inversion point. The Spycher-Pruess model for solubility of CO$_2$ in brine remained our reference for this system, as their EoS was in agreement with accepted literature values (Spycher & Pruess).

6.2.2 Uncertainty Analysis

Following the same procedure as in Subsection 6.1.4, the combined standard uncertainty for the CO$_2$ mole fraction was calculated and the results for each pressure are presented in 6.5.

6.2.3 Conclusions

Keeping in mind that the end goal was novel data obtention, only a very short period of time was allowed to achieve the isotherm measurements and fulfil this last step of the validation of the rig. Smooth analyses were experienced for isobars $p = (10, 20, 40) \text{ MPa}$. For

<table>
<thead>
<tr>
<th>$T / \text{K}$</th>
<th>$p / \text{MPa}$</th>
<th>$x_{\text{CO}_2}$</th>
<th>$U(x) = k \cdot u_c(x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>348.15</td>
<td>10</td>
<td>$8.410^{-3}$</td>
<td>$9.9510^{-4}$</td>
</tr>
<tr>
<td>20</td>
<td>1.1110$^{-2}$</td>
<td>$8.0510^{-4}$</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.2410$^{-2}$</td>
<td>$6.2810^{-4}$</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.3210$^{-2}$</td>
<td>$1.2710^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>
those points, the AAD is plotted in Figure 6.7, with an average value of $5.8 \times 10^{-4}$. However, post-vaporisation, NaCl would form large crystals in the transfer line. These would travel to the restriction tube and reduce the bleeding rate. Most times, it would result in capillary blockages and required replacement. This cycle ended once a 50 mm length 50 µm i.d. smooth wall silica tube was installed. As a change of dimension for the capillary directly translates into a change of pressure drop, which translates into a change of bleeding flow rate, every time a capillary was changed, an adaptation period was necessary to find the optimal bleeding time. The period of trial and error happened during measurements at $p = 30$ MPa. Once the new capillary was installed and the lower pressures re-measured with this configuration, the pressure $p = 50$ MPa was measured only once (which explains the absence of uncertainty quantification for this pressure).

The CO$_2$ content of the saturated water-rich phase of the (CO$_2$+H$_2$O+NaCl) binary was studied at $T = 348.15$ K and $p$ up to 50 MPa and with a salt concentration of $m = 3$ mol/kg. The AAD was 1.5% and maximum deviation of 3.3% from SP salting-out estimations, prove that the solubility model from Spycher & Pruess (2010) is valid within its stated uncertainty (Mean Square Root 7%) at these conditions. The new semi-analytical apparatus successfully generated reliable measurements for solubility of gases in highly concentrated brines for a wide range of pressure and temperature, respectively (0.1 - 50) MPa and (298.15 - 423.15) K. Furthermore, because the salting out effect pushes the solubility inversion point farther, it is likely that the temperature limit for this system is also expanded. However, this theory was not tested. An additional point which brings noteworthy value-added to these measurements is that the isotherm $T = 348.15$ K had not yet been studied for the (CO$_2$+H$_2$O+NaCl) binary at either, the pressures nor the concentration investigated in this work (see Subsection 2.2.1). These encouraging results grant the semi-analytical apparatus a promising potential for novel HPHT gas solubility measurements in water/brine. More valuable binaries were to be investigated to verify this potential, and the next section presents the study of one of such untapped system with that of (CO$_2$+H$_2$O+NaHCO$_3$[0.8 mol/kg]).
6.3 The \((\text{CO}_2 + \text{H}_2\text{O} + \text{NaHCO}_3[0.8\text{mol/kg}])\) System

The work achieved in Sections 6.1 and 6.2 brought us full validation of the rig for a satisfactory range of pressure and temperature \((p \text{ from 0.1 to 50 MPa and } T \text{ from 308.15K to 398.15 K})\). Obviously, the most interesting systems to study, then, would have been the sulphuric gases binaries. However, because the complete array of safety features of the laboratory were not yet designed or tested, the measurements of these systems were postponed until further notice. It would have also been interesting to go back to the \((\text{C}_3\text{H}_8 + \text{H}_2\text{O})\) system, now that the rig was producing reliable data. This binary was not the chosen system to study next however, due to its experimental risks. As a matter of fact, by the time the validation of the rig was fully proven, less than two months were left until the authorised time in the lab came to an end. The propane-water binary contained too many identified unknowns for the remaining time. Potential risks, the effects of which on experiments could not be anticipated, were: a low solubility inversion point (Kobayashi et al. (1953)) and there was uncertainties regarding potential hydrate formation under our condition of operation (especially the cooling of the LSL which could go as low as 280.15 K under 60 MPa of pressure). The first risk would have generated gas coming out of solution during the recirculation process (similar to during the \((\text{CO}_2 + \text{H}_2\text{O})\) measurement at 348.15 K above 40 MPa, see 6.1). The second issue would have also seen the mixture sampled being non-homogeneous but this time due to the presence of hydrates: solid, ice-like particulates, rich in propane. As the likeliness of such situations was non-negligible, it was decided to not go through such risks, and potentially failing at obtaining the sought after novel data.

The \((\text{CO}_2 + \text{H}_2\text{O} + \text{NaHCO}_3)\) system presented a high potential for novel measurements as essentially no data were available at reservoir conditions (2.2). Also, \text{HCO}_3^- is particularly relevant to \text{CO}_2 sequestration in carbonate rocks, the focus of the overall QCCSRC program. It supposedly also had very similar solubility features to the \((\text{CO}_2 + \text{H}_2\text{O} + \text{NaCl})\) system, with an expected similar salting-out effect (common presence of cation \text{Na}^+ in solution) and a solubility inversion point that should not cause any issues under the validated operating conditions. For these reasons, it was decided that the \((\text{CO}_2 + \text{H}_2\text{O} + \text{NaHCO}_3)\) system would be the next and last system studied.
6.3.1 Preliminary study: the \((\text{H}_2\text{O}+\text{NaHCO}_3[0.8\text{mol/kg}])\) brine

Sodium bicarbonate, usually referred to as "baking-soda," has an interesting chemistry, which explains its frequent presence in recipe books. When exposed to heat, the salt decomposes, producing \(\text{CO}_2\) and \(\text{H}_2\text{O}\) in half-stoichiometric proportion, as shown by Equation 6.3 (Barrall Ii: & Rogeas (1966)). This phenomenon has been behind the "rising" of doughs for centuries.

\[
2\text{NaHCO}_3 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \tag{6.3}
\]

The equilibrium constant of this reaction increases with temperature, with instant full thermal decomposition at 473.15 K. This phenomenon is very important for our analysis. As a matter of fact, the sampling protocol includes the vaporisation of the mixture at temperatures close to 473.15 K. Under these conditions, the water evaporates and leaves salt behind. The latter, fully dissociates when exposed to high temperatures and turns into \(\text{CO}_2\) and \(\text{H}_2\text{O}\), leaving behind a crust of sodium carbonate. In cases where the solubility analysis focuses on any other gas than \(\text{CO}_2\), this side reaction has little importance, as the water content introduced is negligible compared to the average size of the matrix of the solvent. However, if the gas of interest is carbon dioxide, then considering the amount of \(\text{CO}_2\) generated by the bicarbonate thermal decomposition is key to a reliable estimation of \(x\text{CO}_2\).  

The brine preparation is similar to the one explained in section 6.2. The sodium bicarbonate salt was purchased from Sigma Aldrich, with a rated purity of \(\geq 99.5\%\). The final weight showed 36.66 g of NaHCO\(_3\) for 544.68 g of DI H\(_2\)O at 294.65 K, yielding a final salt concentration of 67.03 g per kg of water \((m = 0.8 \text{ mol/kg})\). In such concentration, the theoretical molar production of \(\text{CO}_2\) would then be as follows:

\[
n_{\text{CO}_2} = \frac{1}{2} c_m \frac{\rho_{\text{H}_2\text{O}}}{M_{\text{NaHCO}_3}} V_{\text{SL}} \tag{6.4}
\]

\(^1\)The knowledgeable reader would know that, in an aqueous solution, the reaction 6.3 will occur in the direction 2, right to left, meaning that in presence of both \(\text{CO}_2\) and \(\text{Na}_2\text{CO}_3\), additional sodium bicarbonate could be produced. Such production would have had a profound impact on the chemistry and composition of the aqueous phase and would require a clear quantification, thus bringing an additional complexity level to its analysis. However, this reaction is limited by the concentration of sodium carbonate \((\text{Na}_2\text{CO}_3)\) which, in a de-ionised water environment, is necessarily scarce. However, the equilibrium of reaction 6.3 is greatly altered in the reactor R which is filled with HP \(\text{CO}_2\), one of the two products of the reaction. Therefore, in this experiment, the \(\text{CO}_2\) saturated brine and the absence of sodium carbonate will insure that both directions equilibrium constants from reaction 6.3 are negligible. This resolves any doubts regarding the integrity of the initial bicarbonate concentration.
Where $n_{\text{CO}_2}$ is the number of moles of $\text{CO}_2$ produced from the thermal dissociation mentioned in Formula 6.3. $c_m$ is the mass concentration of $\text{NaHCO}_3$ in water, $\rho_{\text{H}_2\text{O}}$ is the density of water at room temperature ($T = 294.65$ K), $M_{\text{NaHCO}_3}$ is the molar mass of $\text{NaHCO}_3$ and $V_{\text{LSL}}$ is the LSL volume. This yields:

$$n_{\text{CO}_2} = \frac{1}{2} \times 67.03 \times \frac{0.998}{84.0066} \times 10 \times 10^{-6} = 3.98 \times 10^{-6} \text{ mol} \quad (6.5)$$

In the 10 µL LSL, at an average room temperature of 303.15 K, resides an amount of $5.55 \times 10^{-4}$ moles of water. Taking this value into consideration, as well as the $\text{CO}_2$ from Equation 6.5, yields a virtual $\hat{x}_{\text{CO}_2} = 7.12 \times 10^{-3}$. As explained earlier, when sampled, the salt thermally dissociates in the heated transfer line and produces $\text{CO}_2$. This latter is detected by the TCD (as well as the water steam). If this measured concentration corresponds to the mole fraction calculated in this paragraph, the thermal dissociation of the salt will have been well-quantified. A systematic amount of $\text{CO}_2$ will then have been proven to be generated for each brine sample.

The brine was analysed at three isobars: $p = (5, 10, 40)$ MPa to establish any sort of pressure dependence. It was accepted that temperature, constantly being the LSL temperature, would not have any impact on the $\text{CO}_2$ generation. Prior to being filled, the seals of the reactor were changed and Viton, a polymer material more suitable to high pressure $\text{CO}_2$ measurements was installed instead (see subsection 6.1.5 for more explanations). The system was then evacuated and washed with clear water. Degassed brine was introduced to the reactor at $T = 348.15$ K, circulation was started, pressure was controlled and thermal equilibrium established before the brine was sampled. The results of the raw measurements and a statistical analysis of this latter are presented in Table 6.6. One can then see that the average of the $\text{CO}_2$ mole fraction measured, $\hat{x}_{\text{CO}_2} = 7.23 \times 10^{-3}$, corresponds (within 4.6% repeatability margin and a standard error of $2.14 \times 10^{-2}$) to the theoretical mole fraction expected $\hat{x}_{\text{CO}_2} = 7.12 \times 10^{-3}$. This in itself was yet another confirmation that all the elements of the analysis process are functioning correctly and that the measurements can be trusted. Another equivalent process to prove the reliability of the rig was to back-calculate the salt concentration from the measured $\text{CO}_2$ mole fraction. This was evidently equivalent to doing the reverse calculations, rather than
Table 6.6: Analysis of the \((\text{H}_2\text{O}+\text{NaHCO}_3[3\text{mol/kg}])\) brine at 3 isobars.

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>Water Content / mol</th>
<th>CO₂ Content / mol</th>
<th>(x_{\text{CO}_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.57 \times 10^{-4}</td>
<td>1.92 \times 10^{-6}</td>
<td>7.48 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>2.52 \times 10^{-4}</td>
<td>1.90 \times 10^{-6}</td>
<td>7.54 \times 10^{-3}</td>
</tr>
<tr>
<td>10</td>
<td>2.32 \times 10^{-4}</td>
<td>1.64 \times 10^{-6}</td>
<td>7.07 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>2.35 \times 10^{-4}</td>
<td>1.59 \times 10^{-6}</td>
<td>6.76 \times 10^{-3}</td>
</tr>
<tr>
<td>40</td>
<td>2.41 \times 10^{-4}</td>
<td>1.73 \times 10^{-6}</td>
<td>7.17 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>2.11 \times 10^{-4}</td>
<td>1.42 \times 10^{-6}</td>
<td>6.76 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>2.31 \times 10^{-4}</td>
<td>1.81 \times 10^{-6}</td>
<td>7.84 \times 10^{-3}</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>7.23 \times 10^{-3}</td>
</tr>
<tr>
<td>AAD</td>
<td></td>
<td></td>
<td>4.60%</td>
</tr>
<tr>
<td>(s(\bar{x})/\bar{x})</td>
<td></td>
<td></td>
<td>2.14 \times 10^{-02}</td>
</tr>
</tbody>
</table>

The one presented earlier in this section. The sodium bicarbonate content in the brine was found to be equal to 0.802 mol/kg, which was less than 0.25% different than the prepared brine composition.

The conclusion drawn from this section is that, when analysing the liquid phase composition of the \((\text{CO}_2+\text{H}_2\text{O}+\text{NaHCO}_3[0.8\text{mol/kg}])\) system, the bicarbonate salt thermally dissociates and systematically generates a predictable amount of \(\text{CO}_2\): \(n_{\text{CO}_2}^{\text{NaHCO}_3}\). To accommodate for this offset introduced to the actual \(\text{CO}_2\) solubility measurements, the produced carbon dioxide should be subtracted from the total amount of \(\text{CO}_2\) measured. The way to reliably obtain \(n_{\text{CO}_2}^{\text{NaHCO}_3}\) is to extract it from the measured water amount as follows:

\[
\begin{align*}
  n_{\text{CO}_2}^{\text{NaHCO}_3} &= x_{\text{CO}_2}^{\text{m}} n_{\text{H}_2\text{O}}^{\text{tot}} \\
  \text{(6.6)}
\end{align*}
\]

Where \(x_{\text{CO}_2}^{\text{m}}\) is the measured \(\text{CO}_2\) mole fraction generated from the \(\text{NaHCO}_3\) thermal dissociation, equal to \(7.23 \times 10^{-3}\) and \(n_{\text{H}_2\text{O}}^{\text{tot}}\) is the total amount of water measured from the liquid sample.
6.3.2 The (CO$_2$+H$_2$O+NaHCO$_3$[0.8mol/kg]) System

Measurements

The experience amassed from the studies of the previous section significantly helped the measurements of the (CO$_2$+H$_2$O+NaHCO$_3$[0.8mol/kg]) system. Unfortunately, due to time limitations, only two isotherms were studied: $T =$ (348.15, 398.15) K. The brine used was the same as that used in section 6.3.1, with a salt concentration $m = 0.8$ mol/kg.

For isotherm $T =$ 348.15 K, the pressure range measured was extended to 60 MPa. For isotherm $T =$ 398.15 K, the pressure range measured followed the validation pressure range with $p = (5 - 50)$ MPa. Following the conclusions from subsection 6.3.1, $x_{CO2}$ was calculated by subtracting the CO$_2$ generated by the bicarbonate thermal dissociation from the TCD measured CO$_2$. This step lead us to remove a proportion of CO$_2$, which varied with pressure (as density does). The operation is as follows:

$$x_{CO2}^{eff} = \frac{n_{CO2}^{eff}}{n_{H2O}^{eff} + n_{CO2}^{eff}}$$  \hspace{1cm} (6.7)

$$= \frac{n_{CO2}^{tot} - n_{NaHCO3}^{tot}}{(n_{H2O}^{tot} + n_{CO2}^{tot}^{NaHCO3}) + (n_{CO2}^{tot} - n_{NaHCO3}^{tot})}$$  \hspace{1cm} (6.8)

$$= \frac{n_{CO2}^{tot} - 7.23 \times 10^{-3}n_{H2O}^{tot}}{(n_{H2O}^{tot} - 7.23 \times 10^{-3}n_{H2O}^{tot}) + (n_{CO2}^{tot} - 7.23 \times 10^{-3}n_{H2O}^{tot})}$$  \hspace{1cm} (6.9)

The results of the calculations are presented in Tables 6.8 and 6.9. The statistical analysis of the measurements are presented in Tables 6.10 and 6.11, and plotted in Figures 6.8 and 6.9. In Table 6.8 and 6.9, $n_{CO2}^{tot}$ and $n_{H2O}^{tot}$ are the effective mole fraction of CO$_2$ and water. $n_{CO2}^{tot}$ is the total amount of CO$_2$ measured during the sampling. One can see that, for both isotherms, data are highly repeatable, with an average deviation of 2.7% (also and expanded uncertainty of $1.38 \times 10^{-3}$) at 348.15 K and 2.2% (also an expanded uncertainty of $1.37 \times 10^{-3}$) at 398.15 K. This is very satisfactory and proves the reliability of the data sets.

As expected from highly concentrated brines, a salting-out effect is noticeable at all temperatures and pressures, with less CO$_2$ dissolved in the saline solution than for pure H$_2$O. However, this salting-out effect is not correctly predicted by the SP model, as can be seen from Figures 6.8 and 6.9. Such a discrepancy can be explained by the absence of HPHT data.
for this system up to this work. Therefore, no input for bicarbonate presence is to be found in solubility models. In the next subsection, we introduce a modification of the SP solubility model, which results in a better prediction of the CO₂ mole fraction obtained through this work.

Uncertainty Analysis

The process for the uncertainty analysis of the measurements of this system was built on that which was detailed in Subsection 6.1.4, with the exception that an additional term $u(A)_{\text{diss}}$ was added to account for the bicarbonate thermal dissociation (see Subsection 6.3.1). The results of the uncertainty estimations are presented in Table 6.7.

Table 6.7: Combined expanded uncertainty, $U(x_{CO2})$ for the solubility measurement of CO₂ in brine for the (CO₂+H₂O+NaHCO₃[0.8mol/kg]) system at $T = (348.15, 398.15)$ K, using a coverage factor $k = 2$.

<table>
<thead>
<tr>
<th>$T$ /K</th>
<th>$p$ /MPa</th>
<th>$x_{CO2}$</th>
<th>$U(x) = k.u_c(x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>348.15</td>
<td>5</td>
<td>$9.80 \times 10^{-3}$</td>
<td>$1.44 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$1.42 \times 10^{-2}$</td>
<td>$1.90 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$1.77 \times 10^{-2}$</td>
<td>$1.50 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$2.01 \times 10^{-2}$</td>
<td>$1.16 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>$2.16 \times 10^{-2}$</td>
<td>$1.21 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>$2.26 \times 10^{-2}$</td>
<td>$1.19 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>$2.36 \times 10^{-2}$</td>
<td>$1.27 \times 10^{-3}$</td>
</tr>
<tr>
<td>398.15</td>
<td>5</td>
<td>$7.48 \times 10^{-3}$</td>
<td>$1.70 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$1.21 \times 10^{-2}$</td>
<td>$1.40 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$1.81 \times 10^{-2}$</td>
<td>$1.15 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$2.18 \times 10^{-2}$</td>
<td>$1.26 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>$2.47 \times 10^{-2}$</td>
<td>$1.33 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>$2.67 \times 10^{-2}$</td>
<td>$1.38 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

6.3.3 Modelling of CO₂ solubility data: The SP model and additions from this work

The ability to reliably predict the solubility of CO₂ in water throughout a large range of temperatures and pressures is key to quantifying and assessing the development of the
Table 6.8: CO₂ mole fraction calculation in the (CO₂+H₂O+NaHCO₃[0.8mol/kg]) system at $T = 348.15$ K.

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>Average Water Content / mol</th>
<th>Average CO₂ Content / mol</th>
<th>Average Actual CO₂/ mol</th>
<th>$x_{CO₂}$ before Subtraction</th>
<th>Actual $x_{CO₂}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.10 $10^{-4}$</td>
<td>3.39 $10^{-6}$</td>
<td>1.88 $10^{-6}$</td>
<td>1.40 $10^{-2}$</td>
<td>9.8 $10^{-3}$</td>
</tr>
<tr>
<td>10</td>
<td>2.10 $10^{-4}$</td>
<td>4.44 $10^{-6}$</td>
<td>2.92 $10^{-6}$</td>
<td>2.12 $10^{-2}$</td>
<td>1.42 $10^{-2}$</td>
</tr>
<tr>
<td>20</td>
<td>1.68 $10^{-4}$</td>
<td>4.16 $10^{-6}$</td>
<td>3.23 $10^{-6}$</td>
<td>2.42 $10^{-2}$</td>
<td>1.77 $10^{-2}$</td>
</tr>
<tr>
<td>30</td>
<td>1.98 $10^{-4}$</td>
<td>5.42 $10^{-6}$</td>
<td>3.99 $10^{-6}$</td>
<td>2.63 $10^{-2}$</td>
<td>2.01 $10^{-2}$</td>
</tr>
<tr>
<td>40</td>
<td>2.04 $10^{-4}$</td>
<td>5.80 $10^{-6}$</td>
<td>4.33 $10^{-6}$</td>
<td>2.70 $10^{-2}$</td>
<td>2.16 $10^{-2}$</td>
</tr>
<tr>
<td>50</td>
<td>1.75 $10^{-4}$</td>
<td>5.08 $10^{-6}$</td>
<td>3.81 $10^{-6}$</td>
<td>2.78 $10^{-2}$</td>
<td>2.26 $10^{-2}$</td>
</tr>
<tr>
<td>60</td>
<td>1.76 $10^{-4}$</td>
<td>5.38 $10^{-6}$</td>
<td>4.11 $10^{-6}$</td>
<td>2.97 $10^{-2}$</td>
<td>2.36 $10^{-2}$</td>
</tr>
</tbody>
</table>

Table 6.9: CO₂ mole fraction calculation in the (CO₂+H₂O+NaHCO₃[0.8mol/kg]) system at $T = 398.15$ K.

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>Average Water Content / mol</th>
<th>Average CO₂ Content / mol</th>
<th>Average Actual CO₂/ mol</th>
<th>$x_{CO₂}$ before Subtraction</th>
<th>Actual $x_{CO₂}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.81 $10^{-4}$</td>
<td>2.68 $10^{-6}$</td>
<td>1.37 $10^{-6}$</td>
<td>1.45 $10^{-2}$</td>
<td>7.5 $10^{-3}$</td>
</tr>
<tr>
<td>10</td>
<td>1.90 $10^{-4}$</td>
<td>3.67 $10^{-6}$</td>
<td>2.29 $10^{-6}$</td>
<td>1.90 $10^{-2}$</td>
<td>1.21 $10^{-2}$</td>
</tr>
<tr>
<td>20</td>
<td>2.23 $10^{-4}$</td>
<td>5.58 $10^{-6}$</td>
<td>3.96 $10^{-6}$</td>
<td>2.44 $10^{-2}$</td>
<td>1.81 $10^{-2}$</td>
</tr>
<tr>
<td>30</td>
<td>1.97 $10^{-4}$</td>
<td>5.72 $10^{-6}$</td>
<td>4.29 $10^{-6}$</td>
<td>2.81 $10^{-2}$</td>
<td>2.18 $10^{-2}$</td>
</tr>
<tr>
<td>40</td>
<td>2.42 $10^{-4}$</td>
<td>7.66 $10^{-6}$</td>
<td>5.91 $10^{-6}$</td>
<td>3.07 $10^{-2}$</td>
<td>2.47 $10^{-2}$</td>
</tr>
<tr>
<td>50</td>
<td>2.43 $10^{-4}$</td>
<td>8.36 $10^{-6}$</td>
<td>6.59 $10^{-6}$</td>
<td>3.32 $10^{-2}$</td>
<td>2.67 $10^{-2}$</td>
</tr>
</tbody>
</table>

Table 6.10: CO₂ solubility measurement (CO₂+H₂O+NaHCO₃[0.8mol/kg]) for isotherm $T = 348.15$ K

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>$x_{CO₂} * 10^2$</th>
<th>AAD /%</th>
<th>Salting out /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.98</td>
<td>6.37</td>
<td>6.30</td>
</tr>
<tr>
<td>10</td>
<td>1.42</td>
<td>2.60</td>
<td>11.2</td>
</tr>
<tr>
<td>20</td>
<td>1.77</td>
<td>2.1</td>
<td>14.3</td>
</tr>
<tr>
<td>30</td>
<td>2.01</td>
<td>1.81</td>
<td>12.2</td>
</tr>
<tr>
<td>40</td>
<td>2.16</td>
<td>2.00</td>
<td>12.6</td>
</tr>
<tr>
<td>50</td>
<td>2.26</td>
<td>1.77</td>
<td>14.0</td>
</tr>
<tr>
<td>60</td>
<td>2.36</td>
<td>2.09</td>
<td>14.7</td>
</tr>
<tr>
<td><strong>AAD</strong></td>
<td><strong>2.68</strong></td>
<td><strong>12.2</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.11: CO₂ solubility measurement (CO₂+H₂O+NaHCO₃[0.8mol/kg]) for isotherm $T = 398.15$ K

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>$x_{CO₂} * 10^2$</th>
<th>AAD /%</th>
<th>Salting out /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.75</td>
<td>4.02</td>
<td>11.1</td>
</tr>
<tr>
<td>10</td>
<td>1.21</td>
<td>2.76</td>
<td>11.0</td>
</tr>
<tr>
<td>20</td>
<td>1.81</td>
<td>2.06</td>
<td>13.2</td>
</tr>
<tr>
<td>30</td>
<td>2.18</td>
<td>2.08</td>
<td>13.0</td>
</tr>
<tr>
<td>40</td>
<td>2.47</td>
<td>1.33</td>
<td>11.8</td>
</tr>
<tr>
<td>50</td>
<td>2.67</td>
<td>1.11</td>
<td>12.9</td>
</tr>
<tr>
<td><strong>AAD</strong></td>
<td><strong>2.23</strong></td>
<td><strong>12.1</strong></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.8: CO$_2$ mole fraction in brine (CO$_2$+H$_2$O+NaHCO$_3$[0.8mol/kg]) at $T = 348.15$ K in function of pressure. • This work, $T = 348.15$ K, — SP for CO$_2$ in NaHCO$_3$ (0.8 mol/kg), — SP for CO$_2$ in pure water, — SP modified, $A = -0.0915$ and — SP modified, $A = -0.0836$
Figure 6.9: CO₂ mole fraction in brine (CO₂ + H₂O + NaHCO₃ [0.8 mol/kg]) at T = 398.15 K in function of pressure. ● This work, $T = 348.15$ K, — SP for CO₂ in NaHCO₃ (0.8 mol/kg), — SP for CO₂ in pure water, — SP modified, $A = -0.0915$ and — SP modified, $A = -0.0836$
CO₂ plume after its injection in the reservoir. All prediction bases start with high quality experimental data, from which models can be developed and provide a continuous range of answers to the limited range of discrete experimental data. As explained in Chapter 3, depending on the operating conditions, the system studied and sometimes the preference of the author, the VLE predictions can be obtained through different means. For the (CO₂+H₂O) and the (CO₂+H₂O+[Salts]) systems, the work of Spycher-Pruess (Spycher et al. (2003), Spycher & Pruess (2005, 2010)) has been proven to be reliable for pressures up to 60 MPa and temperatures up to 573.15 K (Root Mean Square Deviation between model and experimental data for the CO₂ in the water reported as 7%).

Their work relies on activity coefficients for the aqueous phase and fugacity coefficient for the CO₂-rich phase (γ-ϕ). They developed a model which behaves differently depending on temperature, as some simplifying assumptions loose validity as mutual solubility increases:

- For temperatures $T \leq 373.15$ K: the activity coefficient of liquid water and CO₂ in pure water activity coefficients were taken equal to unity as the water content in the CO₂ phase was considered infinitely diluted.
- For temperatures $T > 373.15$ K: a two-parameters Margules activity-coefficient model was implemented for the two phase and the fugacity coefficient was calculated via the cubic RK EoS with mixing rules containing the acentric factor (Equations 3.39 and 3.38).

In their formulation, SP take care of the pressure dependence of solubility by using an equilibrium constant, $K(T, p)$ for each species:

$$K(T, p) = K^0(T, p_{ref})\exp\left(\frac{(p - p_{ref})V}{RT}\right) \quad (6.10)$$

With $p_{ref}$ a reference pressure and $V$ the average partial molar volume of the pure condensed phase (CO₂ or water) between $p$ and $p_{ref}$. The equilibrium constant takes care of the pressure effect in a similar fashion to that of the Poynting factor (from Equation 3.23). $K^0$, $p_{ref}$ as well as $V$ follow a parametrisation in function of temperature detailed in Spycher & Pruess (2010).
SP solubility model - CO₂ and pure water

Spycher-Pruess arrive to an expression of solubility of CO₂ in water (concept of interest in this work) expressed in function of the concentration of water in the CO₂ rich phase and other thermodynamic variables:

\[ y_{\text{H₂O}} = A(1 - x_{\text{CO₂}}) \quad (6.11) \]
\[ x_{\text{CO₂}} = B(1 - y_{\text{H₂O}}) \quad (6.12) \]

with
\[ A = \frac{K_{\text{H₂O}} \gamma_{\text{H₂O}}}{\phi_{\text{H₂O}} p} \quad (6.13) \]
and
\[ B = \frac{\phi_{\text{CO₂}} p}{55.508 K_{\text{CO₂}} \gamma_{\text{CO₂}}} \quad (6.14) \]

Simplifying assumptions provide direct calculations at \( T \leq 373.15 \text{ K} \). As a matter of fact, in their work, Spycher & Pruess (2010) state that at this range of temperature and up to 60 MPa, the solubility of CO₂ in water is sparse and that consequently, one can apply the ideal infinite-dilute-solution theory, which states that: \( \gamma_{\text{CO₂}} = \gamma_{\text{H₂O}} = 1 \) and that \( y_{\text{H₂O}} = 0 \). These assumptions provide a direct mean to calculate \( y_{\text{H₂O}} \) and \( x_{\text{CO₂}} \) (no iterative process) with the substitution equation:

\[ y_{\text{H₂O}} = (1 - B)/(1/A - B) \quad (6.15) \]

As mentioned, the fugacity coefficients were obtained using the cubic Redlich-Kwong EoS. The cubic EoS was solved and the larger value root (which corresponds to the gaseous phase volume) was then injected into the expression for the fugacity coefficient they adopted from A. Z. Panagiotopoulos & R. C. Reid (1986).

For temperatures \( T > 382.15 \text{ K} \), the previous assumption of infinite dilutions loses its validity. It follows that:

- The concentration of water in the CO₂ rich phase is not negligible anymore: \( y_{\text{H₂O}} \neq 0 \)
- The CO₂ activity coefficient cannot be validly taken as unity anymore: \( \gamma_{\text{CO₂}} \neq 1 \).
- The water activity coefficient cannot be validly taken as unity anymore: \( \gamma_{\text{H₂O}} \neq 1 \).

For this range of temperatures, solubility calculations follow an iterative procedure initiated by setting \( y_{\text{H₂O}} = p_{\text{ref,H₂O}}/p \) (Henry’s law at low pressure) and \( x_{\text{CO₂}} = 0.009 \).
SP solubility model - CO₂ and brines

A convenient feature of the SP solubility model is that it offers to take salt effects in consideration with little modification to the initial formulation. Under salt presence, on one hand, the activity-coefficient model and the fugacity-coefficient model from the \((\text{CO}_2 + \text{H}_2\text{O})\) formulation are used. On the other hand, a salt mole fraction is added to \(x_{\text{CO}_2}\), the calculations (based on the full dissociation of the salts) and a salt activity coefficient, \(\gamma_{\text{CO}_2}\), is introduced to quantify the CO₂ salting-out. Under these considerations arise new expressions to obtain \(y_{\text{H}_2\text{O}}\) and \(x_{\text{CO}_2}\) (see Sypcher & Pruess (2010)), and more specifically, Equations 6.12 and 6.14 are re-written as follows:

\[
x_{\text{CO}_2} = B'(1 - y_{\text{H}_2\text{O}}) \tag{6.16}
\]

\[
B' = \frac{\phi_{\text{CO}_2} \ p}{55.508 \ K_{\text{CO}_2} \ \gamma_{\text{CO}_2} \ \gamma_{\text{CO}_2}} \tag{6.17}
\]

To obtain \(\gamma_{\text{CO}_2}\), the authors of the model used a modified Pitzer model by Duan & Sun (2003) to reflect CO₂ activity in brines which they re-parametrised to better fit their range of pressures and temperatures. It is expressed as follow:

\[
\gamma_{\text{CO}_2} = \left( 1 + \frac{\sum_{i \neq \text{CO}_2} m_{i} \chi_{i}}{55.508} \right) \exp \left[ 2\lambda \left( m_{\text{Na}} + m_{\text{K}} + 2m_{\text{Ca}} + 2m_{\text{Mg}} \right) \right. \\
\left. + \xi m_{\text{Cl}} \left( m_{\text{Na}} + m_{\text{K}} + m_{\text{Ca}} + m_{\text{Mg}} \right) - 0.07m_{\text{SO}_4} \right] \tag{6.18}
\]

In Equation 6.18, \(m\) is the salt molality and the first term is a conversion factor from molality to mole fraction. The term \(\gamma'_{\text{CO}_2}\) tends to 0 with decreasing salt concentration, and the coefficients \(\lambda\) and \(\xi\) are interaction parameters which, as done in Rumpf & Maurer (1993), are described as a function of invert power of the temperature.

The saturation curves from Figures 6.4a and 6.4b, as well as these of Figure 6.7, were computer-generated using the solubility model formulation found in the SP papers. Although the predictions resulting from the calculations were in agreement for \(x_{\text{CO}_2}\) in pure water.

---

2\(^{\text{Thanks to the hard work of researchers in the thermofluid lab, the solubility model from SP (Spycher et al. (2003), Sypcher & Pruess (2005, 2010)) was implemented in a user-friendly VBA program, allowing instant predictions for } x_{\text{CO}_2} \text{ in water and brines for our full range of pressure (0.1 - 60 MPa) and temperature (273.15 - 473.15 K). It is their VBA program that was inherited and used to generate the solubility prediction and the modifications to the original SP model formulation.}}\)
and NaCl brines (see sections 6.1 and 6.2), they were over-estimating the salting-out effect encountered in the bicarbonate brine. This is because in the SP formulation of the salt activity-coefficient, the list of salts considered does not include NaHCO₃. In fact, the salt dissociates in a sodium cation Na⁺ and a bicarbonate anion HCO₃⁻. Therefore, these species should be taken into consideration in the activity-coefficient model. Such terms are not found in the SP Pitzer’s formulation of CO₂, where only the Na⁺ molality plays a role (see Equation 6.18). This absence is illustrated in Figures 6.8 and 6.9 where the black curve, only representing the CO₂ salting-out generated by 0.8 mol/kg of Na⁺, is not in agreement with our data at T = (348.15, 398.15) K. An interaction coefficient for the bicarbonate anion was added in Equation 6.18, yielding a slightly modified form:

\[
\gamma'_{CO_2} = \left( 1 + \frac{\sum m_{i \neq CO_2}}{55.508} \right) \exp \left[ 2\lambda (m_{Na} + m_{K} + 2m_{Ca} + 2m_{Mg}) + \xi m_{Cl}(m_{Na} + m_{K} + m_{Ca} + m_{Mg}) - 0.07m_{SO_4} + A m_{HCO_3} \right]
\] (6.19)

By tuning the value of parameter "A" in Equation 6.19, the generated saturation curves for both isotherms, T = (348.15, 398.15) K, were displaced as follow:

- A > 0: The CO₂ salting-out effect was amplified, yielding a bubble curve deviating further from our data.
- A < 0: The CO₂ salting-out effect was lessened.

In optimising parameter A, two options were to be investigated: A as a constant and A as a function of temperature (pressure neglected as per Spycher & Pruess (2010) conclusions).

A as a constant

From Figure 6.10 one can see that the optimal value to minimize the average deviation between the predicted and the measured solubility for the two isotherms is A = -0.0836. For isotherm T = 348.15 K, over the pressure range 5 to 60 MPa and with the optimised Pitzer model, the predicted CO₂ solubility in the bicarbonate brine agreed with our data with an average absolute deviation of 2%, and a maximum deviation of 6% (at p = 5 MPa the solubility is low and therefore virtually magnifies the relative deviation). For isotherm T = 398.15 K, the average absolute deviation was 1% and the maximum deviation was 2%.
Figure 6.10: Spycher-Pruess deviation from measured $CO_2$ solubility in sodium bicarbonate data. Based on data from Tables 6.10 and 6.11. ▲ Deviation from $T = 348.15$ K, ▼ Deviation from $T = 398.15$ K, ■ Average Deviation and -- $y = 79.13x + 6.63$. 
Table 6.12: Addition of bicarbonate parameter in the SP Pitzer activity coefficient: effect on agreement with measured CO$_2$ solubility in sodium bicarbonate brine [0.8 mol/kg] at $T = 348.15$ K.

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>Deviation from measured data / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A=+0.0$</td>
</tr>
<tr>
<td>5</td>
<td>13.5</td>
</tr>
<tr>
<td>10</td>
<td>7.6</td>
</tr>
<tr>
<td>20</td>
<td>3.7</td>
</tr>
<tr>
<td>30</td>
<td>6.3</td>
</tr>
<tr>
<td>40</td>
<td>5.8</td>
</tr>
<tr>
<td>50</td>
<td>4.2</td>
</tr>
<tr>
<td>60</td>
<td>3.3</td>
</tr>
<tr>
<td>Average</td>
<td>6.3</td>
</tr>
</tbody>
</table>
Table 6.13: Addition of bicarbonate parameter in the SP Pitzer activity coefficient: effect on agreement with measured CO₂ solubility in sodium bicarbonate brine [0.8 mol/kg] at $T = 398.15$ K.

<table>
<thead>
<tr>
<th>Pressures / MPa</th>
<th>Deviation from measured data / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A=+0.0</td>
<td>A=-0.04</td>
</tr>
<tr>
<td>5</td>
<td>8.7</td>
</tr>
<tr>
<td>10</td>
<td>9.1</td>
</tr>
<tr>
<td>20</td>
<td>6.5</td>
</tr>
<tr>
<td>30</td>
<td>6.9</td>
</tr>
<tr>
<td>40</td>
<td>8.4</td>
</tr>
<tr>
<td>50</td>
<td>7.1</td>
</tr>
<tr>
<td>Average</td>
<td>7.8</td>
</tr>
</tbody>
</table>
Table 6.14: Dependence of $A$ in temperature.

| $A = a \frac{T}{b + 1} + c \frac{1}{T^2}$ |
|---|---|---|
| $a \times 10^4$ | $b$ | $c \times 10^{-3}$ |
| 2.2 | -13 | 4.64 |

For both isotherms, the agreements between the modified SP solubility model and the measured data are within the uncertainty of the experiments, which is a satisfactory conclusion. However, one can notice better agreement between measurements and modelling for $T = 398.15$ K than for $T = 348.15$ K. This might seem counter-intuitive as the departure from reality increases with temperature, and therefore one expects the agreements between modelling and experimental data to worsen with temperature. In the future, the origin of such discrepancy could be further investigated by obtaining solubility data for this system for other isotherms.

$A$ as a function of temperature

If one investigates the temperature dependence for $A$, following the Pitzer interaction coefficients expression from Rumpf & Maurer (1993), one can express it as follows:

$$A = aT + b/T + c/T^2$$

(6.20)

With $a$, $b$ and $c$ constants obtained from fitting the optimal value for $A$ for both isotherm. Table 6.14 provides the generated value for these coefficients. This form helps set the AD between the SP model and the data to a minimum for both isotherms by yielding $A = -0.0756$ at $T = 348.15$ K and $A = -0.0915$ at $T = 398.15$ K$^3$. However, it brought little improvement in regards to the AAD or maximum deviation values as the AAD was 2% and 1% and the maximum deviation was 6% and 2% for isotherm 348.15 and 398.15 K respectively.

Adding a temperature dependence for $A$ has not brought any significant improvements in the statistical agreement with the data obtained from the two isotherm measured. However, this formulation might be useful as the temperature range widens, as a constant value for $A$ might not be sufficient anymore.

---

$^3$Here an objective function would have provided a more accurate value of $A$. The manual adjustments from this work only provide the first estimation of the coefficient $A$. 

170
6.3.4 Conclusions

In this section we provided first-of-its kind water-rich phase composition for the \((\text{CO}_2 + \text{H}_2\text{O} + \text{NaHCO}_3)\) system at HPHT: \(T = 348.15\) and 398.15 K, and \(p = (0.1 - 60)\) MPa for the lowest isotherm and \((0.1 - 50)\) MPa for the highest. These measurements were drawn from a two-step procedure where, before obtaining the \(\text{CO}_2\) concentration, the amount of gas produced by the salt thermal dissociation was determined. It was proved that, independently of pressure and/or temperature, the \(\text{CO}_2\) generated could be accurately predicted by applying a constant, \(7.23 \times 10^{-3}\), factor to the total amount of water measured in that sampling. The effective \(\text{CO}_2\) mole fraction was then calculated after subtracting the gas and steam offset from the quantity measured.

This method led to highly repeatable data sets for both isotherms, with an average deviation of 2.7% at 348.15 K and 2.2% at 398.15 K. As expected from strongly concentrated brines, a salting-out effect is noticeable at all temperatures and pressures, with less \(\text{CO}_2\) dissolved in the saline solution than for pure \(\text{H}_2\text{O}\). However, this salting-out effect was not correctly predicted by the SP solubility model. Such discrepancy could be explained as the bicarbonate ions played no role in the formulation of their model. A modification to the SP solubility model was thus introduced. More specifically, an addition to their Pitzer activity-coefficient formulation was brought forth, such that a linear dependency in the bicarbonate molality was introduced. This resulted in a better prediction of the \(\text{CO}_2\) mole fraction obtained for this system at the conditions of study.

For isotherm \(T = 398.15\) K, over the pressure range 5 to 60 MPa and with the optimised Pitzer model, the computed \(\text{CO}_2\) solubility in the bicarbonate brine agreed with our data with an average absolute deviation of 2% and maximum deviation of 6%. For isotherm \(T = 398.15\) K, the average absolute deviation was 1% and the maximum deviation was 2%. For both isotherms, the agreements between the modified SP solubility model and the measured data are within the uncertainty of the experiments, which is a satisfactory conclusion. However, one can notice better agreement between measurements and modelling for \(T = 398.15\) K than for \(T = 348.15\) K. This might seem counter-intuitive as the departure from reality increases with temperature, and therefore one expects the agreements between modelling and experimental data to worsen with temperature. In the future, the origin of such discrepancy could be
further investigated by obtaining solubility data for this system for other isotherms.

This work was a milestone in the study of the phase behaviour of the \((\text{CO}_2 + \text{H}_2\text{O} + \text{NaHCO}_3)\) system as, apart from the work of Gao et al. (1997), which was discussed in Chapter 2, no data was available for the range of pressure and temperature gathered here. The pioneer results of this work, illustrate the potential of the new semi-analytical apparatus to provide first-of-their-kind solubility data of gases in aqueous solution at a wide range of pressure and temperature, \(T = (298.15 - 398.15)\) K and \(p = (0.1 - 60)\) MPa.
Chapter 7

Conclusions

7.1 Summary

7.1.1 The Synthetic Rig

The synthetic apparatus presented valuable advantages as it had the capacity to measure high-pressure and high-temperature phase behaviour of highly reactive systems composed of corrosive components (highly concentrated brine) or even explosive compounds (propane). It produced reliable data for CO$_2$ in aqueous solutions ($\pm 1.3$ % with the literature data for solubility) for pressures up to 40 MPa and temperatures up to 473.15 K. However, the set-up failed to generate satisfactory measurements for the (C$_3$H$_8$+H$_2$O) system. This was certainly resulting of the combination of two phenomena: the 0.1 mL internal dead-volume introduced by each window-assembly in the cell, and the fact that propane was sparingly soluble in water under these conditions.

Using the Krichevsky-Kasarnovsky EoS, the bubble pressures of the (N$_2$+H$_2$O), (CO$_2$+H$_2$O) and (C$_3$H$_8$+H$_2$O) were estimated for $T$ under 373.15 K. The impact of the introduction of 0.1 mL in a system of 25 mL on the theoretical bubble pressure was significant. The propane presented the worst deviations, with a shift in the bubble pressure as high as 27%. As there were two windows in the synthetic system, the final measured $p_b$ could carry an error as high as 54%, which was unacceptable. Similarly, the (N$_2$+H$_2$O) presents high deviations, with a biased bubble pressure of 38% in the worst case scenario.

Although the synthetic apparatus could provide satisfactory bubble pressure measurements for systems with solubility levels similar to that of CO$_2$ in water/brines (10,000 ppm), due
to some design limitations, sparingly soluble gases in water/brine (100 ppm) were out of its range of capabilities.

7.1.2 The Analytical Rig

The analytical apparatus offered both, liquid-rich and gas-rich phase composition analyses for pressures up to 20 MPa and temperatures between (298.15 - 473) K. First, the (O₂+H₂O) was investigated at two isotherms, T = (308.15, 348.15) K, and up to 17.95 MPa. Difficulties arose once again from the sparingly soluble character of the gas in water (the amounts of water measured by the detector were four orders of magnitude higher than that of the oxygen). The use of TCD for the composition analysis and the low content of O₂ in water lead to weak S/N ratios during measurements. This lead the measurements to be of low quality with a high average deviation and a low repeatability. Enhancing the S/N ratio was equivalent to an increase in the amount of saturated-water sampled, and subsequently the TCD response to the water content. This resulted in water-peak areas largely superior to the upper limit of the calibration range, which lead to extrapolations. Data obtained through this process were not accepted for obvious data reliability reasons. Therefore, a dead-end was encountered when the only way to improve the S/N ratio for oxygen was to introduce larger samples, but these latter, in turn, introduced more water than allowed by the boundaries of the TCD water calibration.

It was therefore not possible to obtain accurate solubility measurements of the (O₂+H₂O) binaries with the configuration of the analytical apparatus utilised in this work.

The (C₃H₈+H₂O) binary was advantageous compared to the (O₂+H₂O) system, as through the parallel use of the TCD and the FID, an enhanced sensitivity toward the solute was provided while keeping a response in the calibrate range for the water.

The solubility of propane in water at the isotherm T = 308.15 K was investigated up to 17 MPa. The results of the measurements were very repeatable (average standard deviation of 1.44%) and were in very good agreement with the literature. Measurements for isotherm T = 348.15 K were initiated but stopped at p = 2.8 MPa, as the N₂ generator, a key safety feature for HPHT propane operation, broke down. However, the limited resulting data seemed to correspond well the literature (average standard deviation of 2%).

In the absence of a nitrogen flooding, the analysis of the (C₃H₈+H₂O) system were brought

174
to an end. Such a conclusion was unfortunate, as encouraging results were obtained for this system. It was felt that, considering the configuration of the analytical equipment during this study, no other water-based binary could be studied with this equipment. Therefore, priority was given to the design of a new, more versatile apparatus with a wider range of pressure, fit for highly concentrated brine measurements and with a more adapted design to handling HPHT toxic gases.

7.1.3 The New Semi-Analytical Rig

The (CO$_2$+H$_2$O) Binary

A new semi-analytical equipment was designed and assembled during this thesis. It offered solubility measurements capabilities for sour gases (CO$_2$, H$_2$S, SO$_2$) in highly concentrated brines for a wide range of temperatures and pressures: $T = (298.15 - 473.15)$ K and $p = (5 - 70)$ MPa. The apparatus was built and operated in a newly commissioned laboratory (2014) for exclusive use of HPHT sulphuric gases. Under this work, design of the piping patterns, gas detectors distribution and working stations, which were optimised for safety and convenient operations, were developed and brought to full operation.

To validate the new apparatus, it was decided to obtain the composition of the water-rich phase of the well-studied (CO$_2$+H$_2$O) binary. In the process of doing so, complex experimental issues were encountered, some counterbalancing each-other and resulting in apparent satisfactory measurements. These set-backs, erroneous calibrations, handicapping blockages, costly leaks and non-desired phase-separation were all identified and methodically solved. The composition of the water-rich phase was obtained for two isotherms: $T = (348.15, 398.15)$ K for pressures $p$ up to 50 MPa and 60 MPa, respectively. Isotherm $T = 348.15$ K was experimentally obtained, which subsequently lead to the development of an optimised sampling protocol. Through this knowledge, a thought-to-be obsolete isotherm, $T = 348.15$ K, was statistically reappraised and the resulting computed data were consistent with the solubility model used.

The gathered data sets were in high agreement with the literature (1.8% and 2.2% AAD with SP predictions for $T = (348.15, 398.15)$ K, respectively). These results provided the necessary validation of the design of the novel semi-analytical apparatus. They also ascertained
CHAPTER 7. CONCLUSIONS

The reliability of the solubility measurements for a wide range of temperatures and pressures: 
\[ T = (298.15 - 398.15) \text{ K} \text{ and } p = (5 - 60) \text{ MPa}. \]

The \( (\text{CO}_2 + \text{H}_2\text{O} + \text{NaCl}) \) Pseudo-Binary

The \( \text{CO}_2 \) content of the saturated water-rich phase of the \( (\text{CO}_2 + \text{H}_2\text{O} + \text{NaCl}) \) binary was studied at \( T = 348.15 \text{ K} \) and \( p \) up to 50 MPa, and with a salt concentration of \( m = 3 \text{ mol/kg} \). The AAD of 1% and maximum deviation of 3% from SP salting-out estimations, which are well within both, the accuracy of the model and the experimental uncertainty (7% and 2% respectively). This success in measuring the \( \text{CO}_2 \) mole fraction under these conditions demonstrated the reliability of the solubility measurements obtained by the new semi-analytical apparatus for gases in highly concentrated brines for a wide range of pressures and temperatures, respectively \((0.1 - 50) \text{ MPa} \) and \((298.15 - 423.15) \text{ K}\). Furthermore, because the salting out effect pushes the solubility inversion point farther, it is likely that the temperature limit for this system was also expanded. This theory was however not tested. An additional point, which brings noteworthy added-value to these measurements, was that the isotherm \( T = 348.15 \text{ K} \) for the \( (\text{CO}_2 + \text{H}_2\text{O} + \text{NaCl}) \) binary had not been explored in the literature at neither the pressures nor the concentration investigated in this work. These encouraging results granted the semi-analytical apparatus a promising potential for pioneer HPHT gas solubility measurements in water/brine.

The \( (\text{CO}_2 + \text{H}_2\text{O} + \text{NaHCO}_3) \) Pseudo-Binary

New water-rich phase composition were provided for the \( (\text{CO}_2 + \text{H}_2\text{O} + \text{NaHCO}_3) \) system at HPHT: \( T = 348.15 \text{ for } p = (0 - 60) \text{ MPa} \) and \( T = 398.15 \text{ K for } p = (0 - 50) \text{ MPa} \). These measurements were drawn from a two-step procedure where, before obtaining the \( \text{CO}_2 \) concentration, the amount of gas produced by the salt thermal dissociation was determined. It was proven that, independently of pressure and/or temperature, the \( \text{CO}_2 \) generated could be accurately predicted by applying a constant factor \( (7.23 \times 10^{-3}) \) to the total amount of water measured in that sampling. The effective \( \text{CO}_2 \) mole fraction was then calculated after subtracting the gas and steam offset from the quantity measured.

This method led to highly repeatable data sets for both isotherms, with an average deviation of 2.7% at 348.15K and 2.2% at 398.15 K. As expected from strongly concentrated brines,
a salting-out effect is noticeable at all temperatures and pressures with less CO$_2$ dissolved in the saline solution than for pure H$_2$O. However, this salting-out effect was not correctly predicted by the SP solubility model. Such discrepancy could be explained as the bicarbonate ions played no role in the formulation of their model. A modification to the SP solubility model was thus introduced. More specifically, an addition to their Pitzer activity-coefficient formulation was brought forth, such that a linear dependency in the bicarbonate molality was introduced. This resulted in a better prediction of the CO$_2$ mole fraction obtained for this system at the conditions of study.

For isotherm $T = 398.15$ K, over the pressure range 5 to 60 MPa and with the optimised Pitzer model, the computed CO$_2$ solubility in the bicarbonate brine agreed with our data with an average absolute deviation of 2% and maximum deviation of 6%. For isotherm $T = 398.15$ K, the average absolute deviation was 1% and the maximum deviation was 2%. For both isotherms, the agreements between the modified SP solubility model and the measured data were within the uncertainty of the experiments, which was a satisfactory conclusion. However, one can notice better agreement between measurements and modelling for $T = 398.15$ K than for $T = 348.15$ K. This might seem counter-intuitive, as the departure from reality increases with temperature and, therefore, one expects the agreements between modelling and experimental data to worsen with temperature. In the future, the origin of such a discrepancy could be further investigated by obtaining solubility data for this system for other isotherms.

This work was a milestone in the study of the phase behaviour of the (CO$_2$ + H$_2$O + NaHCO$_3$) system as, apart from the work of Gao et al. (1997), which was discussed in the literature review in this thesis, no data was available for the range of pressure and temperature of interest. The pioneer results of this work illustrate the potential of the new semi-analytical apparatus to provide first-of-their-kind solubility data of gases in aqueous solutions at a wide range of pressure and temperature, $T = (298.15 - 398.15)$ K and $p = (0.1 - 60)$ MPa.

### 7.2 Key Points

- The synthetic apparatus was recommissioned for pressures up to 40 MPa and temperatures up to 473.15 K and validated with the (CO$_2$+H$_2$O) system for which measured
compositions at bubble pressures agreed well with the literature data.

- It was experimentally and theoretically demonstrated that, due to inherent design limitations, sparingly soluble gases in water/brine (100 ppm) could not be obtained with this synthetic apparatus.

- The \((O_2+H_2O)\) binary was investigated at two isotherms, \(T = (308.15, 348.15)\) K, and up to 17.95 MPa using the analytical apparatus. It was proven that this system could not be accurately measured with the exclusive use of a TCD.

- The \((C_2H_6+H_2O)\) binary was studied as the solubility of propane in water at two isotherms, \(T = (308.15, 348.15)\) K were measured, respectively up to 17 and 2.8 MPa. The results of the measurements were very repeatable (average standard deviation of 1.44%) and were in very good agreement with the literature. The encouraging measurements obtained for this system could unfortunately not be completed because of safety related impediments.

- From the work with these apparatus, a better understanding of the complex sampling challenges pertaining to sparingly soluble solute in water/brines was built and with it was gathered a robust knowledge of the array of solutions available to the high pressure high temperature experimentalist.

- From this experience, a new semi-analytical equipment was designed and assembled. It offered solubility measurements capabilities for sour gases (\(CO_2, H_2S, SO_2\)) in highly concentrated brines for a wide range of temperatures and pressures: \(T = (298.15 - 473.15)\) K and \(p = (5 - 70)\) MPa.

- The \((CO_2+H_2O)\) system was used to validate the new apparatus as reliable solubility data of \(CO_2\) in water were obtained for two isotherms, \(T = (348.15, 398.15)\) K and for pressures up to 50 MPa and 60 MPa, respectively. The gathered data sets were in high agreement with the SP solubility model (2% AAD).

- The \((CO_2+H_2O+NaCl)\) binary was studied at \(T = 348.15\) K and \(p\) up to 50 MPa, and with a salt concentration of \(m = 3\) mol/kg. This data set extends the domain of the range of pressure, temperature and salinity of solubility measurements for the \((CO_2+H_2O+NaCl)\) system as it had not been studied before.
• The AAD of the measured CO₂ mole fraction was 1% and the maximum deviation of 3% from SP salting-out estimations, which are well within both, the accuracy of the model and the experimental uncertainty (7% and 2% respectively). This confirms further the range of validity of the SP model for these newly investigated conditions.

• New water-rich phase composition were provided for the unstudied (CO₂+H₂O+NaHCO₃) system at HPHT: \( T = 348.15 \) for \( p = (0 - 60) \) MPa and \( T = 398.15 \) K for \( p = (0 - 50) \) MPa.

• The gathered data sets were highly repeatable for both isotherms, with an AAD of 2.7% at 348.15K and 2.2% at 398.15 K. As expected from strongly concentrated brines, a salting-out effect is noticeable at all temperatures and pressures.

• A modification to the SP solubility model was made to fit better the obtained new measurements. The agreements between the optimised SP solubility model and the measured data were within the uncertainty of the experiments for both isotherms.

7.3 Future Work

7.3.1 The Synthetic Apparatus

From the conclusions reached in Section 4.1, the synthetic rig seemed not to be the appropriate equipment to measure the solubility of sparingly soluble solute in water/brines. The sulphur-based binaries could have been attempted to be measured by the synthetic apparatus, as they have a higher solubility in water/brine than the system studied in this work. However, the health and safety hazard these systems introduced disqualified their use with this synthetic system. Therefore, no more work related to Task 2.2.1E.b is to be attributed to this apparatus.

7.3.2 The Analytical Apparatus

The configuration described in Section 4.2 seems not to offer the possibility for additional novel work. The sulphuric gases could not be studied with this apparatus as the modifications required to offer safe HPHT sour gas operations were too great. Moreover, the measurement campaign successfully started for the (C₃H₈+H₂O) could not be reinstated without a steady
source of inert gas to flood the oven volume. The remaining systems of interest were sparingly soluble in water/brines, therefore similar out-of-calibration-range measurements were expected to be encountered if experimented. A Helium Ionised Detector (HID) was purchased and its operation in parallel with the TCD should offer customised sensitivity toward the solutes N₂, O₂ and H₂. This configuration, once installed and running, is expected to broaden the type of systems this apparatus could measure, and should offer the possibility to measure the phase behaviour of the (N₂+H₂O), (O₂+H₂O) and (H₂+H₂O) binaries to pressures up to 20 MPa and temperatures between (298.15 - 473.15) K.

7.3.3 The New Semi-Analytical Apparatus

The new semi-analytical equipment has both, the technical capability to give the accuracy needed for low solubility solutes (as its GC is fitted with an FID, which is appropriate for components like propane) and the corrosion/gas handling ability to deal with toxic sour gases. Although they were a central reason behind this project, the binaries involving H₂S and SO₂ were not studied. The highly serious nature of the health hazards associated with high-pressure and high-temperature handling of sour gases in the centre of a large European capital significantly delayed the necessary authorisations to begin operations.

Until full credentials for HPHT operations with sour gas is obtained by the laboratory, more novel measurements should be gathered with the semi-analytical apparatus. In particular, strong emphasis should be attributed to the (C₃H₆+(water+salts)) pseudo-binaries as there is a lack of data for these systems in the range of temperatures and pressures offered by the semi-analytical set-up, and that (propane being a level lower in the ladder of operational risk when compared to sour gases) the laboratory could have its safety measures tested in a more secure manner.
Bibliography


Bamberger, A., Sieder, G. & Maurer, G. (2004), 'High-pressure phase equilibrium of the ternary system carbon dioxide + water + acetic acid at temperatures from 313 to 353 K', *Journal of Supercritical Fluids* 32(1-3), 15–25.

Bando, S., Takemura, F., Nishio, M., Hihara, E. & Akai, M. (2003), 'Solubility of CO2 in
aqueous solutions of NaCl at (30 to 60)°C and (10 to 20) MPa’, *Journal of Chemical and Engineering Data* 48(3), 576–579.


Department of Energy (2012), *DOE History Timeline*. 

183

Diamond, L. W. & Akinfiev, N. N. (2003), 'Solubility of CO2 in water from -1.5 to 100C and from 0.1 to 100 MPa: Evaluation of literature data and thermodynamic modelling'.


Duan, Z., Møller, N. & Weare, J. H. (1992), 'An equation of state for the CH4-CO2-H2O system: II. Mixtures from 50 to 1000C and 0 to 1000 bar', *Geochimica et Cosmochimica Acta* 56(7), 2619–2631.


URL: https://www.energy.gov/fe/science-innovation/oil-gas-research/enhanced-oil-recovery


ENGO (2015), Closing the Gap on Climate - Why CCS is a Vital Part of the Solution, Technical report, ENGO network on CCS.


**URL**: https://www.globalccsinstitute.com/projects/large-scale-ccs-projects

URL: http://scholar.google.co.uk/

Gregory, F. D. (1996), NSS 1740.15 Safety Standard For Oxygen And Oxygen Systems
Guidelines for Oxygen System Design, Materials Selection, Operations, Storage, and
Transportation, Technical report, NASA.

G-T Rings - 11,000 series \ Product data (2008), Technical report, Greene Tweed.
URL: www.gtweed.com

Herzog, H. J. (2011), ‘Scaling up carbon dioxide capture and storage: From megatons to


and (CO2+H2O+KCl): Measurements and modeling’, The Journal of Supercritical Fluids
78, 78–88.

phase behavior of the (carbon dioxide+water) mixture at temperatures from 298.15K to
448.15K’, The Journal of Supercritical Fluids 73, 87–96.


CO2-H2O-NaCl systems below 647 K: Assessment of experimental data and thermodynamic
models’, Chemical Geology 238(3-4), 249–267.

Hudson, J. (1925), ‘The solubility of sulfur dioxide in water and in aqueous solutions of


IEAGHG (2004), Impact of Impurities on CO 2 Capture, Transport and Storage, Technical


IPCC (2005), IPCC Special Report - Carbon Dioxide Capture and Storage - Summary for Policymakers - A Special Report of Working Group III of the Intergovernmental Panel on Climate Change, Technical report, Intergovernmental Panel on Climate Change - IPCC.


Kozintseva, T. N. (1965), ‘Solubility of hydrogen sulphide in water and in salt solutions at elevated temperatures’, *Geochemical investigation in the field of higher temperatures and pressures* pp. 121–134.


Liu, Y., Hou, M., Yang, G. & Han, B. (2011), ‘Solubility of CO2 in aqueous solutions of NaCl, KCl, CaCl2 and their mixed salts at different temperatures and pressures’, Journal of Supercritical Fluids.


McKee, O. (1953), No Title, PhD thesis, Purdue.


URL: http://ccs-info.org/onewebmedia/mit_the_future_of_coal.pdf


BIBLIOGRAPHY


Redlich, O. & Kwong, J. N. S. (1949), ‘On the thermodynamics of solutions; an equation of state; fugacities of gaseous solutions.’, Chemical reviews 44(1), 233–244.


Rumpf, B. & Maurer, G. (1992), ‘Solubilities of hydrogen cyanide and sulfur dioxide in water at temperatures from 293.15 to 413.15 K and pressures up to 2.5 MPa’, Fluid Phase Equilibria 81(81), 241–260.


Sadus, R. (1992), *High Pressure Phase Behaviour of Multicomponent Fluid Mixtures*.


Takenouchi, S. & Kennedy, G. C. (1964), ‘The binary system H2O-CO2 at high temperatures and pressures'.


Thomson Reuters (2012), ‘Web of Knowledge [v.5.8]’.


Tong, D., Trusler, J. P. M. & Vega-Maza, D. (2013), ‘Solubility of CO2 in aqueous solutions of CaCl2 or MgCl2 and in a synthetic formation brine at temperatures up to 423 K and pressures up to 40 MPa’, *Journal of Chemical and Engineering Data* 58(7), 2116–2124.


VICI (n.d.a), ‘Hayese D Chromatogram’.


VICI (n.d.b), ‘Materials of Construction’.


WEC (2013), World Energy Resources, Technical report, WORLD ENERGY COUNCIL.


Wiebe, R. & Gaddy, V. (1940), 'The solubility of carbon dioxide in water at various temperatures from 12 to 40 and at pressures to 500 atmospheres. critical phenomena', *Journal of the American Chemical Society* 315(1), 61–63.


Wiebe, R. & Gaddy, V. L. (1934), 'The Solubility of Hydrogen in Water at 0, 50, 75 and 1000ÅfC from 25 to 1000 Atmospheres.', *Journal of the American Chemical Society* 56, 76–79.


Appendices
Appendix A

Appendix to Literature Review
Figure A.1: Bubble point (in mole fraction) for the \((N_2+H_2O)\) system. Data from the literature.

Figure A.2: Dew point (in mole fraction) for the \((N_2+H_2O)\) system. Data from the literature.
Figure A.3: Dew point (in mole fraction) for the (H₂+H₂O) system. Data from the literature.

Figure A.4: Bubble point (in mole fraction) for the (H₂+H₂O) system. Data from the literature.
Figure A.5: Dew point (in mole fraction) for the (H₂S+H₂O) system. Data from the literature.

Figure A.6: Bubble point (in mole fraction) for the (H₂S+H₂O) system. Data from the literature.
Figure A.7: Bubble point (in mole fraction) for the \((O_2 + H_2O)\) system. Data from the literature.
Appendix B

Oxygen Material Compatibility for the Analytical Rig

<table>
<thead>
<tr>
<th>Material</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>Been used extensively in HP oxygen systems. More flammable and more easily</td>
</tr>
<tr>
<td></td>
<td>ignited than copper/copper alloys. Better than aluminium/aluminium alloys.</td>
</tr>
<tr>
<td></td>
<td>However, considered flammable in relatively low pressures. Ignited easily</td>
</tr>
<tr>
<td></td>
<td>at HP by friction and particulate impact. Problems when used in dynamic</td>
</tr>
<tr>
<td></td>
<td>locations of high velocity, HP or high flow rates : regulators and valves.</td>
</tr>
<tr>
<td>Elastomers (Viton)</td>
<td>Commonly used in oxygen systems. Ignition resistant.</td>
</tr>
<tr>
<td>Plastics (PTFE)</td>
<td>Commonly used in oxygen systems due to good oxygen compatibility. However,</td>
</tr>
<tr>
<td></td>
<td>poor creep resistance</td>
</tr>
</tbody>
</table>

Figure B.1: Oxygen Material Compatibility (Gregory (1996)).
## APPENDIX B. OXYGEN MATERIAL COMPATIBILITY FOR THE ANALYTICAL RIG

<table>
<thead>
<tr>
<th>Ignition mechanism</th>
<th>Definition</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle impact</td>
<td>Heat-generated when particles strike a material with sufficient velocity to ignite the particles and/or the material. Particle impact is a very effective ignition mechanism for metal. Non metal considered less susceptible. The characteristic elements are as follows: particles that can be entrained in the flowing oxygen, high gas velocities (&gt;30m/s), an impact point ranging from 45° to perpendicular to the path of the particle.</td>
<td>Assembly-generated particles traveling at high velocities can cause particle impact ignition by striking the flammable body just downstream of the control element of a valve.</td>
</tr>
<tr>
<td>Heat of compression</td>
<td>Also known as rapid pressurization and adiabatic compression: Heat generated when a gas is rapidly compressed from a low pressure to a high pressure. Most efficient igniter of nonmetals. Generally not capable of igniting bulk metals. Characteristic elements are as follows: rapid pressurisation of oxygen (generally less than 1s for small-diameter, high pressure systems), an exposed non metal close to the rapidly pressurized dead end and, a pressure ratio that causes the maximum temperature from compression to exceed the situational autoignition temperature of the nonmetal.</td>
<td>A fast-opening valve can cause heat of compression ignition when it releases high-pressure oxygen into a dead-end tube or pipe, which compresses the oxygen initially in the tube and causes heat of compression at the dead-end.</td>
</tr>
<tr>
<td>Flow friction</td>
<td>Presently understood to be heat generated when oxygen flows across or impinges upon a nonmetal (polymer) and produces erosion, friction, and/or vibration. Poorly understood ignition mechanism. Theoretical characteristic elements are as follows: Oxygen at elevated P (&gt;3.4 MPa), a nonmetal exposed to the flow and, flow or leaking that produces erosion, friction or vibration of the nonmetal.</td>
<td>A leak past a damaged nonmetal seal could cause flow friction ignition.</td>
</tr>
<tr>
<td>Mechanical impact</td>
<td>Heat generated as a result of a single or repeated impacts on a material. Most metal cannot be ignited by such a mechanism; however, nonmetal do. Characteristic elements are as follows: single large impact or repeated impacts and, a nonmetal or reactive metal at the point of impact.</td>
<td>A wrench dropping onto a porous hydrocarbon soaked with a liquid oxygen could cause mechanical impact ignition.</td>
</tr>
<tr>
<td>Friction</td>
<td>As two or more parts are rubbed together, heat can be generated as a result of friction and galling at the rubbing interface. Metal more susceptible to ignition by friction and galling. The characteristics are as follow: 2 or more rubbing surfaces, generally metal-to-metal, rapid relative motion and, high normal loading between surfaces.</td>
<td>Damaged or worn soft goods resulting in metal-to-metal rubbing between the piston and the cylinder of a reciprocating compressor could lead to friction ignition.</td>
</tr>
</tbody>
</table>

Figure B.2: Oxygen Ignition Mechanisms.
### APPENDIX B. OXYGEN MATERIAL COMPATIBILITY FOR THE ANALYTICAL RIG

<table>
<thead>
<tr>
<th>Displayed Text</th>
<th>Description</th>
<th>Line Size</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>V5</td>
<td>Vindum Valve</td>
<td>1/8&quot;-1/16&quot;</td>
<td>Vindum</td>
<td>420K</td>
<td>VTBN</td>
</tr>
<tr>
<td>V1</td>
<td>Reducer</td>
<td>Sitec</td>
<td>6205.2321-HC776</td>
<td>HC276</td>
<td></td>
</tr>
<tr>
<td>V2</td>
<td>Pneumatic Valve</td>
<td>Vindum Engineering</td>
<td>CC-310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V3</td>
<td>Pneumatic Valve</td>
<td>Vindum Engineering</td>
<td>CC-310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V4</td>
<td>Feed valve</td>
<td>Swagelok</td>
<td>316.750579</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V6</td>
<td>Needle valve</td>
<td>HIP</td>
<td>35-03AF1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V10</td>
<td>Sampling Valves</td>
<td>ROLLI</td>
<td>Monel, SS 316L, PPS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V11</td>
<td>Sampling Valves</td>
<td>ROLLI</td>
<td>Monel, SS 316L, PPS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V7</td>
<td>Needle valve</td>
<td>HIP</td>
<td>35-03AF1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Check valve</td>
<td>Sitec</td>
<td>720.4431-HC776</td>
<td>HC276, nub</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Check valve</td>
<td>Sitec</td>
<td>720.4431-HC776</td>
<td>HC276, nub</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Check valve</td>
<td>Sitec</td>
<td>720.4431-HC776</td>
<td>HC276, nub</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Check valve</td>
<td>Sitec</td>
<td>720.4431-HC776</td>
<td>HC276, nub</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Needle valve</td>
<td>HIP</td>
<td>35-03AF1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Union Cross</td>
<td>Sitec</td>
<td>620.1324-HC776</td>
<td>HC276</td>
<td></td>
</tr>
<tr>
<td>G0</td>
<td>Gas Chromatograph</td>
<td>Agilent</td>
<td>7890 Customized</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>Pressure transducers</td>
<td>Paroscientific</td>
<td>4300-HT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>Pressure transducers</td>
<td>Honeywell</td>
<td>ST1E</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Pressure transducers</td>
<td>Pressure transducers</td>
<td>Pressure transducers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Pressure transducers</td>
<td>Pressure transducers</td>
<td>Pressure transducers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Pressure transducers</td>
<td>Pressure transducers</td>
<td>Pressure transducers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Pressure transducers</td>
<td>Pressure transducers</td>
<td>Pressure transducers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>100ml View cell</td>
<td>SITEC</td>
<td>HC276</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>Needle Pump</td>
<td>Quickie</td>
<td>C-5000-10K</td>
<td>HC276</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>Needle Pump</td>
<td>Quickie</td>
<td>C-5000-10K</td>
<td>HC276</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>Needle Pump</td>
<td>Quickie</td>
<td>C-5000-10K</td>
<td>HC276</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>Circulation loop pump</td>
<td>SS 316L, SS 435</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calibration tubing</td>
<td>5/16&quot;</td>
<td>PEEK</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td></td>
<td>?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Ignition mechanisms

- **Heat of compression; residual grease, oil.
  - particle impact**
  - Remotely possible: 1
  - Remote possibility: 1
  - Possible: 2
  - Possible: 2
  - Possible: 2
  - Possible: 2
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact; mechanical impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact; mechanical impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact; mechanical impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Flow friction; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Heat of compression; residual grease, oil.
  - Heat of compression; residual grease, oil.
  - Heat of compression; residual grease, oil.**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

- **Heat of compression; particle impact**
  - Remote possibility: 1
  - Remote possibility: 1
  - Remote possibility: 1

### Figure B.3: Oxygen Ignition Risk Assessment for the Analytical Rig.
Appendix C

Justification of Uncertainty Calculations

The combined standard uncertainty $u_c$ associated with the mole fraction measurement $x$ of a component $i$ in a given phase is expressed following the methodology described in the Guide to the Expression of Uncertainty in Measurements (GUM - JCGM (2008)), which is as follows:

$$u^2(f) = \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u^2(x_i, x_j),$$  \hspace{1cm} (C.1)

where $x_{i,j}$ represents the variables of which the function $f$ is dependent, $(\partial f / \partial x_{i,j})$ are the sensitivity coefficients of $f$ with respect to the input of component $i$ or $j$ and $u^2(x_i, x_j)$ is the covariance or the variance, depending on the relationship between $i$ and $j$ (equality or strict difference).

In this case, the variables are considered independent. This is equivalent to taking the covariances in Equation C.1 as nil ($u^2(x_i, x_j)=0$) and only retaining the variance ($i=j$), which are abbreviated as $u^2(x_i)$ for simplicity.

The mole fraction measurements presented in this work were obtained using the absolute area principle which states proportionality between the peak area $A_i$ in the chromatogram of the response of the detector and the amount $n_i$ of component $i$ in the sample. The response factor, or calibration coefficient $\alpha_i$ and mole fractions $x_i$ of each component are found through these expressions:

$$n_i = \alpha_i A_i$$  \hspace{1cm} (C.2)

$$x_i = n_i / \sum_{k=1}^{N} n_k$$  \hspace{1cm} (C.3)
Which yields:
\[ x_i = \alpha_i A_i / \sum_{k=1}^{N} \alpha_k A_k \]  \hspace{1cm} (C.4)

Considering that in the experiments presented in this work, additional variables to consider are the temperature and the pressure, one can write:
\[ u_i^2(x_i) = (\partial x_i / \partial T)^2 u^2(T) + (\partial x_i / \partial p)^2 u^2(p) + \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial x_i}{\partial n_j} \frac{\partial n_j}{\partial \alpha_i} \right)^2 u^2(\alpha_j) + \sum_{i=1}^{n} \sum_{j=1}^{n} \left( \frac{\partial x_i}{\partial n_j} \frac{\partial n_j}{\partial A_j} \right)^2 u^2(A_j) \]  \hspace{1cm} (C.5)

Being partial derivatives, the sensitivity coefficient \( \partial x_i / \partial n_j \) can be explicitly written as:
\[ (\partial x_i / \partial n_j) = -x_i x_j / n_j \hspace{1cm} (j \neq i) \]  \hspace{1cm} (C.6)
\[ = (1 - x_i) x_i / n_i \hspace{1cm} (j = i) \]  \hspace{1cm} (C.7)

Similarly, using Equation C.3, \( \partial n_j / \partial \alpha_i \) and \( \partial n_j / \partial A_j \) can be expressed as follows:
\[ (\partial n_j / \partial \alpha_i) = A_j \]  \hspace{1cm} (C.8)
\[ (\partial n_j / \partial A_j) = \alpha_j \]  \hspace{1cm} (C.9)

Using Equation C.5, C.6, C.7, C.8 and C.9, it follows that, for a system composed of N components, the combined standard uncertainty of \( x_i \) is given by:
\[ u_i^2(x_i) = (\partial x_i / \partial T)^2 u^2(T) + (\partial x_i / \partial p)^2 u^2(p) \]
\[ + \sum_{i \neq j} (x_i x_j)^2 \left[ u_i^2(\alpha_i) + u_i^2(A_j) \right] + (x_i(1 - x_i))^2 \left[ u_i^2(\alpha_i) + u_i^2(A_j) \right] , \]

where \( u_i(X) \) denotes the standard relative uncertainty of variable \( X \). The standard relative uncertainties for the calibration coefficient are given by:
\[ u_i^2(\alpha_i) = \alpha_i^2 \left[ u_i^2(n_i) + u_i^2(A_i) \right] \]  \hspace{1cm} (C.11)

The values of \( n_i \) and \( A_i \) in Equation C.11 are the calibration amount of matter and chromatographic peak area for component \( i \).

Finally, Equation C.10 reduces to the following simpler form for a binary mixture:
\[ u_i^2(x_i) = (\partial x_i / \partial T)^2 u^2(T) + (\partial x_i / \partial p)^2 u^2(p) + [x_i(1 - x_i)]^2 \sum_{i \neq j} \left[ u_i^2(\alpha_i) + u_i^2(A_j) \right] \]  \hspace{1cm} (C.12)
Appendix D

Health Effects of Respiratory Exposure to Sour Gases
Table D.1: Health effects of respiratory exposure to H$_2$S.


<table>
<thead>
<tr>
<th>ppm</th>
<th>mg m$^{-3}$</th>
<th>SIGNS AND SYMPTOMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 - 20</td>
<td>15 - 30</td>
<td>Threshold for eye irritation</td>
</tr>
<tr>
<td>50 - 100</td>
<td>70 – 140</td>
<td>Serious eye damage</td>
</tr>
<tr>
<td>150 - 250</td>
<td>210 - 350</td>
<td>Loss of olfactory sense</td>
</tr>
<tr>
<td>320 - 530</td>
<td>450 - 750</td>
<td>Pulmonary oedema with risk of death</td>
</tr>
<tr>
<td>530 - 1000</td>
<td>750 - 1400</td>
<td>Strong CNS stimulation, hyperpnoea followed by respiratory arrest</td>
</tr>
<tr>
<td>1000 - 2000</td>
<td>1400 - 2800</td>
<td>Immediate collapse with paralysis of respiration</td>
</tr>
</tbody>
</table>

Table D.2: Health effects of respiratory exposure to SO$_2$.

(Baxter, 2000; Nemery, 2001; NIOSH 1981; Wellburn, 1994)

<table>
<thead>
<tr>
<th>Exposure limits (ppm)</th>
<th>Health Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-5</td>
<td>Threshold for respiratory response in healthy individuals upon exercise or deep breathing</td>
</tr>
<tr>
<td>3-5</td>
<td>Gas is easily noticeable. Fall in lung function at rest and increased airway resistance</td>
</tr>
<tr>
<td>5</td>
<td>Increased airway resistance in healthy individuals</td>
</tr>
<tr>
<td>6</td>
<td>Immediate irritation of eyes, nose and throat</td>
</tr>
<tr>
<td>10</td>
<td>Worsening irritation of eyes, nose and throat</td>
</tr>
<tr>
<td>10-15</td>
<td>Threshold of toxicity for prolonged exposure</td>
</tr>
<tr>
<td>20+</td>
<td>Paralysis or death occurs after extended exposure</td>
</tr>
<tr>
<td>150</td>
<td>Maximum concentration that can be withstood for a few minutes by healthy individuals</td>
</tr>
</tbody>
</table>
Appendix E

SolidWorks Drawings of the New Semi-Analytical Apparatus
Figure E.1: Main Vessel - Vessel
Figure E.2: Main Vessel - Cap
Figure E.3: Main Vessel - Plug
Figure E.4: *Flash vessel - Body*
Figure E.5: *Flash vessel - Lid*
Figure E.6: Flash vessel - Assembly
Figure E.7: *In-house gas stirrer*