



SEPARATION OF NOBLE GAS MIXTURES OF (Xe, Ar AND Kr) USING GAS HYDRATE TECHNOLOGY

By

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Declaration

I, **Matizakurima Farai**, student number **218085069**, declare that:

- (i) The research reported in this dissertation, except where otherwise indicated or acknowledged, is my original work.
- (ii) This dissertation has not been submitted in full or in part for any degree or examination to any other university.
- (iii) This dissertation does not contain other persons' data, pictures, graphs or other information unless specifically acknowledged as being sourced from other persons.
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- (vii) This dissertation is primarily a collection of material, prepared by myself, published as journal articles or presented as a poster and oral presentations at conferences. In some cases, additional material has been included.

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30/11/2020

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Declaration 2: Publications and contributions

Parts of this work were presented in the following publications:

Publication 1: Journal of Chemical Engineering (Manuscript in preparation)

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Abstract

The separation and purification of xenon from xenon + argon + krypton mixtures is an important research area owing to the increasing industrial demand for the gas. While cryogenic distillation, membrane technology and adsorption using metal-organic frameworks (MOF's) are used as separation methods, these methods are energy-intensive and sometimes financially non-viable. A comprehensive theoretical investigation of these methods is presented in this work. Hydrate-based separation technology has been reported to provide a possible solution. This study aimed to assess the performance of gas hydrate technology in separating and purifying noble gas mixtures. Hydrate technology is an interesting application, it has and is being investigated for the application in hydrocarbon gas capture and storage, carbon dioxide capture and storage, food concentration and refrigeration amongst other application. The motivation of this work was to find a cost-effective separation technology for separating and purifying xenon from the xenon + argon + krypton mixtures. Previous studies investigated the application of gas hydrate technology in separating xenon from binary noble gas mixtures, including an investigation of the effect of hydrate promoters and other factors in the capture of xenon in the hydrate phase. This study builds upon previous work focusing on the ternary mixtures of (Xe + Ar + Kr). Experimental measurements of gas hydrate phase equilibria for gas mixtures of (argon + krypton + xenon), along with compositional analysis of the hydrate and vapour phases using gas chromatography were performed. The isochoric pressure search method was used for measurements, with the use of a 52 ml stainless steel equilibrium cell. Different gas mixtures with various compositions ranging from 19 to 70 mol% xenon were investigated.

To check the reliability of both the experimental equipment and procedures used in this study, dissociation data for the simple carbon dioxide + water system were measured. The newly measured data were compared with those in literature and were found to be in agreement with an acceptable uncertainty range. The instruments that were used were calibrated and the calibrations were verified.

A thermodynamic model based on van der Waals and Platteeuw (vdW–P) solid solution theory was used to predict the hydrate equilibrium conditions for the Xe + Ar + Kr + water

systems. An average absolute deviation (*AAD%*) of 1.4% between the experimental and predicted hydrate dissociation conditions was obtained. The consistency between modelled results and the novel measured experimental data demonstrated the validity of the proposed method. Concurrent to measuring thermodynamic equilibrium data, equilibrium compositional data for the systems studied were measured. The results indicate that the concentration of xenon has the highest increase in the first and second hydrate stages, reducing the concentration effect as the number of stages increases. For a mixture with 40.7 mol % argon, 33.6% krypton and 25.7% xenon, a concentration increase from 25.7% to 80.4% of xenon was achieved using two hydrate formation and dissociation stages. These findings were used to evaluate energy loads for the hydrate-based separation method. The results obtained were compared to the results obtained from an Aspen® simulation of the conventional cryogenic distillation process to determine energy loads for the conventional cryogenic distillation process. Results of the comparison revealed that the hydrate-based separation method presents a 20% energy cost advantage over cryogenic distillation.

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Nomenclature

English letters

A	Area on GC detector
C	Langmuir constant
C_p	Specific heat capacity [J/mol.K]
f	fugacity
H	Enthalpy [kJ]
L_w	The liquid phase
n	Number of moles [mol]
N	Number of stages
NDP	Number of experimental data points
N_{feed}	Feed stage
P	Pressure [MPa]
ppmv	Parts per million by volume
Q_C	Condenser duty [kW]
Q_R	Reboiler duty [kW]
R	Reflux ratio
R	Universal gas constant [$\text{m}^3 \cdot \text{Pa} / (\text{mol} \cdot \text{K})$]
T	Temperature [K]
t	Time [s]
U_x	Combined expanded uncertainty
V	Volume [m^3]
x	Mole fraction in the liquid phase
y	Mole fraction in the vapour phase
y_H	Mole fraction in the hydrate phase
Z	Compressibility factor

Greek symbols

Δ	Change in property
----------	--------------------

ϑ_m	Ratio of the number of type m cavities to number of water molecules in the hydrate lattice
$\bar{v}_m$	Number of cavities of type m per water molecule
θ_m	Fraction of the type m cavities which is occupied by hydrate former molecules
θ	Cage occupancy
μ	Chemical potential

Subscripts

<i>calc</i>	Calculated
<i>calib</i>	Calibration
<i>exp</i>	Experimental
<i>H</i>	Hydrate
<i>i,j</i>	Component
<i>instr</i>	Instrument
<i>lit</i>	Literature
<i>m</i>	Cavities
<i>min</i>	Minimum
<i>rep</i>	Repeatability
<i>w</i>	Water

Superscripts

<i>g</i>	Gas phase
<i>H</i>	Hydrate phase
<i>L</i>	Liquid water phase
<i>sat</i>	Saturated
<i>v</i>	Vapour phase

Abbreviations

<i>AAD</i>	Average Absolute Deviation
<i>Ar</i>	Argon

<i>ARD</i>	Absolute Relative Deviation
C	Equilibrium Cell
CF	Cold finger
DAS	Data acquisition system
DIP	Direct Injection Point
EoS	Equation of State
GC	Gas chromatography
GCY	Gas cylinders
<i>H-L_w-V</i>	Hydrate - Liquid water - Vapour
MJ	Mechanical Jack
MOF	Metal-Organic Framework
NDD	Non-density-dependent mixing rule
Kr	Krypton
QCM	Quartz Crystal Microbalance
ROLSI™	Rapid Online Sampling Injector
sI	Structure I
sII	Structure II
sH	Structure H
SDS	Sodium dodecyl sulphate
SP	Syringe pump
TBAB	Tetra-n-butylammonium bromide
TB	Temperature bath
TCD	Thermal Conductivity Detector
TP	Temperature probe
TPC	Temperature programmable circulator
V	Valves
VPT EoS	Valderrama modification of Patel–Teja Equation of State
VP	Vacuum pump
Xe	Xenon

1

CHAPTER ONE: INTRODUCTION

The capture of xenon, argon, and krypton and their subsequent separation and purification have over the years attracted a lot of researchers' attention. This is due to the increasing industrial demand of xenon and the environmental concerns brought about by the radioactive isotopes of xenon and krypton. Xenon, an extremely rare noble gas (0.087 ppmv (parts per million by volume) in atmospheric air) (Chen et al., 2014), has emerged as an industrially relevant gas for medical imaging, as an anaesthetic, as a satellite propellant in the space industry and as a carrier gas in analytical chemistry (Banerjee et al., 2014, Barnejee and Winkler, 2016) amongst other uses. Five hundred ppmv of xenon isotopes are released from nuclear fuel reprocessing plants as effluent gas mixture along with krypton and need to be captured from the process off-gas to prevent air pollution (Yu et al., 2018). Existing commercially applicable separation technologies, most common being cryogenic distillation, have a high energy penalty and therefore costly. The high cost of cryogenic distillation hinders the extensive application of xenon. Thus, much research has been focused on finding efficient and cost-effective alternative methods for producing the pure component.

Physical adsorption, chemical absorption, membrane technology, and lately, gas hydrate separation technologies are potential alternative technologies for the capture and separation of these gases (Zang and Liang, 2018). Gas hydrate separation offers several attractive advantages as an alternative to cryogenic distillation. It is a simple separation mechanism, can easily be regenerated, is capable of separating gas mixtures, operates at mild temperatures and pressures, requires low material, has less energy loss, has large gas storage capacity and is environmental

friendly (Duc et al. 2007, Dashti et al., 2015, Wang et al., 2017). As an example, gas hydrate can be formed under certain conditions of pressure and temperature in a single reactor with very simple process flow and the water used can continuously be reused, whilst additives including thermodynamic and kinetic promoters for hydrate formation are environmentally friendly (Taylor et al., 2008). Individual rare gases such as xenon, argon, and krypton are industrially obtained as by-products of the capital-intensive cryogenic distillation of liquid air into oxygen, producing as a by-product, a 20/80 v/v xenon to krypton mixture that needs further distillation to produce high purity xenon (99.999%). The high prices of xenon, at US\$ 1000-US\$ 1200/kg in 2018. Banerjee et al. (2018) reflect on the energy and capital intensiveness of the cryogenic process which is a result of the operating conditions of cryogenic distillation, the temperature of 175 K, and variable pressure (Kerry, 2006, Banerjee et al., 2018). As a result of the high operation costs, it is not economical to perform cryogenic distillation onsite and at a small scale (Kerry, 2006).

In South Africa, xenon and krypton are produced by Sasol in partnership with Air Liquide at its Secunda plant. The air separation plants producing the gases were commissioned in 1990. A xenon-krypton mixture is produced, and the mixture is sent to Air Liquide in France for purification. All the 17 air purification plants producing the xenon + krypton mixture use Air Liquide technology (Arnoldi, 2018). The xenon, krypton and argon produced are used locally and exported.

Literature reported the successful use of the hydrate technology in the recovery and capture of various target gases or organic contaminants from gaseous and or aqueous mixtures as exemplified by the recovery of SF₆ from a nitrogen + SF₆ mixture at a laboratory scale (Cha et al., 2010). In a bid to establish industrially viable hydrate based technologies for the capture of CO₂ from flue gases, Mori (2015) evaluated the scaling up of hydrate forming reactors using stirred tank and tubular reactors and found stirred tank reactor unfavourable (Mori, 2015). Zhao et al. (2016) amongst many other researchers, investigated the recovery of methane from coal mine methane using process optimizing additives (Zhao et al., 2016). A pilot-scale study for the capture of CO₂ from flue gases was performed by Xu et al., (2014). They achieved 90% CO₂ concentration from 17% in the flue gas using two hydrate stages. Results of the study demonstrated the effective application of hydrate based gas separation at pilot scale (Xu et al., 2014). These examples demonstrate that there is a need to conduct much research on gas hydrate

technology for various applications. Currently, a lot of research on gas hydrate based separation focuses on methane recovery (Zang and Liang, 2018), methane storage, CO₂ capture and storage (Belandria et al., 2012, Park et al., 2013), water treatment and desalination (Wang et al., 2013), refrigeration (Hashemi, 2015), separation processes including juice concentration in food technology among other areas of study (Eslamimanesh et al., 2012, Babaei, 2015, Doubra, 2020).

1.1 Pricing, supply, and demand for noble gases

Xenon, krypton, and argon are produced as secondary products of the cryogenic distillation of air. This separation process is discussed in Chapter 2. Various air separation plants globally, produce these rare gases as by-products requiring an added investment as the extra purification units are not part of the main air separation unit. Thus, the installation of such a plant depends on the market. The large investment needed should be justified by the prices of the gases to ensure profitability. These additional purification units are often built onsite to reduce transportation costs. According to Betzendahl (2012), there are 100 air separation units worldwide that produce xenon, and these are usually the large plants with large oxygen gas outputs of at least 2000 tonnes per day. (Betzendahl, 2012). As a result, since xenon and krypton have similar properties, these two gases are usually collected together in the ratio 10:1 krypton to xenon (Herman and Unfried, 2015). For an air separation plant producing 1000 tons of oxygen per day, it can produce 1.2 kg/day of xenon (Welle, 1990).

The price for xenon fluctuates continuously due to a small market volume with very few producers. It also depends on the price for krypton as these two gases are produced together, and the production of these two gases depends on the oxygen output of the air separation plants (Cheung et al., 1991, Betzendahl, 2014).

The demand, on the other hand, is driven by its uses. Xenon is used in the manufacture of light bulbs, for electric propulsion, as an anaesthetic, in plasma displays, for lasers, and in dark matter research (Winkler et al., 2016). The expansion of each of these applications means the consumption of the gas will continue to increase. Figure 1.1 shows the trends for xenon production and demand from 2000, including the forecast for the future.

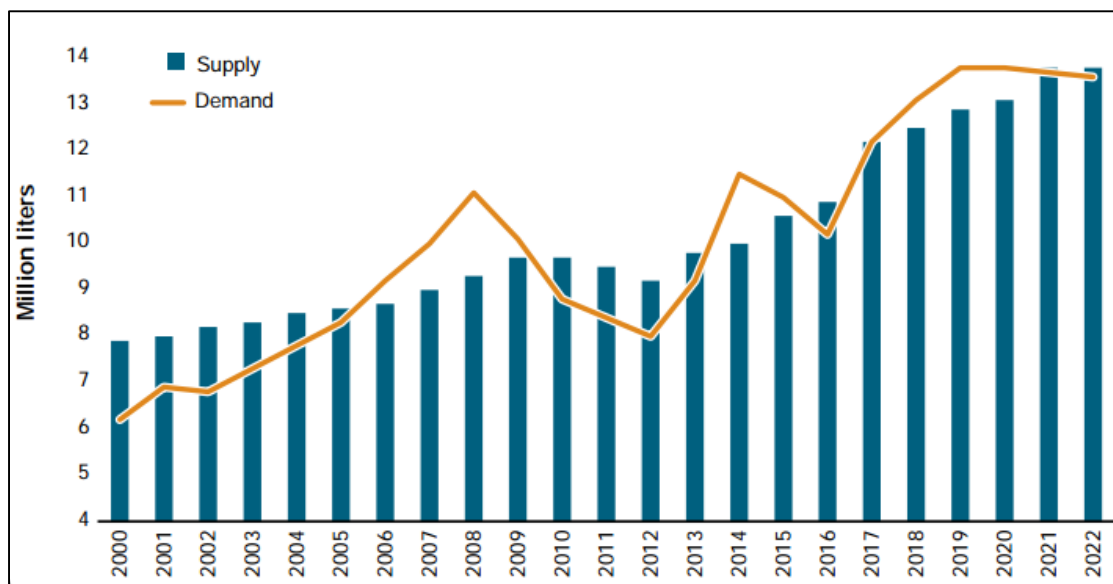


Figure 1.1: Trend for xenon supply and demand since 2000 (extracted from (Spiritus and Betzendahl, 2018)).

Figure 1.1 shows that there has been a significant increase in the production of xenon over the past 20 years, due to the rise in usage shifting from just being used as a specialty gas for research to a commodity, which is relied upon in many industries (Herman and Unfried, 2015). This has resulted in fluctuating prices, US\$5 000/ kg in 2014 (Chen et al., 2014) and US\$1000 - US\$1200/ kg in 2018 (Kim et al., 2017, Banerjee et al., 2018). In the past 30 years, the amount of xenon needed has increased 10-fold due to its use in communications for electric propulsion due to more geostationary satellites which use xenon as the propellant. Also, the amount of xenon being used by each satellite has increased. Furthermore, since the mid-2015, the demand for xenon has increased for the laser process in the semi-conductor industry (Allen et al., 2013, Elsner, 2018). According to the International Market Analysis Research and Consulting (IMARC) group report (IMARC, 2020), the xenon market reached a volume of 17.9 million litres in 2019 with an expected moderate growth during the 2020 – 2025 period.

As mentioned earlier, since xenon and krypton are produced together using the same equipment, the price of xenon is inherently intertwined with the price of krypton. If the demand for xenon grows faster than for krypton, the xenon market has to bear a larger share of the production costs, which leads to an increase in the xenon price and vice versa. Figure 1.2 below shows the trend

for xenon pricing since 1998 and the forecast until 2020. It can be seen that the prices have fluctuated over the years but with a general increase (Spiritus and Betzendahl, 2018).

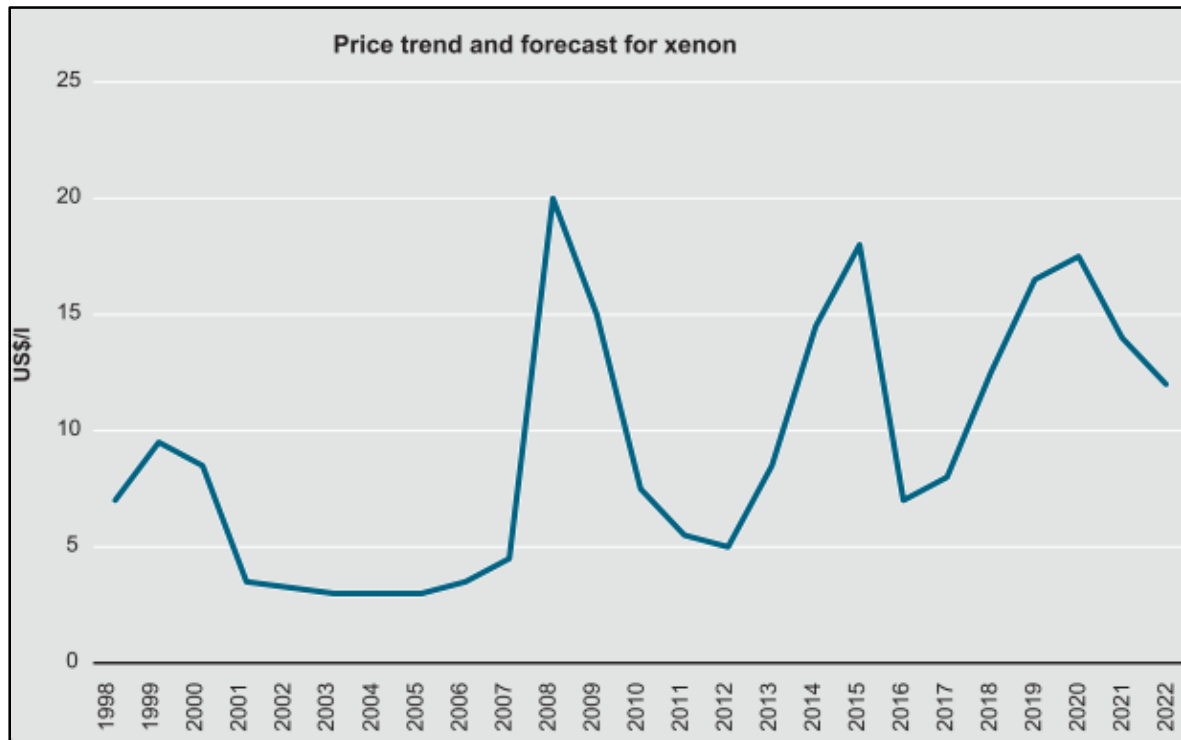


Figure 1.2: Xenon pricing trend and forecast according to (Herman and Unfried, 2015) and (Spiritus and Betzendahl, 2018).

The current price for krypton is approximately 100 times more expensive than argon, which is prohibitively expensive for widespread market adoption. The major use for krypton is in insulated glass window manufacture which consumes as much as 51% of all the krypton produced. Krypton is also used for filling incandescent lamps, with this use accounting for 40% of all the krypton used. Other uses include in the semi-conductor industry in lasers and in research and development (Spiritus et al., 2018).

The four significant companies controlling about 75 percent of all global rare gas sales are Air Liquide, Linde, Praxair, and Iceblick (Betzendahl, 2012, Elsner, 2018) as shown by the market share proportions they each have in Figure 1.3. The "Other" group in Figure 1.3 is comprised of a number of steel mills in Russia and China as well as the industrial gas companies Air Products, Messer, Taiyo Nippon Sanso, and other small-scale purifiers in Eastern Europe.

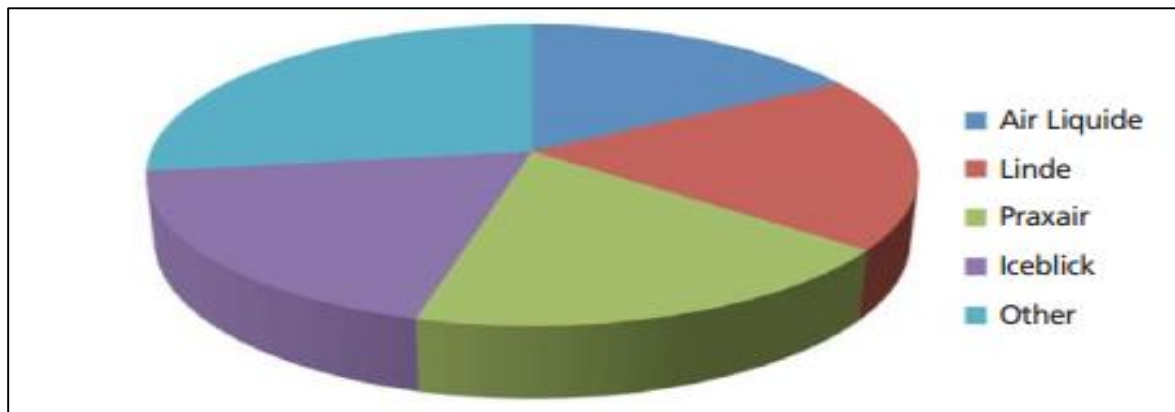


Figure 1.3: Market shareholders of xenon and krypton production (Betzendahl, 2012).

1.2 Aim and objectives

This work is a continuation of the study performed by (Babaei, 2015) in her PhD work and postdoctoral research. She studied the application of gas hydrate in the separation of noble gas mixtures. Her studies covered the following topics:

- The investigation of the effect of TBAB as a promotor on the hydrate dissociation conditions of Ar, Kr, and Xe.
- The investigation of the effect of TBAB, SDS, and the kinetic parameters (temperature and pressure conditions) on the rate of Ar hydrate formation.
- Separation and purification of Xe from binary mixtures of Ar and Xe.

This study aims to determine the feasibility of separating xenon from the ternary mixtures of (Xe + Kr + Ar) using gas hydrate technology as an alternative to distillation.

The specific objectives of this work include:

1. Generating accurate and novel gas hydrate phase equilibrium data for the ternary mixtures of (Xe + Kr + Ar); to be used to design and simulate a gas-hydrate based separation process.

2. Performing a multiple gas hydrate formation/ dissociation experimental procedure to separate xenon from the (Xe + Kr + Xe) mixtures. This section includes the compositional analysis of the vapour and the hydrate phases using gas chromatography technology.
3. Applying a comprehensive thermodynamic model to predict the gas hydrate phase equilibria for the ternary mixture of (Xe + Kr + Ar), comparing the model predictions with the experimental results.
4. Using the phase equilibrium and phase composition data provided by the experiments and the model to assess the performance of gas hydrate-based separation for (Xe + Kr + Xe) gas mixtures. These are important in understanding and proposing a process design.
5. Performing an assessment of the heating and cooling utilities of the hydrate-based gas separation process in comparison to the conventional distillation process.

To date, there is still a need to expand knowledge on the real potential of gas hydrate technology in separating numerous other gas-gas mixtures which have not yet been investigated and reported in the literature. This work presents a combination of experimental and preliminary calculations of the separation process based on the thermodynamic data obtained.

In this thesis, the introductory chapter is succeeded by an in-depth literature review of the processes being used and/or understudy for the separation of noble gas mixtures. This chapter includes an introduction to gas hydrates and their applications; it also describes and analyses the advantages and disadvantages of each process. The theory to the thermodynamic model that was applied will also be presented in this chapter.

Chapter 3 outlines the experimental methods and techniques used for hydrate measurements. The chapter also summarises the data and equipment from open literature for the separation of binary and ternary gas mixtures.

Chapter 4 outlines the equipment used in this study, as well as the experimental procedures performed in the study.

The experimental results obtained are presented and analysed in Chapter 5. These results include results for the equipment calibrations, thermodynamic hydrate equilibrium data for the test system, and the seven gas mixture systems containing different concentrations of argon, krypton, and xenon that were studied. The chapter also presents the compositional analysis of the vapour and hydrate phases during the hydrate formation process as well as preliminary energy calculations for the experimental hydrate-based gas separation process compared to the distillation process.

The last chapter concludes the work as well as outlines recommendations.

CHAPTER TWO: REVIEW OF SEPARATION TECHNOLOGIES FOR GAS MIXTURE SEPARATION

This chapter presents a review of the physical and chemical properties of argon, xenon, and krypton and the technologies which are being used and under study for the separation of noble gas mixtures. These include cryogenic distillation, physical adsorption, and gas hydrates. The chapter also presents background information on gas hydrates as well as their application with an emphasis on gas separation processes.

2.1 Physical and chemical properties

Table 2.1 and Figure 2.1 show the physical and chemical properties of Xe, Kr, and Ar. Owing to the differences in the boiling points, Xe and Kr can be separated using cryogenic distillation. Both the kinetic diameter and the polarizability of Kr are smaller than Xe. The bigger kinetic diameter for Xe enables it to be adsorbed on molecular sieves while the smaller Kr passes through. The two noble gases are chemically nearly inert with symmetric atoms and are both non-polar (Alagappan, 2013). Adsorbate size and polarizability also affect the adsorption of Xe atoms over Kr atoms when in solid-state MOFs (Banerjee et al., 2015).

Table 2.1: Physical and chemical properties of Xe, Kr, and Ar.

Chemical	Formula	^a BP/ K	^b Kinetic diameter / Å	^c Atomic radius (pm)
Argon	Ar	87.28	3.80	71
Krypton	Kr	119.8	3.655	88
Xenon	Xe	164.1	4.047	108

(^a Kerry, 2006, ^b Lallemand et al., 1977, ^c LibreTexts, 2019).

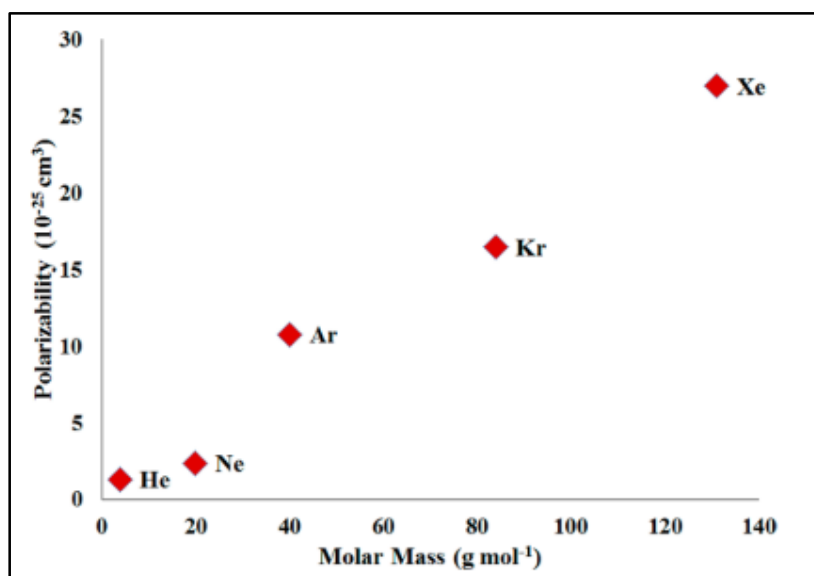


Figure 2.1: Polarizability of Xe, Kr, and Ar (extracted from (Banerjee et al., 2015)).

2.2 Technologies for the separation of noble gas mixtures

There is a variety of technologies currently being used and under study. These include cryogenic distillation, adsorption using activated carbons, zeolites and metal-organic frameworks. This section will discuss the different technologies, including their advantages and disadvantages. The application of gas hydrate technology will also be discussed.

2.2.1 Cryogenic distillation of noble gas mixtures

Generally, cryogenic distillation separates gases based on the disparities in their boiling points. The composition of air components and their respective boiling points are shown in Table 2.2. The main products of the cryogenic distillation of air are oxygen and nitrogen with Ar, Kr, and Xe being produced as by-products.

Table 2.2: Composition of air and respective boiling points for the components, according to (Brimblecombe, 1986).

Component	Molar mass (g)	Volume (%)	Boiling point (K)
Nitrogen	28.01	78.084	77.35
Oxygen	32.00	20.946	90.19
Argon	39.95	0.934	87.27
Hydrogen	1.01	0.00005	20.27
Neon	20.18	0.00192	27.09
Helium	4.00	0.000053	4.22
Krypton	83.80	0.000114	119.81
Xenon	131.29	0.0000087	165.04
Carbon Dioxide	44.01	0.02-0.04	194.68

The cryogenic distillation process is more effective in the separation of gases with large differences in boiling points but more difficult to do so if the boiling points for the substances are close together. Oxygen and argon have very close boiling points (90.19 K and 87.27 K respectively), so the separation between these two gases is less effective and as such argon is obtained upon further distillation of an oxygen-argon mixture.

During the cryogenic distillation process, the gas mixture components are separated through a series of compression, refrigeration, and separation steps. These steps are most technologically advanced and well established in the industry, and their operation and design have been proven (Xu et al., 2014, Winkler et al., 2016). The general arrangement of distillation columns for the recovery of argon is shown in Figure 2.2. The oxygen stream that is enriched with argon from the low-pressure column is purified to remove oxygen by using the crude argon column (Cheung et al., 1991, The Linde Group, 2020).

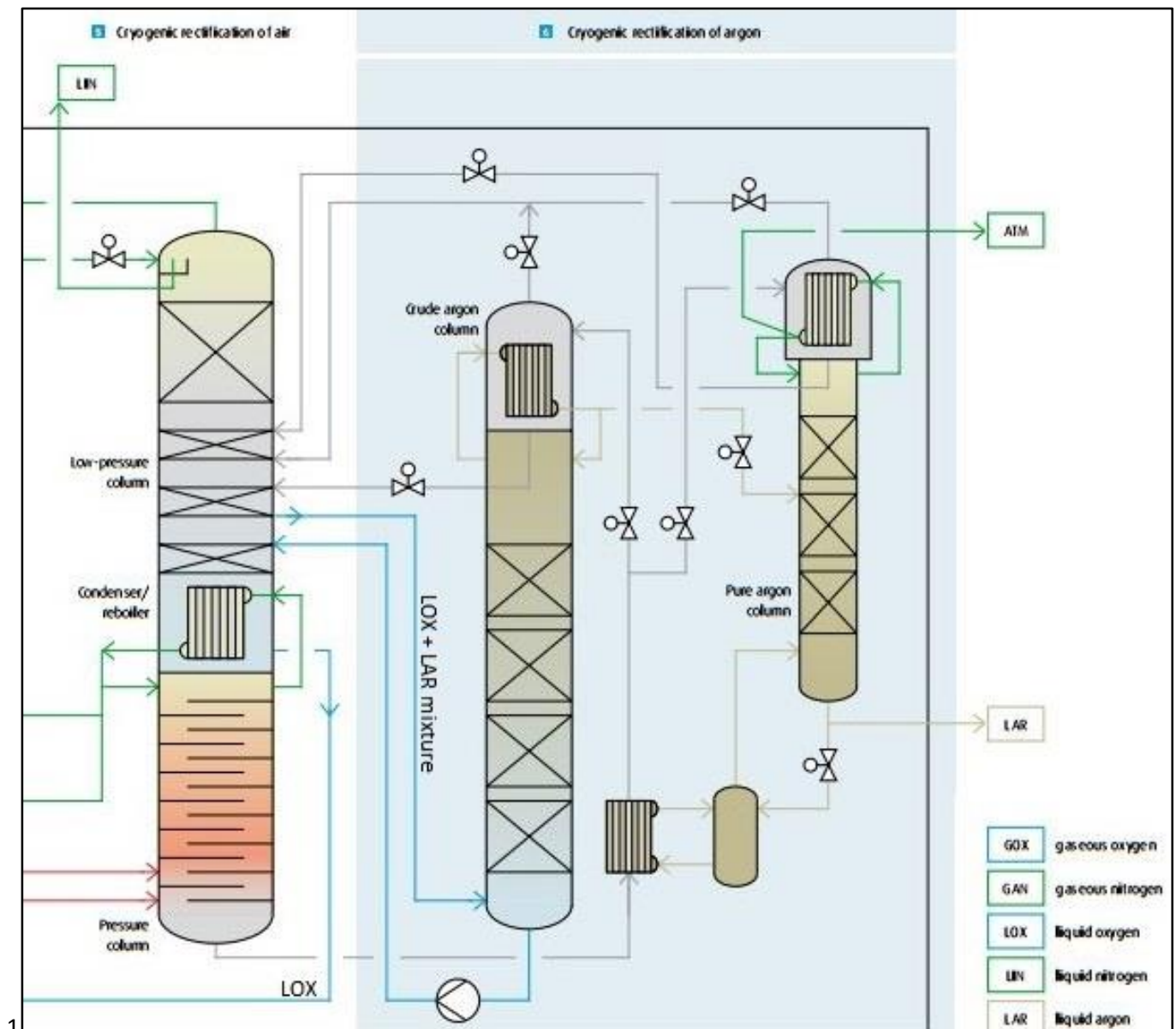


Figure 2.2: Distillation column setup for argon (extracted from (The Linde Group, 2020)).

The process for the recovery of the xenon-krypton mixture is similar to the recovery of argon. Oxygen is drawn from the main distillation column and passed through hydrocarbon absorbers and sent to an auxiliary column similar to the argon auxiliary column. Through a series of condensation and re-boiling steps using nitrogen from the top of the main column, a xenon -krypton mixture is obtained which is then sent for final separation to obtain pure xenon and krypton gases using another distillation column (Kerry, 2006). The cryogenic distillation method is a costly technology, mainly because of the very low operating temperatures required.

In an effort to reduce the cost of production, Wang et al. (2014) designed and constructed a cryogenic distillation device for the separation of Kr from commercially available xenon with a Kr/Xe ratio of approximately 10 based on the McCabe-Thiele method (Wang et al., 2014). The study aimed to reduce the Kr concentration by three orders of magnitude and achieve a xenon separation efficiency of 99%. The developed system was efficient in removing Kr from Xe to a concentration of 10^{-12} mol/mol with the speed of distillation being 5 kg/hr but did not solve the economics of using cryogenic distillation as the purity of the Xe is still dependent on the height of the column. The separated Xe was to be used for dark matter research. An extension of 2.8 m of package material had to be made on the 2.7 m distillation column to increase the separation efficiency of the designed cryogenic distillation (Aprile et al., 2017). This indicates the inherent capital intensiveness of the cryogenic distillation process.

2.2.2 Separation of noble gases using adsorption

Separation of noble gases by physical adsorption on porous materials and absorption by dissolution in a solvent has been considered as cost-effective alternatives to cryogenic distillation in the separation of gas mixtures. However, the challenge lies in finding the best suitable material for a particular gas mixture and determining the separation efficiencies (Barnejee, 2018). In the liquid absorption process, the separation coefficient is determined by the solubility of the target gases in a given solvent and varies with temperature and pressure. Figure 2.1 showed the difference in the polarizability of the noble gas molecules, and these differences affect their adsorption on surfaces. Xenon has a polarizability value of approximately 60% above that for krypton, as such Xe has a higher probability of adsorption on adsorbent surfaces. (Bazan et al., 2011). Figure 2.3 shows a process flow diagram for separating Xe and Kr using adsorption from a flue gas stream.

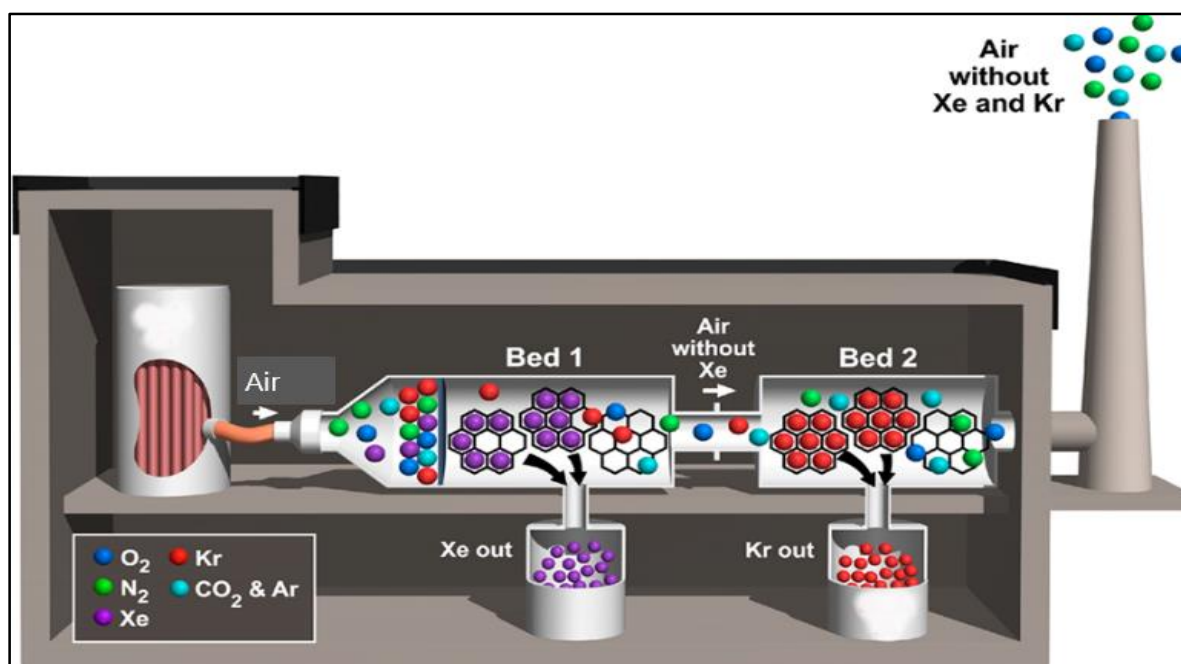


Figure 2.3: Noble gas extraction process using adsorption (extracted from (Banerjee et al., 2015)).

The separation of noble gases using physical adsorption has proved to be better than using absorption. This is because the adsorbents have high surface areas which allow a greater storage capacity. Many adsorbents have been investigated for this application ranging from activated carbons, modified zeolites (Xiong et al., 2015, Xiong et al., 2018) to metal-organic frameworks (MOFs). Banerjee et al. (2018) achieved a separation factor of up to 1000 and separation efficiencies of 99.9% by using liquid absorption in dichlorodifluoromethane as a solvent (Banerjee et al., 2018).

2.2.2.1 Zeolites

Zeolites are readily available and widely used commercial adsorbents, also known as molecular sieves because they separate molecules based on their differences in shapes and sizes. The increased surface area and larger pores of the zeolite adsorbents allow easier interaction with non-polar adsorbates (Xiong et al., 2015). As such, zeolite NaA and zeolite NaX were shown to be selective adsorbents for xenon over krypton with selectivity factors of approximately 4 to 6 but with a downside of low capacities (Jameson et al., 1997). There has

been a remarkable increase in the zeolite-based membrane technology for Kr/Xe separation (Anderson et al., 2018).

2.2.2.2 Activated carbons

Activated carbons are attractive adsorbents owing to their low cost, large surface area, high chemical and thermal stability (Wang and Li, 2018). Bazan et al. (2011) investigated the adsorption of Ar, Kr, Xe, and O₂ on activated carbon and zeolites and for every case studied, Xe was the most strongly adsorbed, followed by Kr, then O₂ and Ar (Bazan et al., 2011). Experimental ternary data obtained confirmed the preferential adsorption of Xe over the other gases. The main disadvantage of using activated carbon is that it poses a severe fire hazard in the presence of NO_x (Banerjee et al., 2018). Another disadvantage is that they have a low uptake capacity and selectivities. CO₂ and water molecules must also be extracted in advance when such sorbents are used, as CO₂ and water compete for the same adsorption sites as Xe and this presents operational challenges (Banerjee et al., 2018). These studies show that activated carbons are lucrative potential adsorbents but they also have serious disadvantages that hinder their application at large scale.

2.2.2.3 Metal-organic frameworks (MOFs)

The nano-sized pores and consequently high internal surface area (>7000 m²/g) of MOFs make them suitable for application in separating gases. They are classified into MOFs with high specific surface area, MOFs with open metal sites, and MOFs with small pores without open metal sites (Yu et al., 2018, Kukulka et al., 2019).

Gonzales et al. (2018) investigated the separation of Xe and Kr in the two different MOFs Ni₂(m-dobdc) and Co₂(m-dobdc). They concluded that xenon has a stronger interaction with the open metal sites of both materials, and hence can effectively be separated but recommended further work to be done under more realistic mixtures (Gonzalez et al., 2018).

Another experimental study investigated the MOF, MOF-505, and attributed the high Xe selectivity to the small pores with strong adsorption properties (Bae et al., 2013). These MOFs do absorb gases such as methane and xenon, but they are air-sensitive, and they collapse upon solvent removal. Banerjee (2018) demonstrated the applicability of MOFs for Xe

recovery and recycling from an anaesthetic gas mixture using two benchmark MOFs, Ni-DOBDC and HKUST-1 (Banerjee et al., 2018). MOFs are also being investigated for potential use in recovering and recycling of Xe from portable breathing units used for anaesthetics (Abrahams et al., 2017). Another MOF, PCN-12 showed remarkable performance for the separation and recovery of Xe as demonstrated by its superior Xe adsorption capacity and Xe/CO₂, Xe/N₂, and Xe/O₂ selectivities when recycling anaesthetic gas mixtures. The use of the MOFs in this application is cost-effective when xenon is used as an anaesthetic gas (Banerjee et al., 2018).

Although MOFs are an exciting group of materials used for adsorption, Forster (2014) addressed the question of whether they were better sorbents than zeolites and concluded that zeolites were more robust and less expensive (Forster, 2014). Moreover, MOF-5 was investigated for noble gas uptake and had a xenon uptake of 27 wt % at atmospheric pressure and room temperature, which is half that of commercial activated carbon at the same pressure and temperature (Kukulka et al., 2019). Results from experiments performed with pellets of commercially available HKUST-1 showed the preferential adsorption of xenon over krypton. However, the xenon capacity (3.18 mol/kg) was still lower than that of the benchmark activated carbon (3.72 mol/kg). Furthermore, the selectivities measured for three gas compositions (i.e., xenon/krypton = 20/80 v/v, 50/50 v/v, 80/20 v/v) were consistently lower than those for activated carbon (Banerjee, 2014).

In conclusion, MOFs are promising materials for the separation of xenon from noble gas mixtures, but so far they are not well established for real-world applications, and they are still a relatively new research area with only a few MOFs having been studied to date (Banerjee et al., 2014). The main challenge that remains in the separation of Xe by the adsorption method is the inefficiency of the technology in the separation of low concentration gases.

2.2.3 Separation of noble gases using gas hydrate technology

2.2.3.1 Definition

Gas hydrates are crystalline compounds made up of water molecules that form cages inside of which guest molecules (former gas) are trapped (Sloan and Koh, 2008, Carroll, 2014). Figure 2.4 shows a gas hydrate crystal.

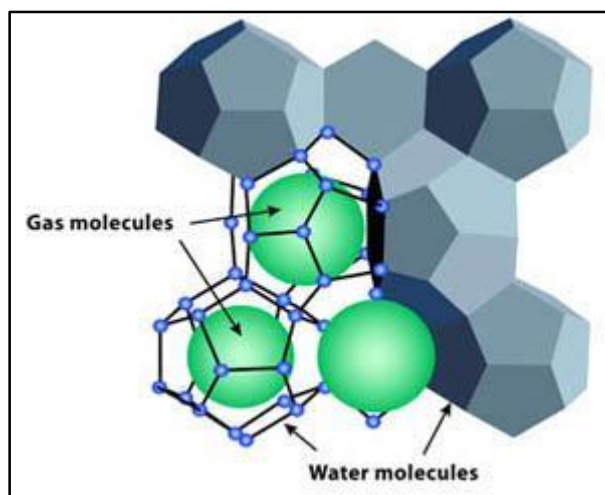


Figure 2.4: Gas hydrate crystal structure (MIDAS Consortium, 2011).

The cages are stabilized by water molecules which connected through hydrogen bonds. The three-dimensional arrangement of the cages leads to various nano-porous ice-like structures depending on the chemical nature of the encapsulated guest molecules as well as the conditions of temperature and pressure. Depending on the atomic diameters of the guest molecules in comparison with the hydrate structure formed, one component is trapped inside the cage structure whilst the other is not. These hydrate structures can form with various host molecules and take on different types of structures. The hydrogen-bonded water network that makes up the framework for the clathrate is responsible for the stability of these clathrates. These gas hydrate structures form under favourable conditions of high pressure and low temperature (He et al., 2017). Gas hydrates have the main advantage of being able to form at temperatures above the freezing point of water. Former gases used to form gas hydrates are usually hydrogen (H_2), methane (CH_4), sulphur dioxide (SO_2), carbon dioxide (CO_2), nitrogen (N_2), hydrogen sulphide (H_2S), ethane (C_2H_6), propane (C_3H_8), iso-butane ($i-C_4H_{10}$), ethylene (C_2H_4) and propylene (C_3H_6) (Xu and Li, 2014). These gas molecules are small enough to form hydrates (Carroll, 2014).

The most common hydrate structures are sI, sII and sH. These structures differ on the number of water molecules that make up the cage, the size of the guest molecules and their properties. The sI hydrate unit cell consists of 46 water molecules and forms two 12-sided polyhedron with a pentagon for each face (5^{12}) and six $5^{12}6^2$ cages in one unit cell. The sII structure contains 136 molecules of water and forms sixteen 5^{12} and eight $5^{12}6^4$ cages in one

unit cell, and the sH contains 36 water molecules and form three 5^{12} , two $4^35^66^3$, and one $5^{12}6^8$ cages in one unit cell (Sloan and Koh, 2008). The summary of the structures and cavities is well represented in Figure 2.5.

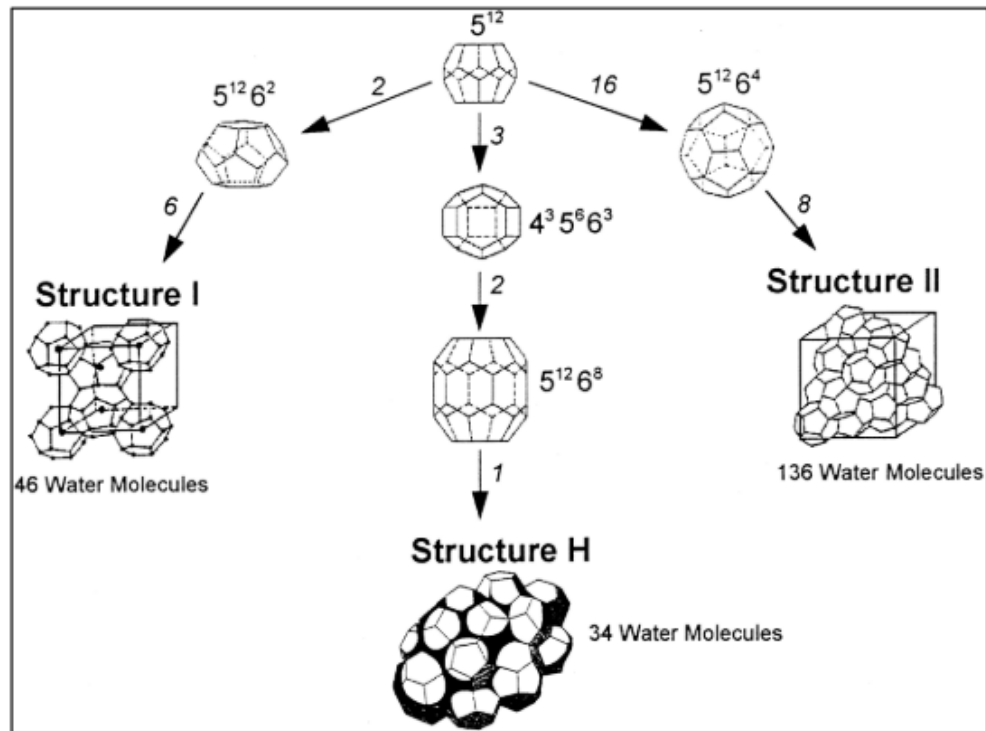


Figure 2.5: Hydrate structures (extracted from (Khokhar et al., 1998)).

2.2.3.2 Gas hydrates applications

Hydrate based separation has been proposed and studied for application in many fields including, methane recovery and storage (Zang and Liang, 2018), CO₂ capture and storage (Belandria et al., 2012, Park et al., 2013), water treatment and desalination (Wang et al., 2013), refrigeration (Hashemi, 2015), separation processes including noble gas separation and juice concentration in food technology amongst other areas of study (Babaei, 2015, Eslamimanesh et al., 2012, Zhao et al., 2016, Doubra, 2020).

2.2.3.3 Principles of hydrate-based gas separation

No alternative separation technique has gone beyond the pilot plant scale as researchers continue to explore technologies such as the hydrate-based technology as alternatives to the

energy-intensive cryogenic distillation. A mixture containing at least one hydrate former can be separated by exploiting the difference in hydrate formation conditions between its components (Tumba, 2019). Separation of gas mixtures using gas hydrate technology exploits the selective encapsulation of gases between the vapour and hydrate phases as one component is trapped in the hydrate phase and the other is not (Zhao et al., 2016). The stability of the hydrate cage formed differs according to the type of guest molecule. Some molecules form more stable hydrate cages than others; thus, some gases are encapsulated more in the hydrate phase than others. The concentration of the gas with low encapsulation will then increase in the gaseous phase. Sloan and Koh (2008) showed that water might not wholly transform into hydrate in the absence of vigorous agitation; hence, agitation is an essential part of hydrate formation and dissociation systems.

An appropriate adjustment of pressure and temperature can lead to the partitioning of a component between the hydrate and the fluid phases, which is favourable to its recovery. The feed stream is successively compressed and cooled to achieve appropriate conditions for hydrate formation in a reactor. The hydrate phase is separated and then dissociated in order to recover the product gas, whereas water is recycled through the process. Figure 2.4 illustrates the separation of a gas mixture using gas hydrates. It shows the separation of a $\text{CHF}_3 + \text{N}_2$ by selective encapsulation of CHF_3 from the mixture (Kim et al., 2017).

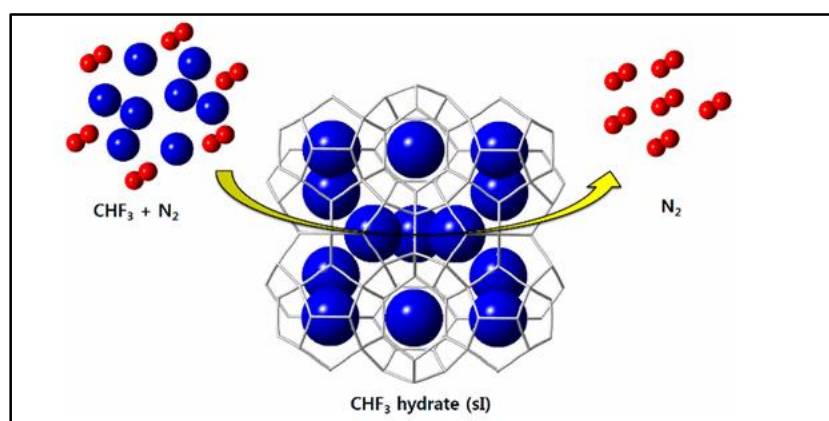


Figure 2.6: Separation of a CHF_3 and N_2 mixture to individual components using hydrate technology (extracted from (Kim et al., 2017)).

2.2.3.4 Separation of gas mixtures using gas hydrate technology

There is a lot of ongoing research and experimental studies in the open literature about the separation of gas mixtures using gas hydrates. Mixtures with two or more gas components can be separated using gas hydrates by selective encapsulation into hydrate cavities. Belandria et al. (2012) amongst many other researchers, conducted studies on the separation of carbon dioxide from binary mixtures using gas hydrate technology (Belandria et al., 2012, Wang et al., 2017). Eslamimanesh et al. (2012), Babu et al. (2015), Zang and Liang (2018) and many other researchers reported on various successful studies that focused on the separation of carbon dioxide from binary mixtures containing carbon dioxide (Eslamimanesh et al., 2012, Babu et al., 2015, Zang and Liang, 2018). Sun et al. (2015) experimentally recovered N_2 and H_2 from a $N_2 + H_2 + CH_4$ mixture using multiple hydrate formation and separation stages. The study also investigated the effect of pressure, temperature and gas flow rate on the separation efficiency. The experimental procedure followed by Sun et al. (2015) is relevant to this study as it informs on the procedure that was observed in this study. Other researchers, Tumba (2015), Zang and Liang (2018) and Liu et al. (2019), conducted studies on the separation of gas mixtures with three or more gas components, and these studies are vital to this current study. Of importance is the compositional analysis that they performed on the gas mixtures before and after each hydrate formation and dissociation stage (Tumba, 2015, Zang and Liang, 2018, Liu et al., 2019).

2.2.3.5 Application of gas hydrates in the separation of noble gas mixtures

This study is concerned with the separation of noble gas mixtures using gas hydrate technology. There is limited research on the separation of noble gas mixtures using gas hydrate technology. The studies conducted on separation of noble gases by Vorotyntsev and Malyshev (2011), Sergeeva et al. (2019) and Babaee et al. (2020) are relevant to this study (Vorotyntsev and Malyshev, 2011, Sergeeva et al., 2019, Babaee et al., 2020). Vorotyntsev and Malyshev (2011) developed a model to calculate the separation coefficients for $Ar + Kr + Xe$ mixtures. They found that the separation coefficient for xenon is 65 times greater than that for krypton and 400 times higher than that for argon. Their results showed that a mixture with 33% Xe, 34% Ar and 33% Kr can be concentrated to produced a mixture with 97% Xe, 3.9% Kr and 0.1% Ar. Babaee et al. (2020) perfomed studies on the separation of binary mixtures of xenon

+ argon and xenon + krypton and the results obtained demonstrated that xenon can be concentrated from the binary mixtures she studied.

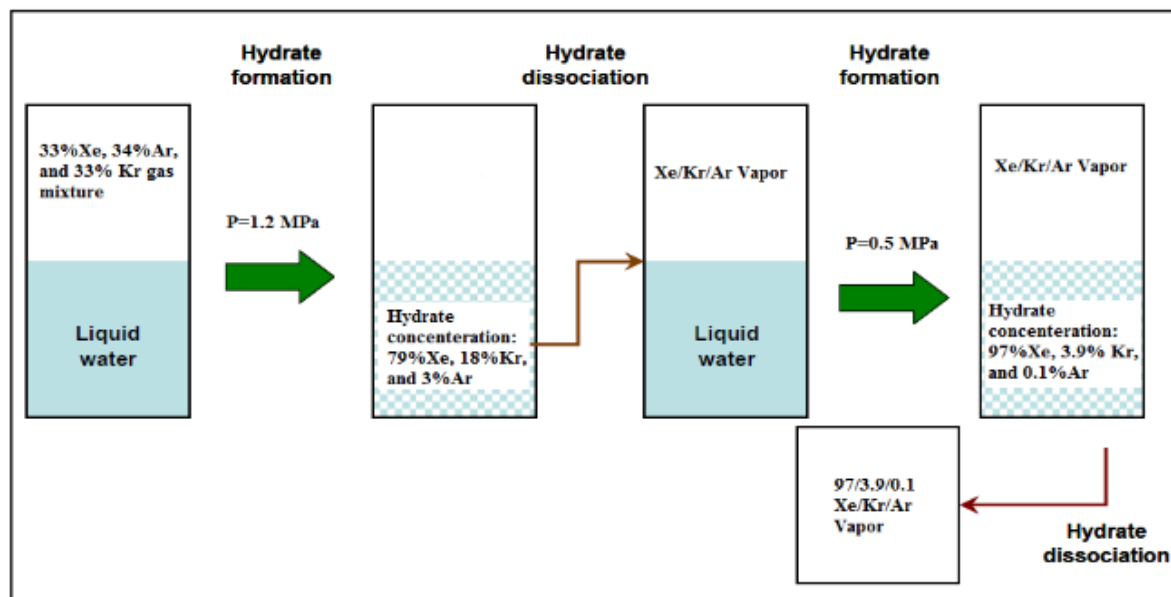


Figure 2.7: A schematic diagram of the 2 stage xenon separation from the mixture of Ar, Kr, Xe using gas hydrate method (Vorotyntsev and Malyshev, 2011) (extracted from (Babaei, 2015)).

In order to design a practical separation process, experimental hydrate equilibrium and compositional data were needed in addition to the study conducted by Vorotyntsev and Malyshev (2011). Such data would be vital in designing the process and determining the number of stages practically needed to achieve the level of separation that Vorotyntsev and Malyshev, (2011) achieved by calculation.

Sergeeva et al. (2019) simulated the recovery of xenon from $\text{CH}_4 + \text{H}_2\text{S} + \text{CO}_2 + \text{Xe}$ mixtures using multiple hydrate formation and dissociation stages (Sergeeva et al., 2019). Results from their simulation showed that as the number of separation stages increases to more than two, the concentration effect of xenon decreases, and this is a very important observation in the application of the technology for separation and purification of gas mixtures using multiple hydrate stages. Sergeeva et al. (2019) also investigated the effects of the gas hydrate distribution coefficient, concentrations, temperature and pressure on the efficiency of separation. Among other important results, they discovered that increasing temperature and pressure leads to a decrease in the Xe gas hydrate distribution coefficient.

Babaei (2015) investigated the promoting effect of hydrate formers, TBAB and SDS, on the rate of hydrate formation for Ar/Xe/Kr/CF₄ and hydrate dissociation equilibria. Her results indicated that an increase in TBAB concentration led to an increase in the equilibrium temperature conditions as well as the rate of hydrate formation. Babaei et al. (2020) conducted experiments to separate xenon from Xe + Ar mixtures. The experimental procedure used by Babaei et al. (2020) informed the procedure used in this work. In their study, the hydrate dissociation conditions for the system of Ar + Xe + water were experimentally measured and various mixtures of Ar, and Xe were studied. The compositions of the gas phase in equilibrium with gas hydrate and aqueous phase were experimentally measured by gas chromatography technique. A material balance approach based on Newton numerical method (Constantinides and Mostoufi, 1999) accompanying the differential evaluation optimization technique (DE) (Price, 2013) was applied for determining the compositions of the vapour, hydrate, and aqueous phases. According to their study, using one stage of the hydrate formation, the composition of Xe can be increased to more than 0.97-mole fraction. The calculated separation factor of Xe for the different conditions of temperatures and pressures was more than 50. The results of Babaei et al.'s study demonstrated that gas hydrate technology has a high capability for the separation of Xe from the mixture of Ar and Xe.

The use of hydrate technology for the separation of Xe from the Ar + Xe + Kr ternary mixtures requires extensive studies to determine the feasibility of the process. Therefore, this study continued the work performed by Babaei (2015) and Babaei et al. (2020) and aims to give further insights through assessing the performance of gas hydrate-based separation for Ar + Xe + Kr gas mixtures.

A pressure–composition phase diagram for the gas mixture system as the one shown in Figure 2.8 is required to assess the possibility of separation via gas hydrates and determine the number of separation stages to achieve a specific composition. In Fig 2.8, Tumba (2015) used the McCabe-Thiele approach to determine the number of equilibrium stages required to increase the concentration of 5 mol% ethyne or propene to 95 mol% (Tumba, 2015). As such, equilibrium concentrations in the vapour and hydrate phases were measured.

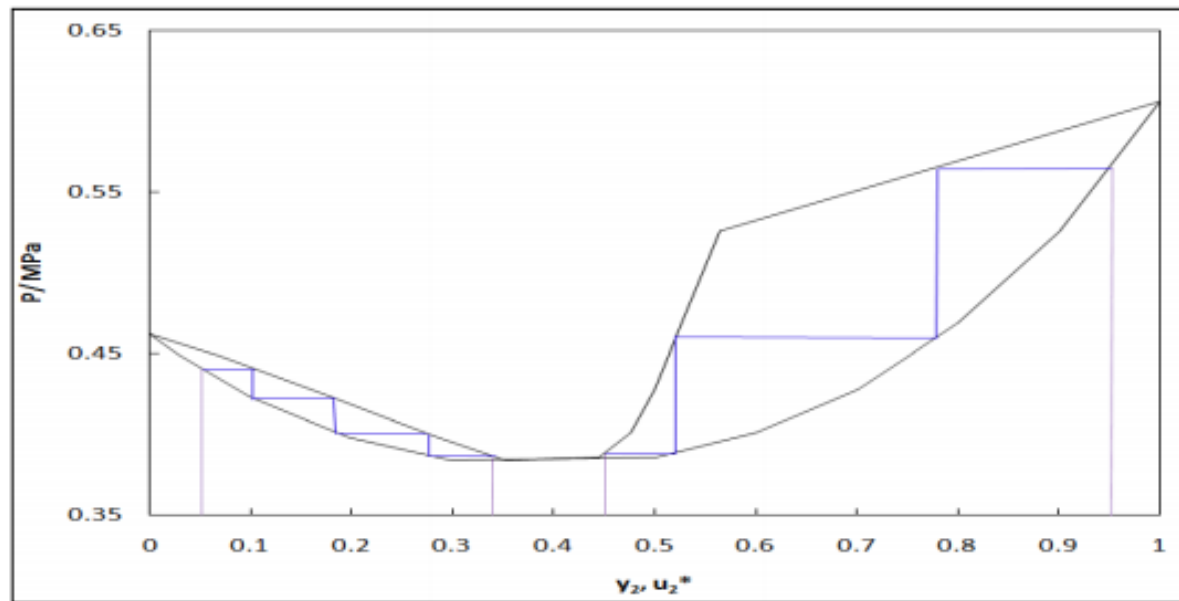


Figure 2.8: Hydrate pressure-composition graph for mixtures depending on feed conditions (extracted from (Tumba, 2015)).

Thermodynamic equilibrium data are also very important as they inform on the conditions for gas hydrate formation and dissociation. The pressure and temperature conditions for hydrate to form, and the final hydrate dissociation point (the pressure and temperature conditions for complete release of gas from the hydrate phase), are important parameters in understanding gas hydrate-based gas separation. Reviewed studies have reported such data for the systems they studied, this study will also report on such data for the system of Xe + Ar + Kr + water.

In the pursuit to increase the efficiency of the gas hydrate technology, Vorotyntsev et al. (2016) proposed a hybrid method in which gas-hydrate crystallization is combined with membrane gas separation in the same module. The membrane allowed the elimination of the admixture accumulated in the crystallizer, which inhibits its concentration and reduces the purification efficiency. This improved the efficiency of separation by approximately 10 times without sacrificing the yield (Vorotyntsev et al., 2016).

2.3 Thermodynamic modelling

Thermodynamic modelling is important in predicting hydrate equilibrium conditions. This section presents the fundamentals of the thermodynamic model that was applied in this study to predict the gas hydrate phase equilibria for the ternary mixture of (Xe + Kr + Ar).

In the phases; liquid, vapour, and hydrate, the equality of water fugacity was used as the criterion for equilibrium conditions (Mohammadi et al., 2005, Babaei & Hashemi, 2012, Javanmardi et al., 2012):

$$f_w^v = f_w^l = f_w^H \quad (2.1)$$

where f_w represents the fugacity of water and v , l , and H represent the vapour, liquid, and hydrate phases, respectively. The solid solution theory of van der Waals and Platteeuw was used to model the gas hydrate phase in the following equation (van der Waals and Platteeuw, 1959):

$$f_w^H = f_w^\beta \exp\left(-\frac{\Delta\mu_w^{\beta-H}}{RT}\right) \quad (2.2)$$

where f_w^H and f_w^β represent the fugacity of water in the hydrate phase and the empty hydrate lattice, respectively. R is the universal gas constant, and T is the system temperature. $\Delta\mu_w^{\beta-H}$, the water chemical potential difference between the empty hydrate lattice and the hydrate phase is defined as follow:

$$\Delta\mu_w^{\beta-H} = RT \sum_m \bar{\nu}_m \ln\left(1 + \sum_j C_{jm} f_j\right) \quad (2.3)$$

In this equation, $\bar{\nu}_m$ represents the number of cavities of type m per water molecule in the unit hydrate cell, and f_j represents the fugacity of the hydrate former j . C_{jm} is the Langmuir constant of hydrate former j in the m cavity which can be calculated was assessed using the Lennard-Jones Devonshire theory, and the Kihara potential function (Babaei, 2019).

The fugacity of water in the empty hydrate lattice, f_w^β was calculated using the equation:

$$f_w^\beta = f_w^L \exp\left(\frac{\Delta\mu_w^{\beta-L}}{RT}\right) \quad (2.4)$$

where f_w^L is the fugacity of water in the liquid phase. In this study, the Valderrama modification of the Patel and Teja equation of state (VPT EoS) (Valderrama, 1990) along with non-density-dependent (NDD) mixing rule (Avlonitis et al., 1994) were used for estimation of the water and gas fugacities in the liquid and vapour phases. As reported in the previous work (Mohammadi et al., 2005, Javanmardi et al., 2012, Eslamimanesh et al., 2012) this combination of VPT EoS (Valderrama, 1990) and NDD mixing rules (Avlonitis et al., 1994) can describe the phase behaviour of systems containing water, and polar components, perfectly.

The water chemical potential difference between the empty hydrate lattice ($\Delta\mu_w^{\beta-L}$) is calculated as follow (Holder et al., 1980, Mohammadi et al., 2005):

$$\frac{\Delta\mu_w^{\beta-L}}{RT} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^T \frac{\Delta h_w^{\beta-L}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{\beta-L}}{RT} dP \quad (2.5)$$

where μ_w^β and μ_w^L are the chemical potentials of the empty hydrate lattice and pure water in the liquid state, respectively. $\Delta\mu_w^0$ represents the reference chemical potential difference for water between the empty hydrate lattice and the ice phase at 273.15 K. Additionally, P and T_0 respectively represent the equilibrium pressure and the absolute temperature of the system at the ice point. $\Delta v_w^{\beta-L}$ represents the volume difference between the empty hydrate lattice and liquid water whereas $\Delta h_w^{\beta-L}$ indicates the molar enthalpy difference between the empty hydrate lattice and liquid water. $\Delta h_w^{\beta-L}$ is calculated using the following equation (Holder et al., 1980, Mohammadi et al., 2005):

$$\Delta h_w^{\beta-L} = \Delta h_w^0 + \int_{T_0}^T \Delta C_{Pw} dT \quad (2.6)$$

where Δh_w^0 represents the enthalpy difference between the empty hydrate lattice and ice, at the ice point and zero pressure and ΔC_{Pw} shows the heat capacity difference between the empty hydrate lattice and the pure liquid water phase and can be determined by the following equation:

$$\Delta C_{pw} = -38.12 + 0.141(T - T_0) \quad (2.7)$$

The following objective function was minimised using the H-L_w-V (Hydrate-Vapour-Liquid) equilibrium data for pure Ar, Kr, and Xe in order to obtain the Kihara potential parameters for these two gases (Kihara, 1953):

$$f_w^H = f_w^\beta \exp\left(-\frac{\Delta\mu_w^{\beta-H}}{RT}\right) \quad (2.8)$$

where, NDP is the number of data points, and T_{exp} and T_{cal} show the experimental and calculated hydrate dissociation temperature. Table 2.3 reports the obtained Kihara parameters for Ar, and Xe hydrate as well as hydrate structures.

Table 2.3: Kihara potential parameters for Ar and Xe hydrates (Babaei, 2016).

Compound	α / Å	σ / Å	(ϵ/k) / K	Hydrate Structure
Ar	0.226	2.770	170.500	II
Kr	0.17	3.047	183.041	II
Xe	0.28	3.310	191.500	I

The absolute relative deviation in the model calculations was evaluated using the following equation:

$$ARD\% = \left(\left| T_{exp} - T_{cal} \right| / T_{exp} \right) \times 100. \quad (2.9)$$

2.3.1 Thermodynamic modelling for the calculation of the number of moles of water that formed hydrate

The number of molecules of the hydrate former per water molecules in the hydrate lattice is calculated using the following equation (Javanmardi & Moshfeghian, 2002):

$$F = \sum_{m=1}^2 \vartheta_m \theta_m \quad (2.10)$$

where ϑ_m is the ratio of the number of type m cavities to number of water molecules in the hydrate lattice and θ_m is the fraction of the type m cavities which is occupied by hydrate former molecules (Javanmardi & Moshfeghian, 2002). Summation over the two types of hydrate

structures (small and large) yields the number of the hydrate former molecules per water molecules in the hydrate lattice. According to the result of this study, which are presented in Chapter 5, the mixture of Ar, Kr, and Xe at this specific condition of temperature 272 K, pressure ranges of 0.63 – 4.29 MPa, and compositions 19 – 44 mol% Xe, forms hydrate structure of I with two small cavities and six large cavities.

Then Equation 2.10 is changed to the following equation for SI:

$$F = 2\theta_S + 6\theta_L \quad (2.11)$$

Where:

$$\theta_S = \sum_{j=1}^3 \theta_{j,S} \quad (2.12)$$

$$\theta_L = \sum_{j=1}^3 \theta_{j,L} \quad (2.13)$$

where, $\theta_{j,S}$ and $\theta_{j,L}$ are the fractional occupancy of the hydrate former j in the small and large cavities, respectively and can be calculated using the Langmuir adsorption theory, illustrated below:

$$\theta_{jm} = \frac{C_{jm}f_j}{1 + \sum_j C_{jm}f_j} \quad (2.14)$$

where, C_{jm} is the Langmuir constant of hydrate former j in the m cavity and f_j represents the fugacity of the hydrate former, Ar, Kr, and Xe. C_{jm} can be calculated using the Lennard-Jones Devonshire theory, and the Kihara potential function (Babaei, 2019). Table 2.3 reported the obtained Kihara parameters for Ar, Kr, and Xe hydrate.

In this study, the fugacities of the hydrate formers (f_j) is determined using the VPT EoS (Valderrama, 1990) with NDD mixing rules (Avlonitis et al., 1994). According to this calculations, the number of molecules of the hydrate former per water molecules in the hydrate lattice, F , is 7.707. The number of water molecules in the hydrate phase $n_{W,H}$ was determined using the equation:

$$n_{W,H} = \frac{n_{g,H} \times n_{W,SI}}{F} \quad (2.15)$$

where, $n_{g,H}$ is the total mole of gas in the hydrate phase, which is 0.008 in this work and $n_{W,SI}$ is the number of water molecules in a SI unit cell, which is 46. Results of this thermodynamic model are presented in Section 5.6.

In summary, various studies on the application of the various technologies for the separation and purification of Xe from noble gas mixtures have been reviewed, noting the advantages and disadvantages of each separation technology. Gas hydrate technology has shown to be an attractive alternative separation method because of its simplicity and operating temperatures. Various studies were reviewed that showed the successful application of gas hydrate in separating gas mixtures, including noble gas mixtures. More research still needs to be conducted as no separation technique based on gas hydrates has yet progressed beyond the pilot plant scale. The thermodynamic model that was applied in this study, was also presented in this chapter. The results of the model will be used to compare with experimental results and to predict for hydrate equilibrium conditions for the mixture of (Xe + Ar + Kr).

3

CHAPTER 3: REVIEW OF EXPERIMENTAL METHODS

Numerous laboratory-scale gas hydrate equipment have been developed over the years to investigate and measure hydrate formation and dissociation data. Modifications are sometimes made to suit the requirements of a particular study especially if the original setup is being used for a different system than the one it was originally intended for. The development and construction of the apparatus is as important as the data that is obtained from them. This chapter presents a review of the equipment used in laboratory-scale research on gas hydrates as well as the experimental methods used in this study.

The chapter begins by classifying the types of experimental methods used for hydrate measurements, followed by an overview of the published data for specific gas systems using hydrate technology.

3.1 Classification of experimental hydrate measurements

There exist different techniques for equilibrium measurement, which are classified into two categories. The first category is based on how equilibrium is attained (Raal et al., 1998):

1. Static methods: equilibrium is achieved by continuous mechanical agitation of the phases. This quickens the time for attaining equilibrium.
2. Dynamic methods: equilibrium is attained without mechanical agitation; one of the phases is circulated until equilibrium is achieved.

The second classification category is based on how equilibrium composition is attained (Raal et al., 1998). Under this classification category, there are:

- i. Synthetic methods: this is when mixture compositions are determined gravimetrically or by introducing known volumes of each component into the vessel.
- ii. Analytic methods: this is when the equilibrium mixture composition is determined by an analytical technique. Such analysis may be done by withdrawing samples of the mixtures and analyzing the sample using gas chromatography or in-situ analysis using gravimetric or spectroscopic methods.
- iii. Combined methods: both synthetic and analytic methods are applied in a single apparatus presenting the benefits of both methods. The system can be operated in either mode depending on the conditions of the system.

Belandria et al. (2012), asserts that the applicability of these methods depends on the system under investigation, properties to be measured and, required accuracy. In this study, both the analytic and synthetic methods were used with modern measuring devices to attain accurate results. An in-depth review of the equipment and methods for hydrate measurements will not be presented here, as the subject has been extensively reviewed by many authors. The reader is referred to the following sources for further information: (Ruffine et al., 2010, Koh et al., 2011, Belandria et al., 2012, Babaee, 2015, Hashemi, 2015, Tumba, 2015). However, it is useful to highlight the most popular techniques used for hydrate measurements and review the recently published work.

Publications of $H-L_w$ -V measurements involving mixed gas systems in the open literature are rare because the experiments are difficult, elaborate and expensive. Hydrate based gas separation is a relatively new technology, hence there is limited reported data in the open literature on the separation of mixtures with three or more components using the technology. Most of the present work on hydrate-based separation focuses on individual and binary gas systems. In this chapter, some of the published $H-L_w$ -V data for gas-gas systems since 2012 are summarised. Whilst published data on methane, hydrogen, carbon dioxide and other gases are relevant, this review is not intended to cover all the measured systems in existence. The review in this chapter only includes systems with two or more gas components involving the determination of equilibrium gas compositions, including systems with xenon, argon and krypton. To the best of the authors' knowledge, the separation of Ar + Kr + Xe mixtures has not been investigated to date. Thus, the review of the apparatus and procedure used for other

gas-gas mixture systems informed the choice of equipment and procedure for the Ar + Kr + Xe system.

3.1.1 Visual vs non-visual methods

One distinction between the most commonly used experimental methods using a static apparatus for hydrate equilibrium studies is based on whether visual and non-visual hydrate detection is used. Constant pressure (isobaric) and constant temperature (isothermal) methods are based on visual observation, whilst the isochoric method is based on the non-visual method. Visual observation of the hydrate formation and dissociation of crystals was successfully done at low pressures by Hammerschmidt in 1934 in a Pyrex tube flow apparatus and in 1937 by Deaton and Frost (Sloan & Koh, 2008).

The process described above requires visual monitoring of the hydrate crystals (at a constant temperature or pressure). It thus can only be used at temperatures above the freezing point of water to prevent mixing with ice crystals (Belandria et al., 2012). The equilibrium may take some time to attain. Alternatively, the hydrate equilibrium measurements may be carried out in a fixed volume cell with no need for visualization of the hydrate crystals that have been formed. Hydrate formation is determined by observing the variation of pressure as the temperature is reduced. When hydrate formation is complete, the pressure inside the cell stabilizes. No visual monitoring is required to determine the hydrate dissociation point.

3.2 Experimental H-L_w-V methods

Table 3.1 shows the different methods used in hydrate measurements and the methods used for detecting hydrate formation and dissociation. Isochoric data (P - x - z) is generally preferred for the hydrate formation measurement. Firstly, with respect to the time for measurements, P - x - z data can be measured more quickly because equilibrium can be established quickly after a change in temperature rather than after a change in pressure (Nelson, 2012). Secondly, it is easier to operate the equipment, as the temperature can easily be controlled using a temperature controller and temperature bath.

Table 3.1: Experimental techniques for equilibrium hydrate-liquid-vapour measurements.

Method	Technique	Method used to detect hydrate formation	Method used to detect hydrate dissociation
Isothermal	Visual	Temperature rise due to the heat produced at hydrate formation.	Visually observing the disappearance of hydrate crystals.
Isobaric	Visual	Sudden significant addition of fluid (gas or liquid) from an external reservoir.	Visually observing the disappearance of hydrate crystals.
Isochoric	Non-visual	Sharp decrease in the pressure inside the reactor.	The intersection point of the cooling and heating curves on a graph of pressure vs temperature.

3.2.2. Isochoric pressure search method

In isochoric experiments, reducing the system temperature may cause the formation of hydrates. Differential pressure and temperature changes are measured in a reactor of constant volume. For each gas mixture or hydrate forming gas loaded into the cell, the pressure is monitored as a function of changing temperature. The isochoric method does not require viewing of the cell contents to distinguish the final hydrate dissociation point. This method was applied in the experiments conducted in this study. A pressure-temperature diagram generated during the hydrate formation and dissociation conditions in the isochoric procedure is presented in Figure 3.1. Measurements commence with a mixture of water and gas at a pressure and temperature outside the hydrate stability zone, point A. The gradual cooling of the cell contents reaches the system to the hydrate formation conditions at which gas hydrate crystals start to form, encapsulating gas molecules inside them. This causes a rapid pressure drop as the gas enters the hydrate phase. At equilibrium between the hydrate, liquid and gas phases, the system pressure remains constant, at which the system temperature is gradually increased to dissociate the gas hydrate crystals. Heating of the system continues until all of the encapsulated gas is released from the crystals. The system pressure and temperature is then said to have reached equilibrium, known as the dissociation condition. According to Sloan and Koh (2008), the

hydrate equilibrium point/final dissociation point is considered as the intersection between the hydrate dissociation curve and the initial cooling curve (Sloan and Koh, 2008). If the cooling and heating curves do not intersect, the point where there is a sharp change of gradient of the heating curve is used, as the final dissociation point (Javanmardi et al., 2012, Tumba et al., 2013). This procedure was followed in determining the final dissociation point as shown in Figure 3.1, the heating and cooling curves obtained in this work for the CO₂ + water system.

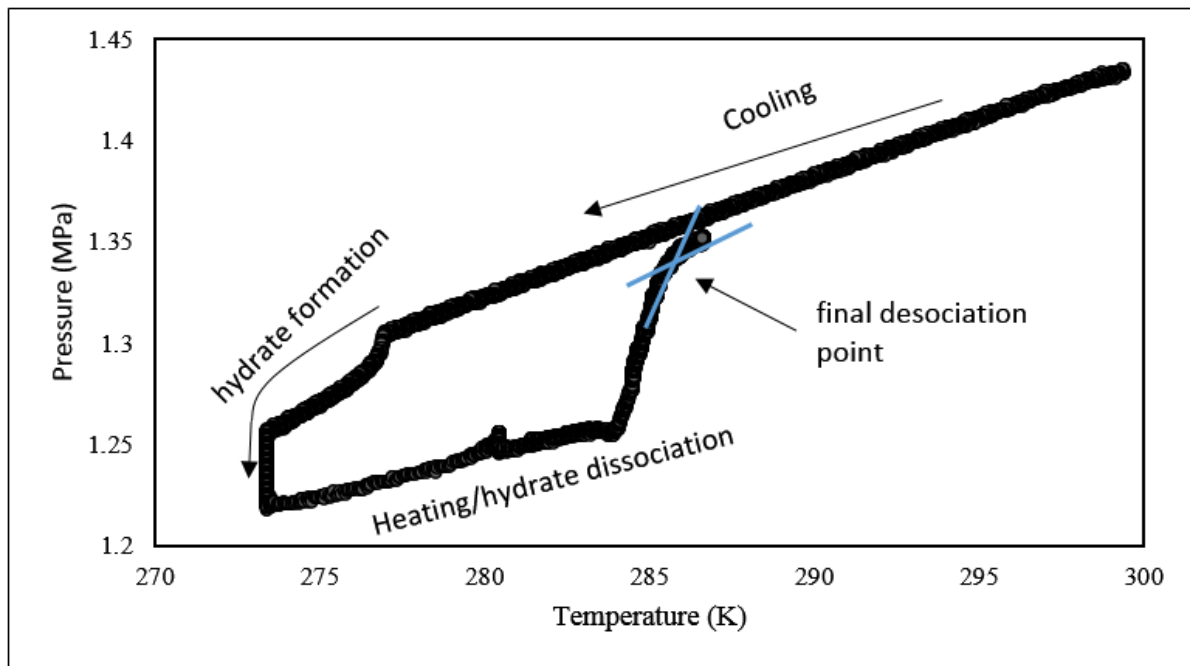


Figure 3.1: Final hydrate dissociation point from heating and cooling curves for the CO₂ + water system (From this work).

Table 3.2 summarises the reported data for gas-gas systems from the open literature from 2012 to date. The review focussed on systems that had gas mixtures with two or more gas components coupled with phase composition analysis. Included in the review is the study by Babaei et al. (2020) as this study is a continuation of their work.

Table 3.2: A brief review of experimental H-L-V data published on gas-gas mixture separation¹

Author(s)	System studied	Method	T/ K	P/ MPa	Comments
(Belandria et al., 2012)	CO ₂ + CH ₄ + H ₂ O	Isochoric pressure search	275 to 289	1.51 to 7.19	Separation using hydrate technology was effective. A maximum CO ₂ concentration of 87.7mol% was obtained in the hydrate phase from a feed gas with 18.1 mol% of CO ₂ .
(Zhong et al., 2015)	CO ₂ + CH ₄ + H ₂ O	Isochoric pressure search	277.15	2.69	Recovery of 58.1% for CO ₂ , was achieved in the hydrate phase after one hydrate stage.
(Tumba, 2015)	Ethane + Ethene + H ₂ O	Isochoric pressure search	273.7 to 288.3	0.522 to 3.191	Distribution coefficients and recovery coefficients calculated. It was found that the hydrate-based process is not the favourable process for separation of the gas mixture.
(Tumba, 2015)	Ethyne + propane + H ₂ O	Isochoric pressure search	275.6 to 283.4	0.392 to 1.827	Separation using hydrate technology was found to only be possible and effective for feeds containing more than 65 mol% propane. The process required seven equilibrium stages to increase concentration to 99 mol%.

Table 3.2 continued.

Author(s)	System studied	Method	T/ K	P/ MPa	Comments
(Sun et al., 2015)	$\text{N}_2 + \text{H}_2 + \text{CH}_4 + \text{H}_2\text{O}$	Isobaric visual	283.15 to 284.15	0.2 to 8.0	Separation was done over 2 continuous hydrate stages. Recovery above 90% was achieved. The concentration of 95.28 mol % ($\text{H}_2 + \text{N}_2$) was increased from 91.8 mol %.
(Sabil & Partoon, 2018)	$\text{H}_2 + \text{CO}_2 + \text{H}_2\text{O}$	Isobaric visual	277.4 to 285.8	5	The concentration of H_2 increased from 0.6 in feed to 0.8 in the hydrate phase. The concentration of CO_2 obtained in the hydrate phase with no hydrate former was 1.
(Zang & Liang, 2018)	$\text{CH}_4 + \text{CO}_2 + \text{N}_2 + \text{H}_2\text{O}$	Isochoric pressure search	273 to 280	4.0 to 8.0	The maximum CH_4 recovery factor was 1.42 at 4 MPa and 277 K for a feed mixture with $\text{CH}_4 / \text{CO}_2 / \text{N}_2 = 50:40:10$.
(Liu et al., 2019)	$\text{BVG}^2 + \text{H}_2\text{O}$	Isobaric visual	274.15 to 280	0.5 to 2.0	The concentration of C_3 ($\text{C}_3\text{H}_8 + \text{C}_3\text{H}_6$) was increased from 59.98 mol % to 84.40 mol %.
(Babaei et al., 2020)	$\text{Xe} + \text{Ar} + \text{H}_2\text{O}$	Isochoric pressure search	274.1 to 298.1	0.4 to 8.0	The composition of Xe was increased to more than 0.97 mole fraction over one hydrate formation stage.

1. Review from 2012 to date.

2. BVG (a mixture of C_3H_8 , C_3H_6 , CH_6 , CO_2 , CH_4 , CO , N_2 , and H_2).

3.3 Equipment review

3.3.1 The equipment of Deaton and Frost (1937)

The static apparatus by Deaton and Frost (1937), shown in Figure 3.2, was used to perform experimental work on gas hydrates. Their equilibrium cell had a glass window where they could observe the inside of the cell. The cell was placed inside a thermo-regulated temperature bath. The flow of gas into and out of the cell was regulated using an installed valve system. Pressure and temperature measurements were made using thermocouples and pressure transducers. Agitation of the system was done using a system that rocked the cell on a horizontal axle. Hydrate formation and dissociation were observed through the glass window by the appearance or disappearance of the hydrate. Over the years, there have not been major changes to the procedure for hydrate measurements except changes that improved the operating pressure ranges and improvements that reduce experimental uncertainties. The significant disadvantage which still remains is the time required for hydrate formation under static conditions, which is still lengthy.

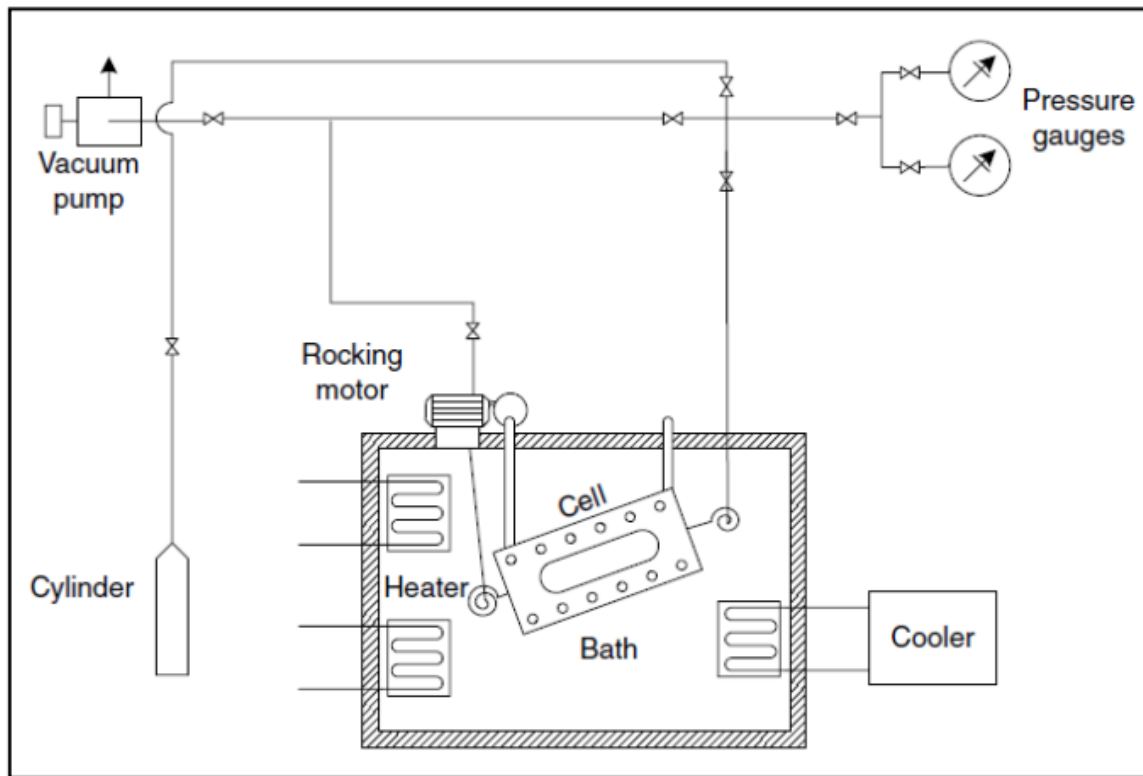


Figure 3.2: Apparatus for hydrate phase equilibrium measurements used by Deaton and Frost (1937) (extracted from (Sloan and Koh, 2008)).

Deaton and Frost (1937) 's apparatus is advantageous in that:

- i. The technique and experimental set-up is simple
- ii. It is applicable at any temperature and over a broad pressure range
- iii. It is suitable for single and multiple component systems
- iv. Compositions and amount of fluid samples can be changed easily
- v. It needs a small quantity of material
- vi. phase behaviour can be observed at high pressures

3.3.2 The Quartz Crystal Microbalance (QCM)

Another alternative method and equipment for measuring gas hydrate data is the Quartz Crystal Microbalance (QCM) shown in Figure 3.3 (Burgass et al., 2002, Mohammadi et al., 2003).

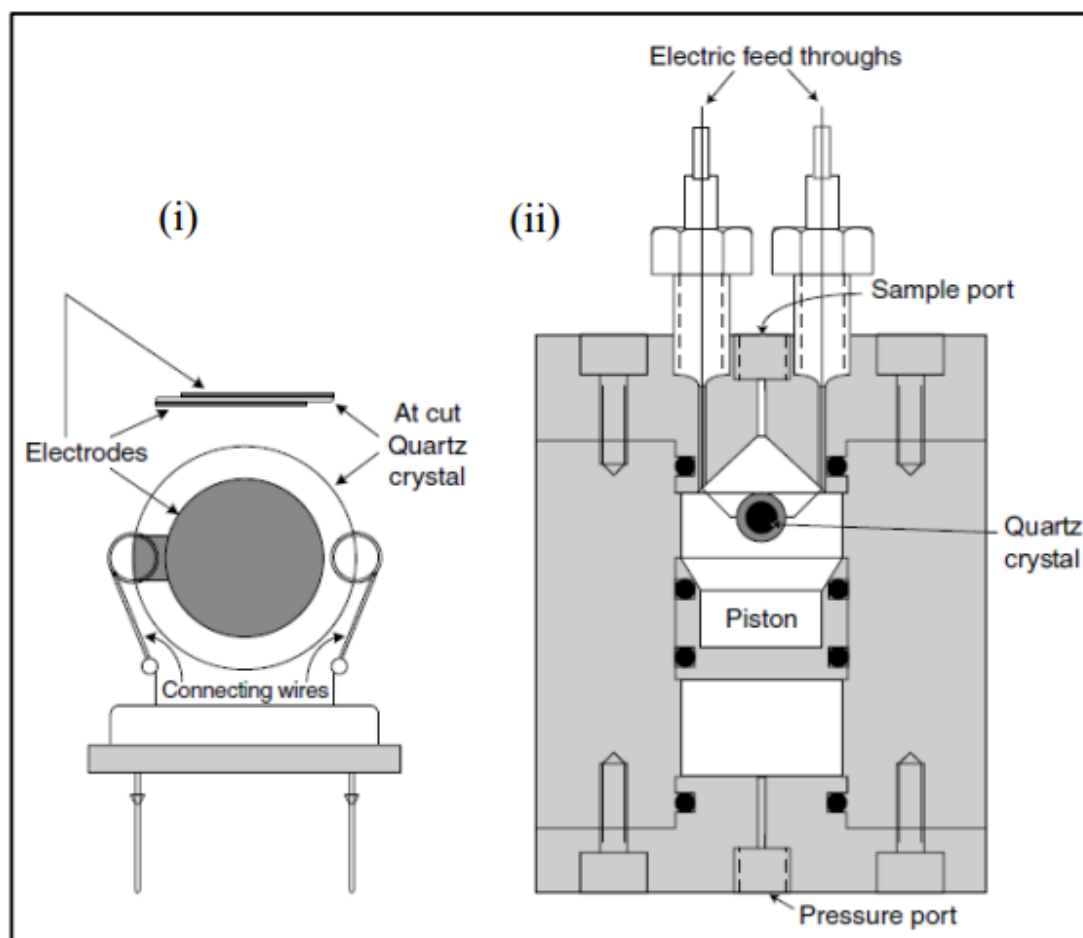


Figure 3.3: (i) The Quartz Crystal Microbalance (QCM). (ii) QCM inside a high-pressure equilibrium cell (Mohammadi et al., 2003).

The QCM was made up of a thin disk of quartz placed between two electrodes. When an electric current passed across the electrodes, the quartz disk then oscillated at a certain resonating frequency. Hydrate formation and dissociation were observed by a change in the resonance frequency as hydrates that would have formed adhered to or detached from the surface of the quartz crystal. A pressure transducer and thermocouple were used to measure the system pressure and temperature, respectively. The apparatus was advantageous in that the time taken to reach equilibrium at each temperature step (15 minutes) was significantly lower than that for conventional methods as the method of Deaton and Frost (1937) (Mohammadi et al., 2003). While the QCM approach was considered unfeasible because of the good contact that is needed between the surface of the quartz crystal and hydrates, Lee et al., (2012) demonstrated that it produces reasonable results by adjusting the droplet size, in particular, for fast hydrate application purposes (Sloan & Koh, 2008).

3.3.3 The gas hydrate apparatus of Tumba (2015)

Figure 3.4 shows the experimental setup used by (Tumba, 2015) who modified the static analytical high-pressure equipment used by Chen (2010). Tumba replaced the air bath with a liquid bath to increase temperature stability.

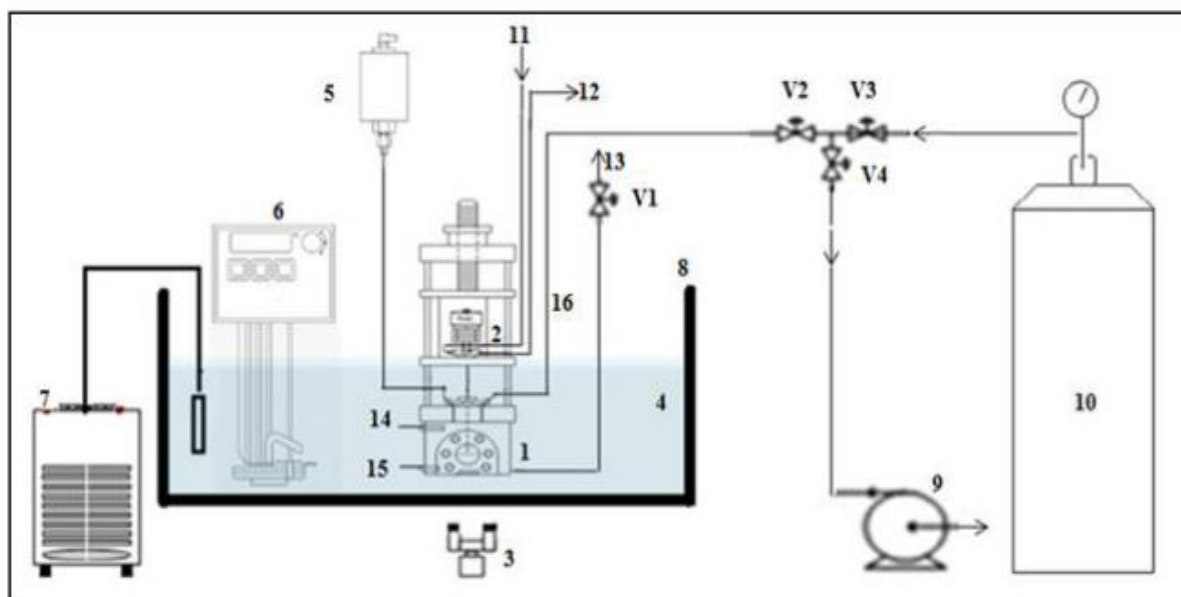


Figure 3.4: Schematic diagram of the apparatus used by Tumba (2015): (1) equilibrium cell; (2) RolsiTM sampler; (3) motor and magnet; (4) water/ ethylene glycol bath; (5) pressure transducer; (6) immersion temperature controller; (7) refrigeration unit; (8) acrylic tank; (9) vacuum pump; (10) gas cylinder; (11) RolsiTM inlet line from the GC; (12) RolsiTM outlet line to the GC injector; (13) drain line; (14) temperature probe in the upper flange; (15) temperature probe in the lower flange; (16) liquid and gas feeding line; and (V1 to V4) valves.

The equipment had an equilibrium cell with an internal volume of approximately 60 cm³, with two sapphire windows on the sides (15 mm thick and 33 mm in diameter). The equipment was advantageous in that even though the isochoric pressure search method (which does not need visual observation of the cell contents) was used for hydrate dissociation measurements the sapphire windows allowed for observation of the cell contents (Tumba, 2015). The windows could withstand pressures up to 20 MPa thus limiting experiments beyond pressures higher than 20 MPa. The equipment had a liquid temperature bath for control of temperature inside the equilibrium cell. The experimental setup of Tumba (2015) had an advantage as it could be used to analyse the molar composition of different phases inside the

equilibrium cell by adjusting the position of the Rolsi™ to move the capillary and target a specific phase inside the cell. Helium gas was used as the gas sample carrier. A sample of the phases was taken five times each in 30-minute intervals. Tumba (2015) reported uncertainties of ± 0.1 K, ± 0.007 MPa and ± 0.01 for temperature, pressure and composition, respectively.

3.3.4 The gas hydrate apparatus of Belandria (2012)

Figure 3.5 shows the apparatus used by (Belandria, 2012) who performed simultaneous hydrate equilibrium measurements and compositional analysis.

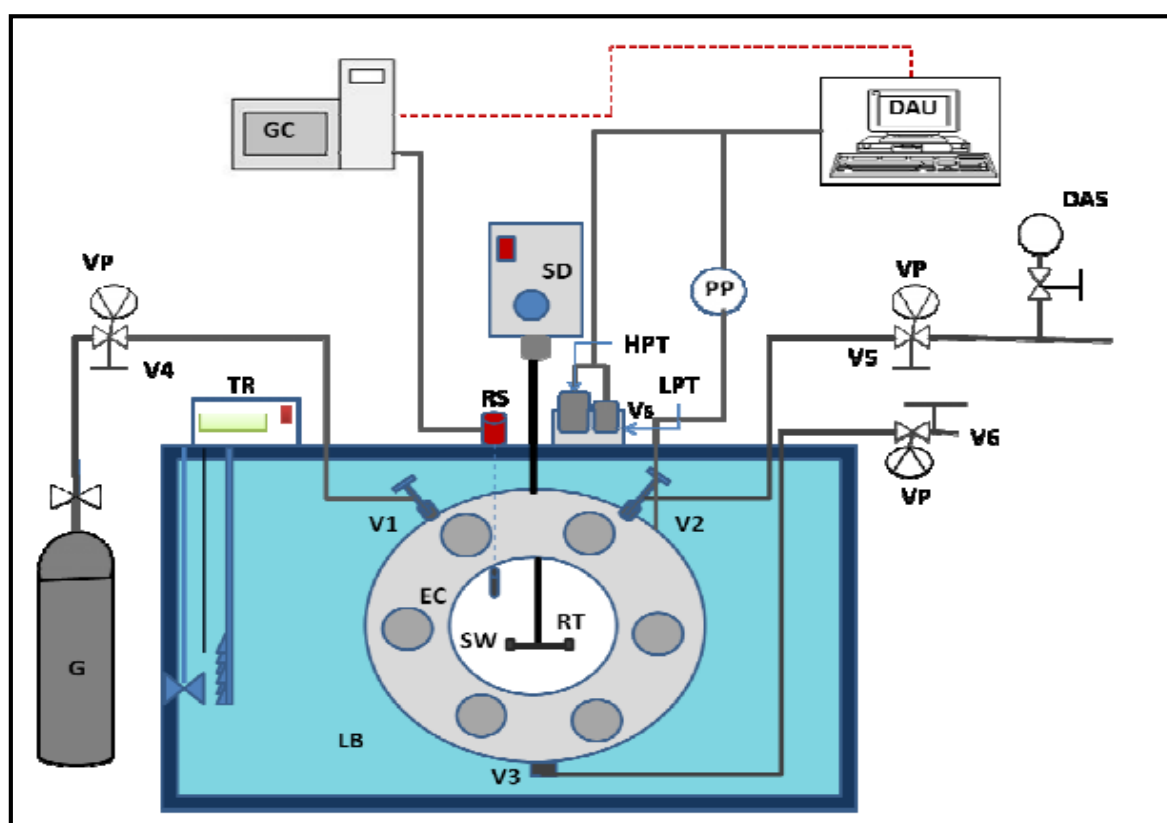


Figure 3.5: Schematic flow diagram of the apparatus used by (Belandria, 2012). DAS: degassed aqueous solution; DAU: data acquisition unit; EC: equilibrium cell; G: Gas cylinder; GC: gas chromatograph; HPT: high pressure transducer; LB: liquid bath; LPT: low pressure transducer; PP: platinum probe; RS: ROLSI™ sampler; RT: Rushton turbine; SD: stirring device; SW: sapphire windows, TR: temperature regulator; V1, V2, V4, V5: feeding valves; V3, V6: purge valves; VP: vacuum pump; Vs: isolation valve for LPT; WP: high pressure pump.

The capability of the apparatus to simultaneously perform hydrate equilibrium and compositional analysis measurements was a major advantage. The experimental setup is made up of four major components; a SS316 equilibrium cell of volume 210 cm³, a sample supplying system, a composition analysing system, and a pressure and temperature measurement system. The apparatus was also advantageous in that it was suitable for experimentation with corrosive fluids and at high pressures (up to 60 MPa). Gas mixtures were prepared inside the equilibrium cell and analysed by an online gas chromatograph. Samples were taken using an electromagnetic RolsiTM sampler. The isochoric pressure search method was used for hydrate equilibrium studies, which did not require viewing of the cell contents. The equilibrium cell presented greater advantage as it had two sapphire windows located at the front and the back of the cell, allowing the presence of gas hydrates and phase behaviour occurring inside the equilibrium cell to be visually observed. The system operated for temperatures from 233 to 373 K. Gas mixture compositions were measured using the gas chromatography detector and verified by PVT calculations, thus the mixture preparation procedure was very reliable.

3.3.5 The two stage hydrate apparatus of Sun et al. (2015)

Figure 3.6 shows the schematic of the apparatus used by Sun et al. (2015) in the continuous separation of hydrogen and nitrogen from tail gases of varying composition of N₂ + H₂ + CH₄ gas mixtures.

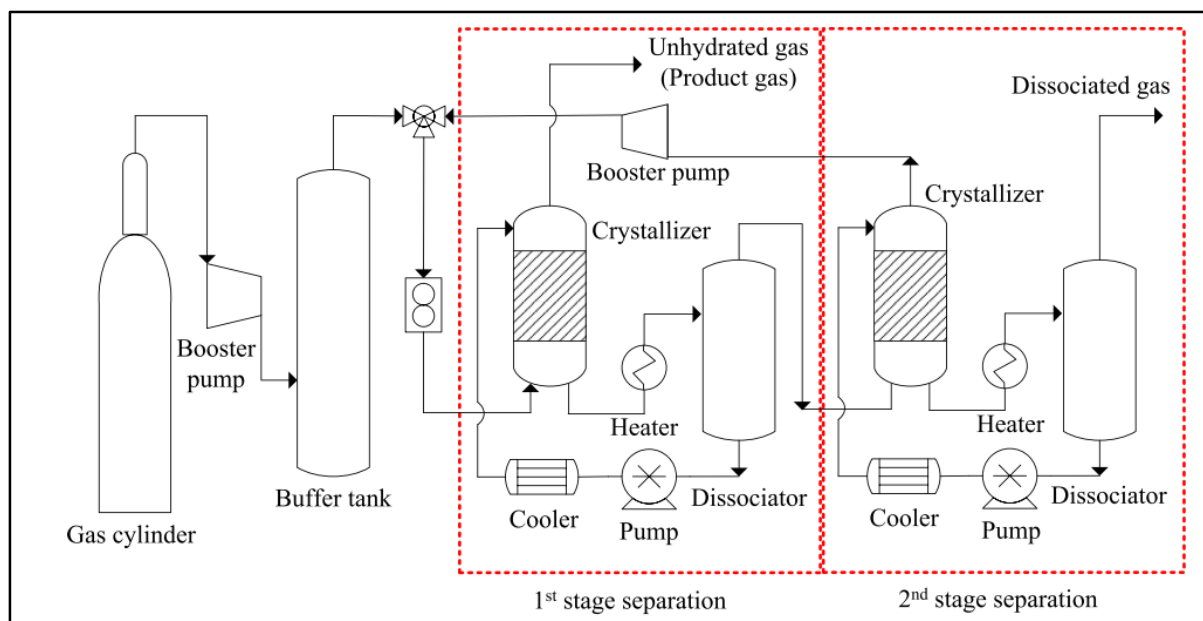


Figure 3.6: Schematic diagram of the two-stage continuous hydrate based separation of $N_2/H_2/CH_4$ used by Sun et al. (Extracted from (Sun et al., 2015)).

The apparatus consisted of a gas inflow system and two sets of hydrate separation stages. Each hydrate separation stage had a hydrate formation and dissociation system and a liquid circulation system. The gas booster, the inlet gas flow meter and gas cylinders made up the gas inflow system. The hydrate formation and dissociation system was composed of a visual crystallizer vessel with a volume of 28 L, a stirrer inside the cell, temperature and pressure measurements transducers, the hydrate dissociator and heater. A centrifugal pump was used to circulate the liquid from the crystallizer to the hydrate dissociator and sending the water back to the crystallizer again for hydrate formation.

The product from the first stage was directly fed into the second stage as feed; the gas dissociated from the hydrate phase of the first stage was fed the into the second stage crystalliser. The unhydrated gas from the second stage was fed back to the first stage, ensuring that maximum amount of the desired component was captured. For each hydrate separation stage, the authors reported the measured quantities of gas supplied, the molar flowrate of unhydrated gas and the molar flowrate of hydrated gas using wet-type flow meters to calculate the gas recovery. Samples of the gases collected from the crystallizer (unhydrated gas in vapour phase) and the dissociator (dissociated gas) were taken synchronously and analyzed by the gas

chromatography to determine the composition. The authors reported a pressure deviation of less than ± 0.01 MPa and a temperature deviation of ± 0.1 K in their measurements. The setup used by Sun et al. was advantageous in that it was continuous, also recovering the unhydrated gas from the second stage ensured the maximum recovery of the desired gas.

3.3.6 The apparatus of Liu et al. (2019)

Liu et al. (2019) separated C_3 ($C_3H_8 + C_3H_6$) from butyl alcohol–octyl alcohol vent gas, HBV (a mixture of C_3H_8 , C_3H_6 , CH_4 , CO_2 , CH_4 , CO , N_2 , and H_2) using gas hydrate technology. Figure 3.7 shows the apparatus used for the experimental work.

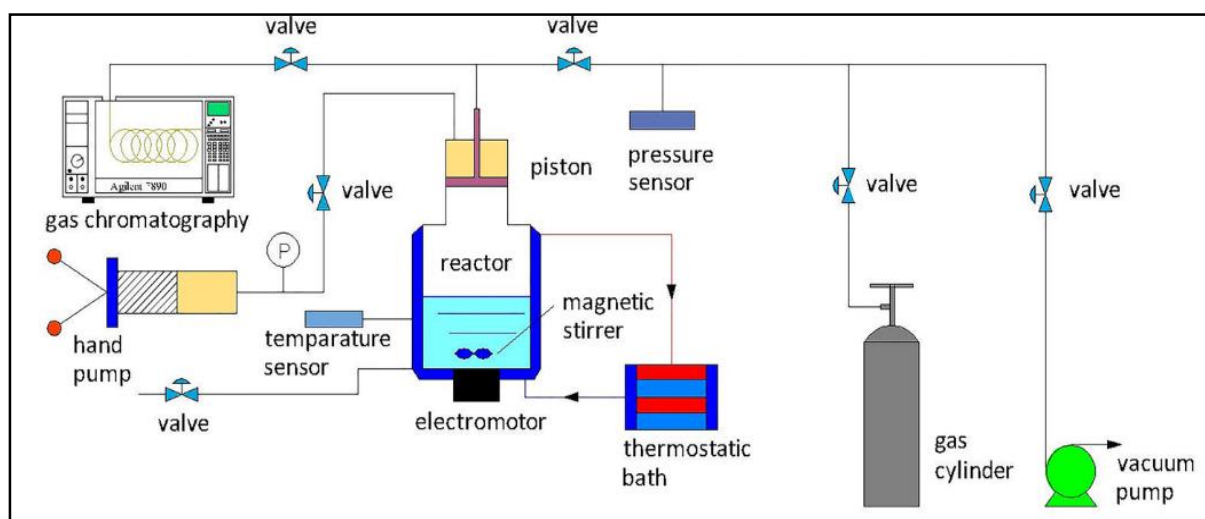


Figure 3.7: Experimental setup for hydrate based separation of C_3H_8 and C_3H_6 from HBV (extracted from (Liu et al., 2019)).

The apparatus consisted of a visual reactor, a thermostat, magnetic stirrer, hand pump and gas chromatography. The stainless-steel reactor cell had a maximum working pressure of 20 MPa and a working temperature of 223.15 K to 323.15 K. The pressure and temperature were measured using pressure and temperature sensors with measuring accuracy of ± 0.02 MPa and ± 0.1 K respectively. The cell was divided into two sections, with the upper part of the cell with a volume of 200 ml and the bottom part with a volume of 220 ml.

The authors used the isobaric, visual observation method for hydrate formation and dissociation measurements. The pressure in the cell decreased as hydrate formed, and the hand pump was used to keep the pressure constant. Samples of the vapour phase were taken until the pressure in the cell was constant for 4 - 6 hours showing that complete hydrate formation had occurred. The samples were analyzed using gas chromatography for composition. Before the vapour phase was released to the atmosphere, the temperature was decreased to 286.15 K to ensure the stability of the hydrate phase. The vapour phase was then released to the atmosphere. The temperature of the hydrate cell was increased to allow the hydrate crystals to decompose and samples of the decomposed gas were taken and analyzed using the gas chromatography for composition. A recovery yield of 80.19% was achieved for C₃ components (C₃H₈ + C₃H₆). Measurement uncertainties were not reported.

The high-pressure apparatus used by Babaee (2015) and Babaee et al. (2020) will be presented and discussed in Chapter 4 as this equipment was used for the measurements in this study.

In summary, this chapter presented a review of the experimental methods and equipment used in hydrate measurement. The key features of the equipment reviewed above were the hydrate reactor which varied in volume from 60 cm³ to 210 cm³. Most researchers used a temperature liquid bath for improved stability and control, a gas loading system, and high accuracy temperature and pressure measuring devices. The most commonly used experimental method was the non-visual isochoric pressure search method and the visual isobaric method, which used sapphire windows to observe the contents inside the equilibrium cell. Advantages and disadvantages of each experimental equipment and corresponding method were presented. Of particular interest was the use of the online RolsiTM sampler and gas chromatography in sampling and analyzing gas concentration in the hydrate and gaseous phases. The review highlighted the method that was used for sampling the hydrate phase, in releasing the vapour phase at equilibrium conditions and then dissociating the hydrate phase then sample and analyse the concentration of the gas released from the hydrate. Continuous agitation was also used in the experimental procedure as this quickens the time for hydrate formation and decrease total experimental time to a few hours. The review also highlighted a

method for continuous stepwise gas separation using the gas hydrate based technology. These concepts were applied in the experimental method developed in this study.

4

CHAPTER 4: EXPERIMENTAL METHOD

This chapter describes the features of the equipment used and the experimental procedures followed in calibrations, thermodynamic equilibrium study and compositional analysis. The equipment used in this study was also used by Babaei (2015) for her thermodynamic and kinetic studies for the hydrates of Xe, Ar, Kr and CH₄.

4.1 Equipment description

The schematic in Figure 4.1 shows the setup of the apparatus. The individual components in the setup are listed below. An in-depth description of the major components in the setup subsequently follows.

- 40 cm³ stainless steel equilibrium cell
- agitation system for the equilibrium cell contents
- WIKA (0-16 MPa) pressure transmitter
- two class A Pt-100 thermocouple thermometers (model REB)
- Rolsi™ sampling device
- TCD equipped Shimadzu 2014 gas chromatography with a Porapak type Q, packed column, of length 2.2 m
- Stainless steel temperature bath with dimensions 43 cm × 35 cm × 26 cm
- Cold finger (Polyscience® immersion probe cooler)
- Agilent data acquisition of model LXI Agilent 34972A

- 699 cm³ stainless steel (SS316L) gas mixing vessel
- 1.5 T scissors mechanical jack
- ISCO syringe pump model 260D
- Grant 200 temperature controller
- RV12 Edwards rotary vane vacuum pump.

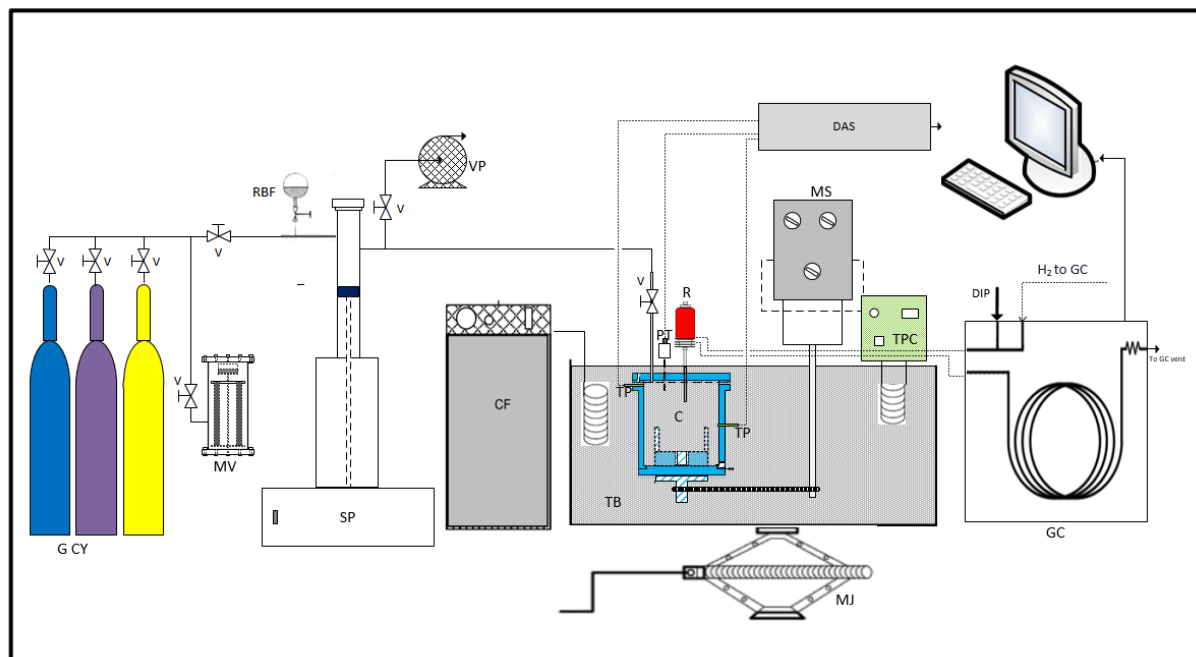


Figure 4.1: Schematic of the apparatus used in this study (This work). The equilibrium cell (C), cold finger (CF), data acquisition system (DAS), mechanical stirrer (MS), gas chromatography (GC), gas cylinders (GCY), gas mixing vessel (MV), mechanical jack (MJ), ROLSITM (R), pressure transmitter (PT), temperature bath (TB), temperature probe (TP), temperature programmable circulator (TPC), vacuum pump (VP), round bottom flask (RBF), syringe pump (SP), valves (V), Direct gas injection point (DIP).

4.1.1 The equilibrium cell

The hydrate formation and dissociation experiments were performed in a stainless steel 316 equilibrium cell used by Babaee (2015). The equilibrium cell, of dimensions 45 mm height and an internal diameter of 36 mm, and internal volume 52 ml had a maximum working pressure of 10 MPa. Figure 4.2 shows the schematic of the cell, and Photograph 4.1 shows a pictorial view of the equilibrium cell used in the study.

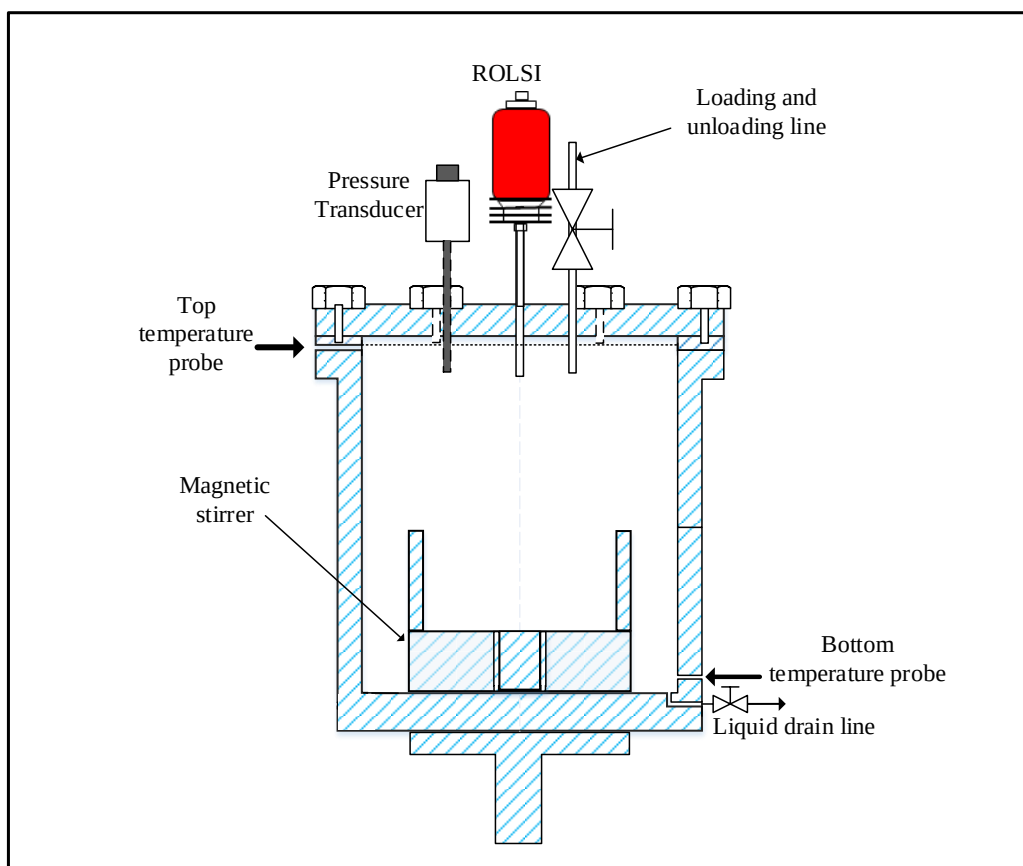
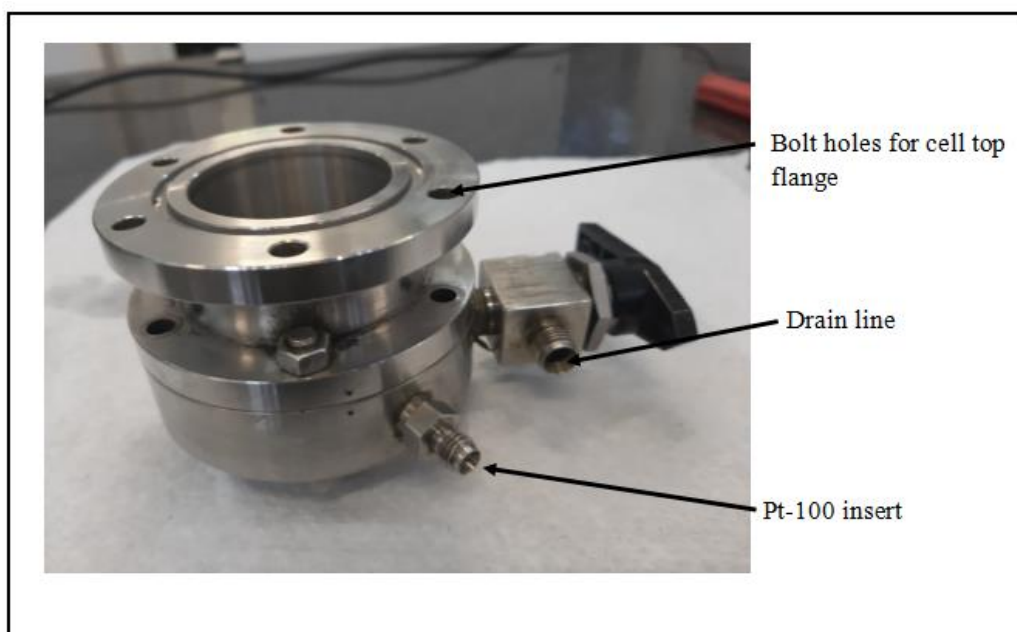


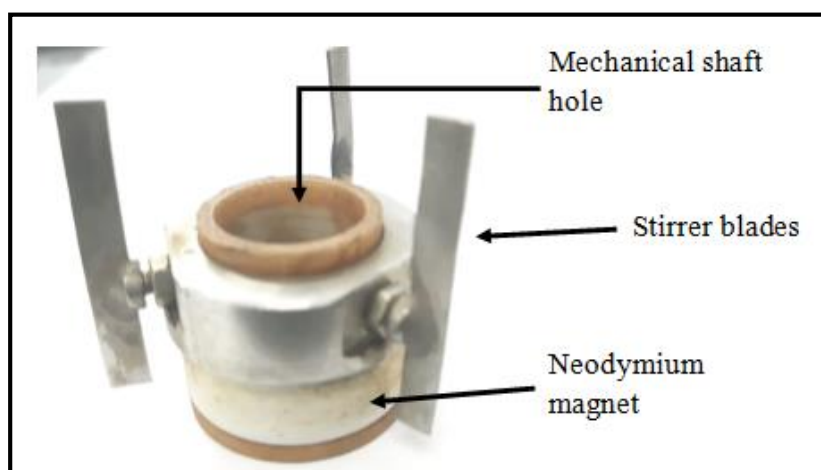
Figure 4.2: Schematic of the equilibrium cell (This work).



Photograph 4.1: The hydrate cell used in this work (This work).

4.1.2 The agitation system for the equilibrium cell

Stirring of the cell contents increases the rate of mass transfer between water and the vapour phase and increases the rate of hydrate formation significantly. The agitation system used in this work was made up of a Heidolph RZR 2041 motor (equipped with two gears of 40 - 400 rpm and 200 - 2000 rpm), a gear system connected to a shaft that had a strong magnet attached to it at its end and a stirring device placed inside the equilibrium cell. As the motor rotates, it turns the gear system, which in turn rotates the external magnet. As the external magnet rotates, the internal neodymium magnet also rotates due to magnetic attraction and thus rotates the stirring device. The stirring device had four blades and was gold-coated to reduce friction. Photograph 4.2 shows the stirring device used in the equilibrium cell. A speed of 180 rpm is suitable for adequate agitation of the equilibrium cell contents.



Photograph 4.2: Agitation device used inside the equilibrium cell (From this work).

4.1.3 Pressure and temperature measurement

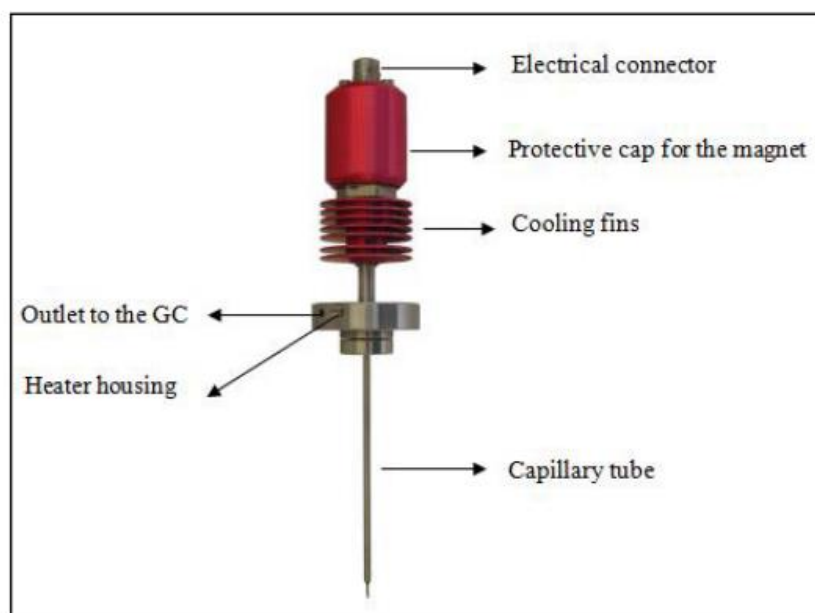
A WIKA pressure transducer with an operating range of 0-16 MPa and an accuracy of 0.05% was used to measure the pressure inside the cell. Two WIKA model REB Pt-100 thermocouple temperature probes with an accuracy of 0.05 K were used to measure the temperature inside the cell. The temperature sensors were not in direct contact with the system under investigation, as they were located in the flanges of the cell (as shown in Figure 4.2). The pressure and temperature sensors were connected to a 34972A LX Agilent data acquisition system that was connected to a computer installed with a LabVIEW software to periodically

capture and store real-time pressure and temperature measurements and log the data on a Microsoft Excel spreadsheet.

4.1.4 The vapour phase sampling device

The vapour phase in the cell was sampled using a Rapid Online Sampling Injector (ROLSI™) device (Guilbot et al., 2000), shown in Photograph 4.3. The ROLSI™ operates from cryogenic temperatures to 583.15 K and pressure ranges of atmospheric pressures to 60 MPa. A comprehensive description of the components of the device, its operation, its advantages and disadvantages, is provided in the reference of Guilbot et al. (2000).

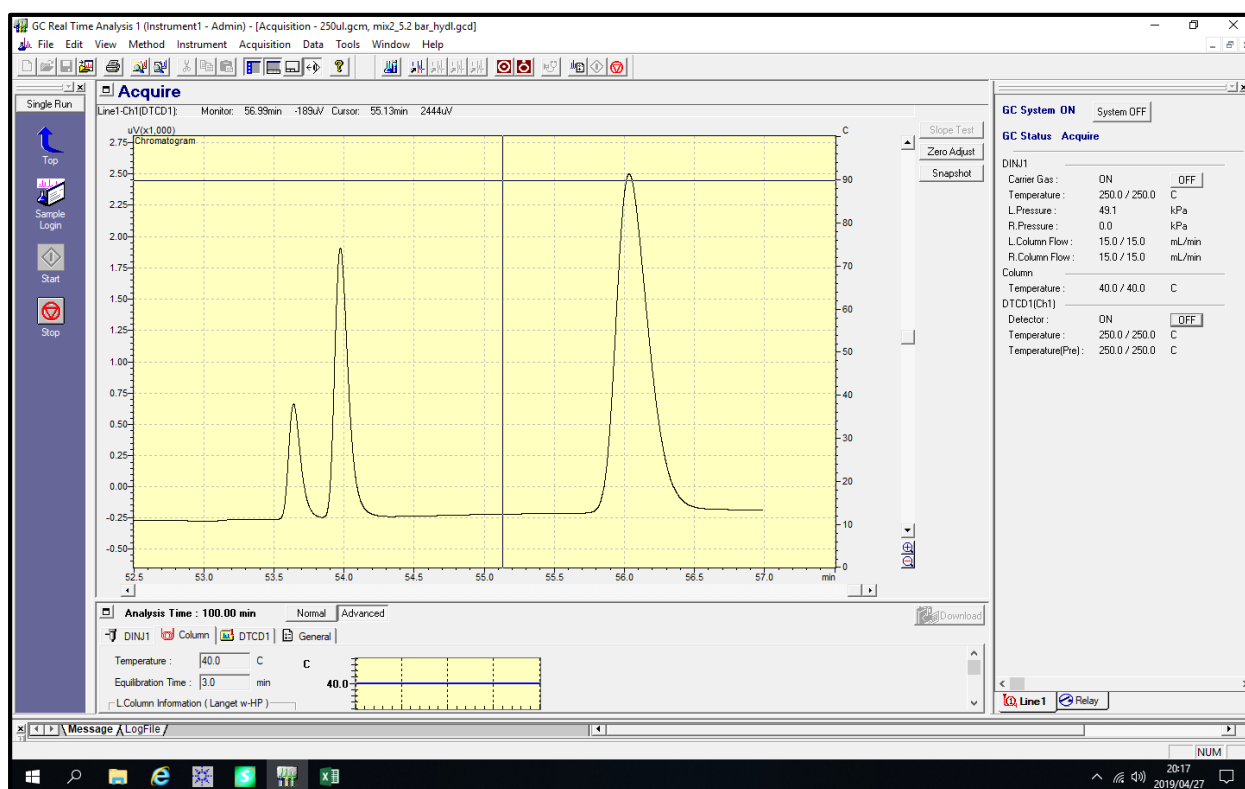
The volume of the sample taken was determined by the opening time (the time during which the seal between the piston and the capillary of the ROLSI™ was temporarily broken). The duration of the opening time and the time between successive sampling were both set on a timer that is coupled to the ROLSI™. During the sampling mode, the carrier gas (hydrogen) carried the sample (gas mixture) to the Gas Chromatography (GC) for analysis.



Photograph 4.3: The ROLSI™ (extracted from (Tumba, 2015)).

4.1.5 Compositional analysis

A Shimadzu 2014 gas chromatograph, equipped with a thermal conductivity detector (TCD) and interfaced with the GC Solutions software, was used to analyze the feed, vapour and hydrate phases. A picture of the GC user interface is shown in Photograph 4.4. Analysis using the GC was done online by use of the ROLSI™ device. Table 4.1 shows the specifications for the column that was used in the GC and the operating conditions.



Photograph 4.4: User interface for the GC Shimadzu 2014.

Table 4.1: Gas chromatograph specifications.

Property	Specification
Data acquisition software	GC Solutions
Detector	Thermal conductivity Conductor (TCD)
Stationary phase	Carbon molecular sieve phase
Column type	Packed column, Porapak Q
Column length (m)	2.2
Polarity	Polar
Maximum temperature (K)	250
Carrier gas	Hydrogen
Carrier gas flow rate (mL/min)	15
Injector temperature (K)	523.15
Detector temperature (K)	523.15
Column temperature (K)	303.15
Detector current (mA)	70

4.1.6 The equilibrium cell housing

In order to have better control and stability of temperature, the cell was immersed in a liquid bath. The equilibrium cell housing was made using 316 stainless steel with dimensions of $43 \times 35 \times 26$ cm. The bath was filled with 50% water and 50% ethyl glycol (a good coolant and antifreeze). Immersion of the cell in the liquid bath maintains the cell conditions and insulation on the bath walls minimises heat loss.

4.1.7 Temperature control

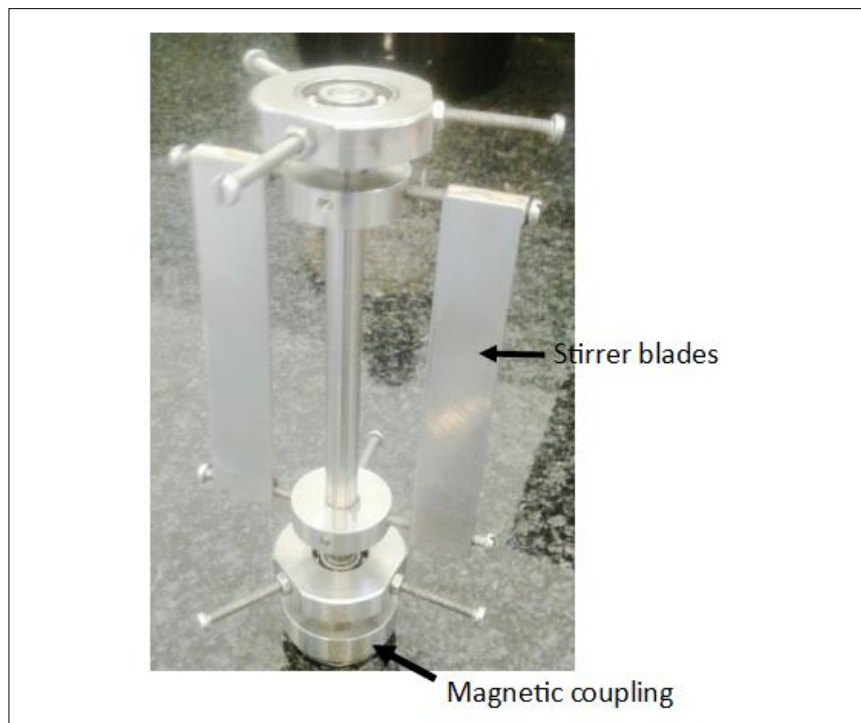
A cold finger (chiller) that consisted of a condenser, throttling valve, compressor and evaporator was used to cool the liquid bath to the operating temperature. The chiller could reach a temperature of 173.15 K. A Model TXF200 programmable controller supplied by Polyscience® with an operational temperature range of 243.15 to 323.15 K was used to maintain or increase the bath temperature. The controller had an internal temperature probe for cooling or heating.

4.1.8 Syringe pump

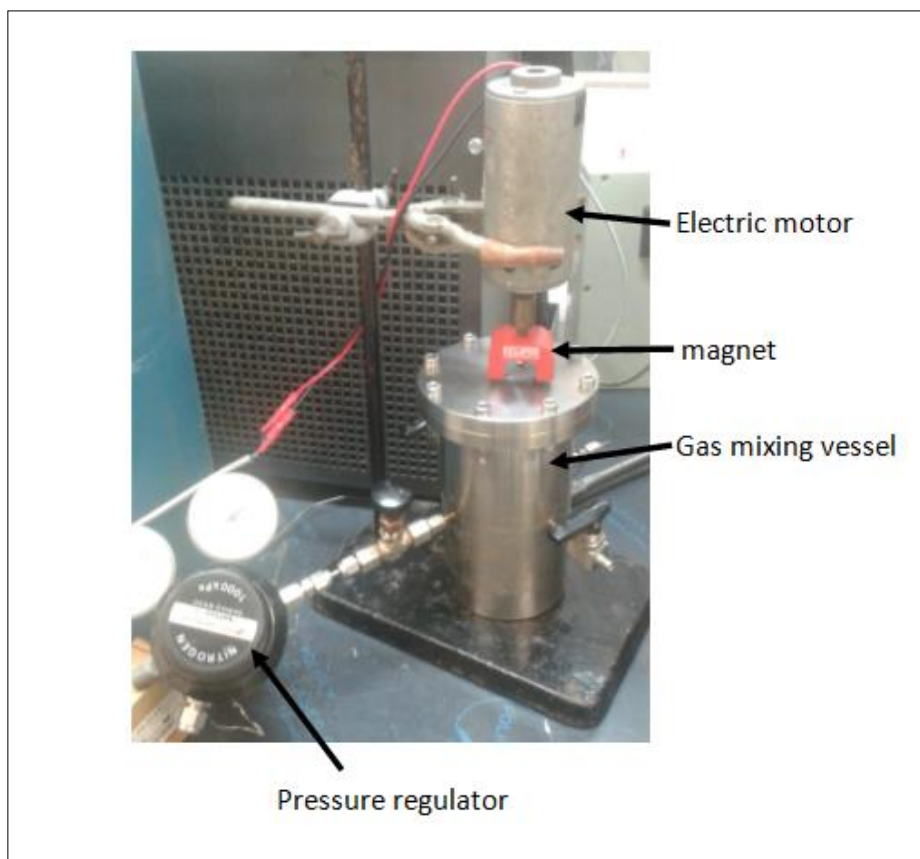
A Model 260D ISCO Syringe pump was used for the loading of both water and gas mixture into the equilibrium cell at the desired pressure. The pump has a capacity of 266 ml and can produce output pressures in the range 0.07 – 51.7 MPa.

4.1.9 Mixing Vessel

In this work, a new experimental procedure was followed. Thus, modifications to the existing equipment were necessary. A new vessel for making gas mixtures was added to the equipment setup. This vessel had a volume of 699 ml and could withstand pressures up to 8 MPa. It was essential for the composition of the gas mixture to be continuously maintained once the gas mixture had been made; thus, a stirring system for the vessel was manufactured. Photograph 4.5 shows the stirrer that was installed inside the vessel and Photograph 4.6 shows the stirring system of the vessel using a magnetic stirrer.



Photograph 4.5: The stirrer for the gas-mixing vessel (From this work).



Photograph 4.6: Magnetic stirring system for gas mixing vessel (From this work).

4.1.10 Vacuum pump

A RV12 rotary vane vacuum pump was used to evacuate the syringe pump, loading lines, mixing vessel and the equilibrium cell before loading or making the gas mixtures. The pump has a capacity of evacuating to a pressure of 0.002 mbar.

4.1.11 Mechanical jack

A 1.5T scissors mechanical jack was used to lift and hold the liquid bath housing in place during experiments.

4.1.12 Gas lines, valves and fittings

Gas lines were used to connect the gas cylinders, mixing vessel, equilibrium cell, GC, vacuum pump, syringe pump for the loading and removal of gas and water into the equilibrium cell and carrying the gas for analysis via the GC. Valves were used to allow or prevent the flow of any fluids (gas mixtures or water) in the equipment.

4.2 Experimental procedure

4.2.1 Pressure calibration

The pressure inside the equilibrium cell was measured using a calibrated WIKA (0-16 MPa) pressure capacitance transducer. This pressure transducer was calibrated using a model CPH 6000 standard pressure calibration device. Both the standard pressure calibration unit and the pressure transducer were kept at a temperature of 313.15 K, a temperature higher than any possible temperature for the experiments, to prevent any condensation of water or gases on the pressure measuring system and eliminate effects of the environment on the pressure readings. The temperature inside the equilibrium cell was kept at 298.15 K throughout the calibrations.

Nitrogen was loaded into the equilibrium cell and allowed to stabilize. Pressure measurements were then taken using both the pressure transducer and the standard pressure calibration device. Each recorded pressure value was an average of several measurements taken for a duration of three minutes before changing the pressure inside the cell. Pressure measurements were taken at different pressures in the range from 0.35 MPa to 14.5 MPa. After different sets of pressure measurements were taken, the values recorded using the standard calibration device were plotted against the values recorded using the pressure transducer. A 1st order polynomial was fitted to the plotted data to obtain the calibration curve. Results of the calibration are presented in Section 5.3.1.

4.2.2 Temperature calibration

The temperature probe used in this study was calibrated using a CTH 6500 standard temperature calibration unit, with a certified calibration from WIKA. Both the temperature probe and the calibration unit were immersed in the silicon oil bath to measure its temperature.

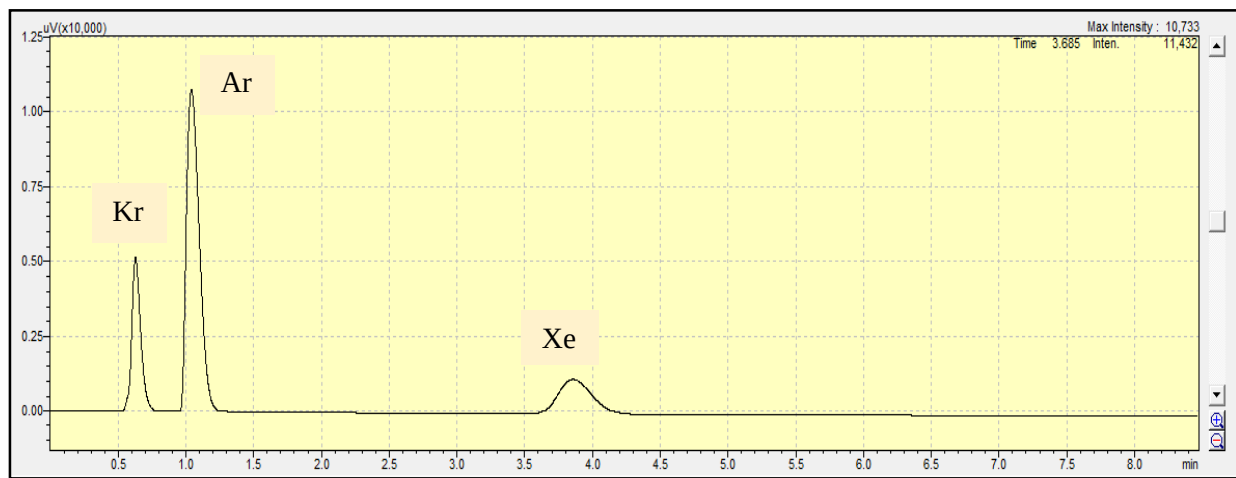
The temperature of the bath was increased and decreased using the TXF200 programmable controller at uniform intervals from 210 K to 310 K to detect any temperature hysteresis with the temperature sensors. The temperature reading from the sensors was allowed to stabilize first before taking measurements using the micro-ohmmeter data acquisition unit (Hewlett-Packard, model 34420A). The temperature of the bath was changed in steps between the ranges 210 - 310 K. Temperature values measured using the Pt-100 platinum resistance thermometer were plotted against the temperature values measured using the standard temperature calibration unit. A first-order polynomial was fitted to the plotted data to obtain the temperature calibration curve. Results of the calibration are presented in Section 5.3.2.

4.2.3 Calibration of the gas chromatography detector

The compositions of gases in the feed, vapour, and hydrate phase were analyzed using an online Shimadzu 2014 Gas Chromatography detector. The TCD of the GC was calibrated using gas mixtures and the calibration was validated by performing additional calibrations using pure gases. The composition of the gas in the feed was confirmed by comparing the areas determined by the GC detector using the obtained calibration curves and the compositions determined by mass during gas mixture preparation.

In order to find the best acceptable chromatographic conditions, a range of experiments were conducted for effective separation of the ternary mixture using gas chromatography. Factors that affect the extent and efficiency of gas separation that were considered were column type, column packing, column temperature, carrier gas flow rate, physical properties of the gases and the detector current.

The GC used in this study was also used in the previous study of hydrate experiments of the (Xe + Ar) binary mixtures, thus, the column type, packing, phase, were not changed. When analyzing the ternary gas mixtures using the GC detector, argon and krypton initially had very similar elution times in the GC detector; thus, the carrier gas flow rate and column temperature were varied until an optimum column temperature of 313 K and carrier gas flow rate of 15 ml/min were found. Photograph 4.7 shows a typical GC result that was obtained when an effective separation of the gas mixture was achieved. The operating conditions (method) for the GC were presented in Section 4.1.5.



Photograph 4.7: Photograph of a GC interface showing a good separation of gases in a mixture. (Peak 1 at 0.7 min corresponds to krypton, peak at 1.1 min corresponds to argon, and peak at 3.8 min corresponds to xenon.

Mixtures of the three gases was prepared using the procedure outlined in Section 4.2.8, and the direct injection method of gas samples was used to calibrate the GC detector (Raal and Muhlbauer, 1999, Ramjugemath, 2000). Curves of ratios of compositions $\frac{y_i}{y_j}$ versus the ratio of component peak areas $\frac{A_i}{A_j}$ were drawn. Binary and ternary systems exhibit the following relationships between the ratio of areas to the ratio of compositions:

$$\frac{y_i}{y_j} = G \frac{A_i}{A_j} + D \quad (4.1)$$

Where G is the gradient of the curve, and D is the Y-intercept. The gradient of the curve was determined using linear regression. The generated relationship between peak area, $\frac{A_i}{A_j}$, and the ratio of composition, $\frac{y_i}{y_j}$, was then used to determine the composition of an unknown quantity using Equations 4.2 to 4.5.

$$\frac{1}{y_{Ar}} = 1 + \frac{y_{Kr}}{y_{Ar}} + \frac{y_{Xe}}{y_{Ar}} \quad (4.2)$$

$$\frac{1}{y_{Kr}} = 1 + \frac{y_{Ar}}{y_{Kr}} + \frac{y_{Xe}}{y_{Kr}} \quad (4.3)$$

Generally,

$$y_j = \frac{1}{1 + \sum_{i=2}^n \left(\frac{y_i}{y_j}\right)} \quad (4.4)$$

And

$$y_{Xe} = 1 - (y_{Ar} + y_{Kr}) \quad (4.5)$$

Using Equation 4.1, two plots for $\frac{y_{Ar}}{y_{Kr}}$ against $\frac{A_{Ar}}{A_{Kr}}$ and for $\frac{y_{Xe}}{y_{Kr}}$ against $\frac{A_{Xe}}{A_{Kr}}$ were generated. Equations 4.4 and 4.5 were then applied to determine the composition of each component, and these compositions were compared to the compositions obtained gravimetrically (see Section 4.2.8). Results of the calibration are presented in Section 5.3.3. The procedure and measurements for the validation of the gas chromatography calibrations are presented in Appendix B. In this method, the detector was calibrated for varying number of moles of pure gases. Then the results compared to the results obtained for the synthesized mixtures.

4.2.5 Cleaning of the cell

The equilibrium cell, its fittings and the gas mixing vessel were cleaned with acetone to remove any impurities present. The cell, impellers and cell fitting were then blown with high-pressure nitrogen to dry it and remove any particulate matter which could be attached.

4.2.6 Leak testing

Leak testing of the equilibrium cell and gas mixing vessel was done before any experiments could be performed. Nitrogen at 6.9 MPa was filled into the cell, whilst the temperature of the cell was kept constant at 298.15 K. The pressure inside the cell was monitored for 15 hours to determine if there were any leaks. If the pressure inside the cell decreased significantly, this indicated the presence of a leak in the seal or fittings of the cell.

A leak detection fluid (Snoop®) was applied to all the fittings and joints throughout the apparatus to check for leaks. If a leak existed, the Snoop® produced foam at the point of the leak as a result of the pressurized gas in the cell exiting the cell through that point. The leak was then fixed by tightening or replacing the respective fittings.

4.2.7 Evacuation of the cell

After performing a leak test, the nitrogen used for leak testing was released. The equilibrium cell, connecting lines and the syringe pump were evacuated using a vacuum pump to a pressure of 0.00032 MPa to remove all the air and any residual gases. The evacuation was done overnight to be sure that the cell was completely evacuated.

4.2.8 Preparing gas mixtures

The mixing vessel was used to prepare the ternary mixtures. The vessel was evacuated as described in Section 4.2.7 above and dried using a hot air blower to remove any water molecules that may introduce errors in the measurement of the mass of the vessel. The mass of the gas mixing vessel was measured using a mass balance (OHAUS PA4202C) that measures masses up to 4200 g with 10 mg uncertainty. For each mass measurement, several values were recorded, and an average value was taken. When making the mixtures, krypton was loaded first into the mixing vessel. This was done because it had the lowest pressure in its pure gas cylinder compared to the other gases investigated. The mass of the vessel was measured before and after loading of the krypton, and the difference gave the mass of the krypton loaded into the vessel. The pressure in the krypton gas cylinder was approximately 0.2 MPa; therefore when loading

the next gas (xenon), the loading pressure had to be higher than 0.2 MPa to avoid backflow of the gas already loaded in the cylinder. The xenon was loaded at a pressure of approximately 0.8 MPa. The mass of the mixing vessel was also measured after loading of xenon to determine the mass of xenon loaded into the cell. Argon was loaded last since it had the highest pressure in its gas cylinder (7 MPa). This pressure was high enough not to allow backflow of the gas mixture already in the vessel. The difference between the mass of the gas mixing vessel before and after adding a gas gave the mass of the argon added.

The added masses of each gas were used to calculate the number of moles added using the equation ($number\ of\ moles = \frac{mass\ added}{Molar\ mass}$) and the molar composition of the mixture was subsequently determined by dividing the number of moles of each gas added by the total number of moles of the three gases. An alternate method for obtaining the number of moles of gas, which uses the ideal gas equation, was used to perform the validation of the gas chromatography calibrations. is explained in Appendix B. The mixing vessel was placed in an ice bath to reduce the temperature of the gases inside the vessel so as to lower the pressure and thus allow more gas to be loaded into the equilibrium cell. The contents of the mixing vessel were continuously stirred to ensure a homogenous mixture.

The composition of the feed gas was measured using two methods; gravimetrically as described above and using the GC to confirm the feed composition measurements. The maximum molar deviation between gravimetric compositions and GC compositions was 0.01 mole as shown in Figure 5.5 and Figure 5.7 on Page 73-74.

4.2.9 Loading the cell

The gas mixture was loaded into the equilibrium cell first, thereafter, water was added. This was done in this order to avoid the splashing of water particles onto the ROLSITM capillary (which could possibly cause blockage), if the water was loaded first. The mixing vessel was connected to the evacuated, which was loaded with the gas mixture and then used to pressurize it to the desired pressure. The syringe pump was connected to both gas mixing vessel and the equilibrium cell as shown in Figure 4.1. It was used to load the gas mixture from the gas mixing

vessel into the cell. The syringe pump was first evacuated and then it was filled with the gas mixture from gas mixing vessel. The syringe pump was then set to pressurise the gas to a desired value. When the inlet valve to the equilibrium cell was opened, the pressurised gas mixture flowed from the syringe pump into the equilibrium cell. Water was loaded from the round bottom flask into the syringe pump and pressurised, thereafter the inlet valve to the cell was opened to allow the water to flow into the cell.

4.2.10 Procedure for the measurement of hydrate dissociation conditions

The isochoric pressure search method was employed when performing hydrate dissociation measurements, and the reliability of this experimental method has been proven in published literature (Afzal et al., 2007, Belandria, 2012, Babaei, 2015, Tumba, 2015, Hashemi, 2015). Its advantage is that there is no need for one to view the cell contents to note the point at which hydrate forms and dissociates.

Measurements for the CO₂ + water test system were performed first before measurements of the (Xe + Ar + Kr) systems to validate the experimental technique through a comparison of the measured data with reliable literature sources. The same procedure was used for both the CO₂ + water test system and the (Xe + Ar + Kr + water) systems.

Before measurements were done, the cell was prepared, and the gas mixture was loaded into the cell as described in Sections 4.2.5 to 4.2.9 above. After that, deionized water was introduced into the cell using the syringe pump at a pressure that exceeded the pressure inside the cell by 0.8 - 1 MPa to ensure that the gas did not escape. The temperature and pressure of the cell were allowed to stabilize before the stirrer was switched on to allow for dissolution of the gases into the liquid phase. The stirrer operated at a speed of 180 rpm for all measurements to agitate the phases inside the cell. The temperature of the cell contents was gradually reduced to about 6 – 7 K below the estimated hydrate formation point. This cooling process was done to ensure that the majority of the gas could be encapsulated in the hydrate phase. As the temperature decreased, the pressure inside the cell also gradually decreased. This process is known as the cooling step. Figure 4.3 shows the cooling and heating curves, hydrate formation, hydrate dissociation curve and the final dissociation point. A change in the gradient of the cooling curve

and the sudden drop in pressure due to the gas encapsulation within the hydrate cavities showed hydrate formation (Hashemi, 2015). After hydrate formation, the cell conditions were allowed to stabilize to attain equilibrium, then a stepwise increment of the temperature was started. The temperature was increased by 1 K at each step, and the pressure and temperature in the cell were allowed to first stabilize for a sufficient time (approximately 3 hours) before the next stepwise increase was done to allow for equilibrium to be reached. This process is known as the heating step. As the temperature was increased, the hydrate crystals dissociated; thus, a pressure increase was observed. The 1 K temperature increments were done up to a point which was about 1 - 2 K below the estimated final dissociation point, or the reported final dissociation point in literature if such data existed. From this point on, 0.1 K per hour stepwise increments were effected until and past the final dissociation point.

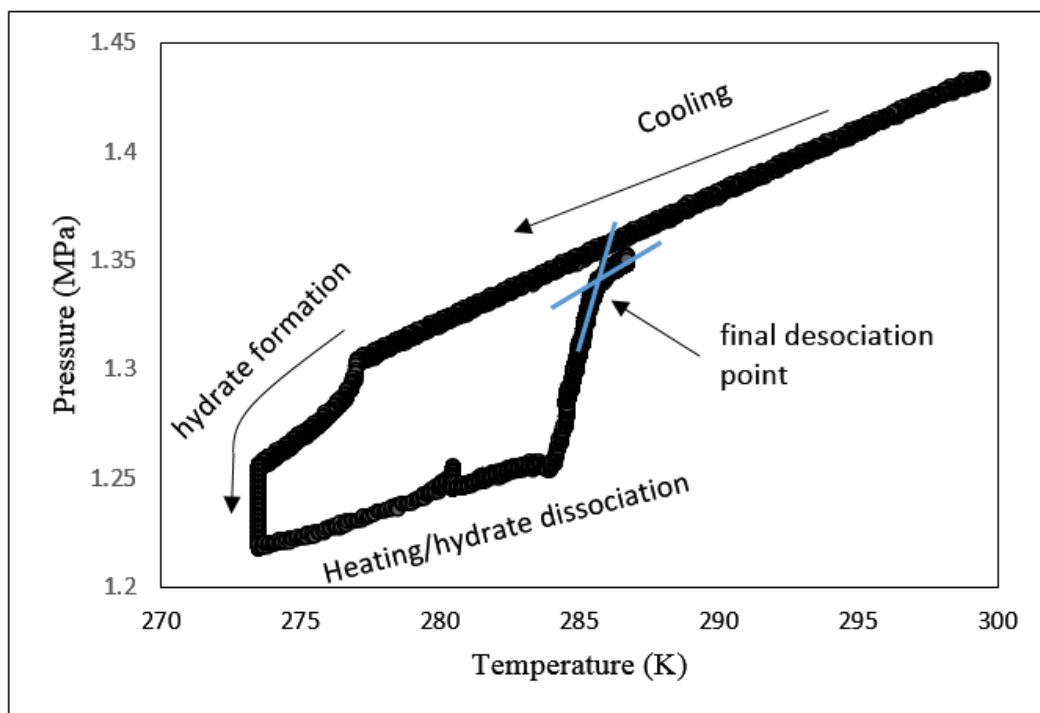


Figure 4.3: The primary heating and cooling curve obtained in this study for the carbon dioxide test system.

According to Sloan and Koh (2008), the hydrate equilibrium point/final dissociation point is considered as the intersection between the hydrate dissociation curve and the initial cooling curve (Sloan and Koh, 2008). If the cooling and heating curves do not intersect, as in

Figure 4.3, the point where there is a sharp change of gradient of the heating curve is used as the final dissociation point (Javanmardi et al., 2012, Tumba et al., 2013).

4.2.11 Composition analysis

The hydrate dissociation measurements were completed first, followed by compositional analysis measurements. As such, after the final dissociation point was determined for each mixture, the cooling step was performed again to form hydrate and attain equilibrium. After hydrate formation at 272 K, the cell conditions were allowed to stabilize to attain equilibrium, then sampling of the vapour phase was done to determine its composition where the hydrate phase was stable. The equilibrium gas phase composition was determined using the online GC, set at conditions detailed in Table 4.1. Before sampling using the ROLSITM, the stirrer was switched off to prevent the splashing of liquid and hydrate onto the sampling device, which would cause an inconsistent result from the GC. The temperature and pressure of the cell contents were kept constant during sampling to maintain the phase equilibrium. The sampling volume for the ROLSITM is 0.1 μ l to about 1 μ l (Guilbot et al., 2000; Veeneman, 2010). A few samples taken using the ROLSITM did not significantly upset the equilibrium in the equilibrium cell; about five samples caused a pressure drop of 0.002 bar.

The GC was switched on as per the GC start-up procedure, and sufficient time was allowed for the baseline to stabilize before the analysis of any samples. Sampling of the gas phase was done repeatedly until at least several consistent GC areas with an absolute deviation of 2% from each other were achieved. This was done to reduce errors in the final measured composition of the gas phase. The TCD calibration curves in Section 5.3.3 was then used to determine the molar composition of the sampled gas from the GC peak areas.

To determine the composition of the gas trapped in the hydrate phase, the vapour phase was released from the cell to the atmosphere. Instantly thereafter, the vacuum pump was switched on for 5-10 seconds to remove any residual vapour phase gas in the equilibrium cell and sampling lines. The vacuuming was too fast and instant not to upset the gas hydrate phase during the process, thus the hydrate phase could not dissociate during the vacuum process. This was done without altering the temperature inside the hydrate cell (272 K). The hydrate phase was then dissociated by heating the liquid bath to increase the temperature inside the cell to 298

K, allowing the hydrate phase to dissociate and thus releasing the gas that was trapped in the hydrate phase. The ROLSITM was then used to take samples for analysis by the GC to determine its composition.

4.2.12 Purification steps

The concentration of xenon was done in a stepwise manner. A hydrate stage ended when the composition of the hydrate phase was measured as outlined in Section 4.2.11. The subsequent hydrate separation stage commenced when the gas in the cell was then cooled to hydrate forming conditions and hydrate formed. The feed conditions for the new separation stage was taken as the final pressure, temperature and composition conditions in the hydrate cell just before that hydrate stage commenced. As outlined above, each hydrate stage comprised of; cooling to form hydrate, measuring the vapour composition at equilibrium conditions, releasing the vapour phase to the atmosphere and dissociating the hydrate phase to determine its compositions. It was observed that the composition of xenon in the product gas increased after each hydrate separation stage. The purification steps were done as long as the feed pressure was high enough to form hydrate. The drawback with the equipment setup that was used was that the experimenter could not increase the equilibrium cell pressure manually; one had to only depend on the pressure of the gas already inside the equilibrium cell. New gas could not be externally added to boost the pressure inside the equilibrium cell. The gas would need to have the same composition as the gas inside the equilibrium cell and gas mixtures with specific desired compositions could not be synthesized due to the gas mixture preparation procedure that was employed in the study.

4.2.13 Start-up procedure

- i. Prepare a gas mixture and store in the gas mixing vessel, switch on gas mixing vessel stirrer.
- ii. Switch on the vacuum pump to evacuate the equilibrium cell and connecting lines.
- iii. Close the valve to the vacuum pump and switch off the vacuum pump.
- iv. Load the gas mixture into the equilibrium cell using the syringe pump.
- v. Load the water into the equilibrium cell using the syringe pump and round-bottomed flask.

- vi. Close and check all valves.
- vii. Check that the equilibrium cell is immersed in the temperature bath.
- viii. Switch on the chilling unit and the temperature controller and set the temperature at 25°C.
- ix. Start the motor for the equilibrium cell stirrer.
- x. Switch on the data acquisition system and GC and allow the unit to stabilize.
- xi. Set the operating temperature and start the data acquisition system.
- xii. Then follow the procedures in Section 4.2.10 to 4.2.11.

4.2.14 Shutdown procedure

- i. Stop the data acquisition system.
- ii. Shutdown the GC as per procedure (Shimadzu Cooperation, 2004).
- iii. Switch of the motor for the equilibrium cell stirrer.
- iv. Switch off the chiller.
- v. Switch off the temperature controller.
- vi. Vent off the residual gas from the equilibrium cell to the atmosphere.
- vii. Drain the water from the equilibrium cell.
- viii. Clean the equipment.

In summary, this chapter described the experimental equipment that was used in this study for hydrate formation and dissociation measurements, as well as the purification steps in purifying xenon in the mixture. The results that were obtained from the experimental work are presented in the following chapter.

5

CHAPTER 5: RESULTS AND DISCUSSION

This chapter presents the experimental results of the hydrate phase equilibria for the test system and new work reported in this study. The test system of carbon dioxide + water was performed to confirm the accuracy and reliability of the experimental method. Novel hydrate-liquid-vapour (H-L_w-V) phase equilibrium data for the (Ar + Kr + Xe + water) system are presented together with the corresponding thermodynamic modelling approach and results. Compositional analysis and separation efficiencies of xenon from the (Ar + Kr + Xe) gaseous mixtures using the hydrated based separation process are also presented as well as a comparison of the energy usage of the simulated conventional cryogenic distillation process with the proposed hydrate-distillation hybrid system. A proposal for the integration of a hydrate-distillation hybrid system for the separation of the system studied is also discussed.

5.1 Systems experimentally investigated

Table 5.1 presents the systems that were investigated for H-L_w-V phase equilibrium measurements in this work. The temperature and pressure ranges for the systems investigated as well as the number of experimental data points (*NDP*) obtained are also provided.

Table 5.1: Summary of the systems for H-L_w-V phase equilibrium measurements in this work.

System ^a	Temperature /K	Pressure/ MPa	NDP ^b
CO ₂ + H ₂ O (test)	278.1 to 283.5	2.210 to 4.520	3
Ar (0.16) + Kr (0.65) + Xe (0.19) + H ₂ O	276.6	0.635	1
Ar (0.40) + Kr (0.34) + Xe (0.26) + H ₂ O	276.5 to 286.4	0.783 to 1.955	3
Ar (0.21) + Kr (0.51) + Xe (0.29) + H ₂ O	279.9 to 289.9	0.825 to 2.390	3
Ar (0.52) + Kr (0.34) + Xe (0.14) + H ₂ O	273.1 to 275.4	2.591 to 5.106	3
Ar (0.18) + Kr (0.17) + Xe (0.66) + H ₂ O	288.2	0.635	1
Ar (0.14) + Kr (0.16) + Xe (0.70) + H ₂ O	282.1 to 296.4	0.383 to 2.010	3
Ar (0.31) + Kr (0.25) + Xe (0.44) + H ₂ O	291.3 to 295.6	2.137 to 4.292	2

^aMole fractions of the gaseous mixture.^bNumber of data points.

Based on a review of published literature data to date, the hydrate dissociation data for the Ar + Kr + Xe + water systems investigated and reported in this work constitutes new data.

5.2 Chemical and materials

Table 5.2 shows the chemicals used in this study, the supplier details and product specifications. Deionised water with an electrical conductivity of 18 MΩ.cm was used in all experiments. The purities reported for the gases were measured using a Shimadzu 2014 Gas Chromatography with column details that were discussed in Section 4.1.5.

Table 5.2: Details of chemicals used in this study.

Chemical	Formula	CAS Number	Supplier	Purity ^a	Purity ^b
Carbon dioxide	CO ₂	124-38-9	Air Liquide	0.999	1.000
Argon	Ar	7440-37-1	Air Liquide	0.999	1.000
Krypton	Kr	7439-90-9	Air Liquide	0.999	0.999
Xenon	Xe	7440-63-3	Air Liquide	0.999	1.000
Deionised water	H ₂ O	-	-	-	-

^aMole fraction purity, as stated by the manufacturer.^bMole fraction purity based on GC peak areas.

Deionised water was sourced from the laboratory.

5.3 Calibrations

Calibration data for the gas chromatography detector were generated for compositional analysis of the Ar + Kr + Xe + water system. The gas mixtures were prepared as outlined in Section 4.2.8 and the compositions determined gravimetrically. Calibrations of the GC detector were validated by preparing additional mixtures and performing composition measurements, with the results presented in Section 5.3.3.

Calibration of the pressure and temperature sensors were validated by performing measurements for the CO₂ + water test system which is presented in Section 5.5.1.

5.3.1 Pressure calibration

The pressure probe was calibrated for a wide range of pressures from 0.25 MPa to 14.4 MPa. Figure 5.1 shows the calibration curve that was obtained and Figure 5.2 shows the deviations of the measured values to the calibration polynomial. In the graph, ΔP represents the difference between the pressure that is recorded by the standard probe and the pressure measured by the WIKA pressure transducer.

A 1st order polynomial was fitted to the plotted data to obtain the calibration curve. The pressure calibration error was deduced from the highlighted point in Figure 5.2.

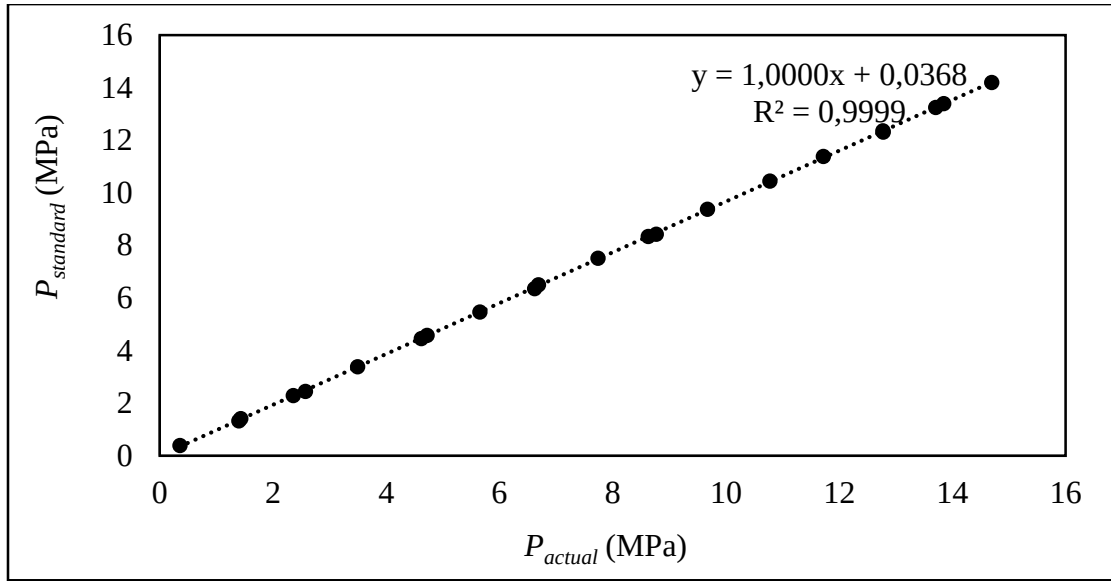


Figure 5.1: Calibration of the WIKA pressure transducer (0-16 MPa) used in this study.

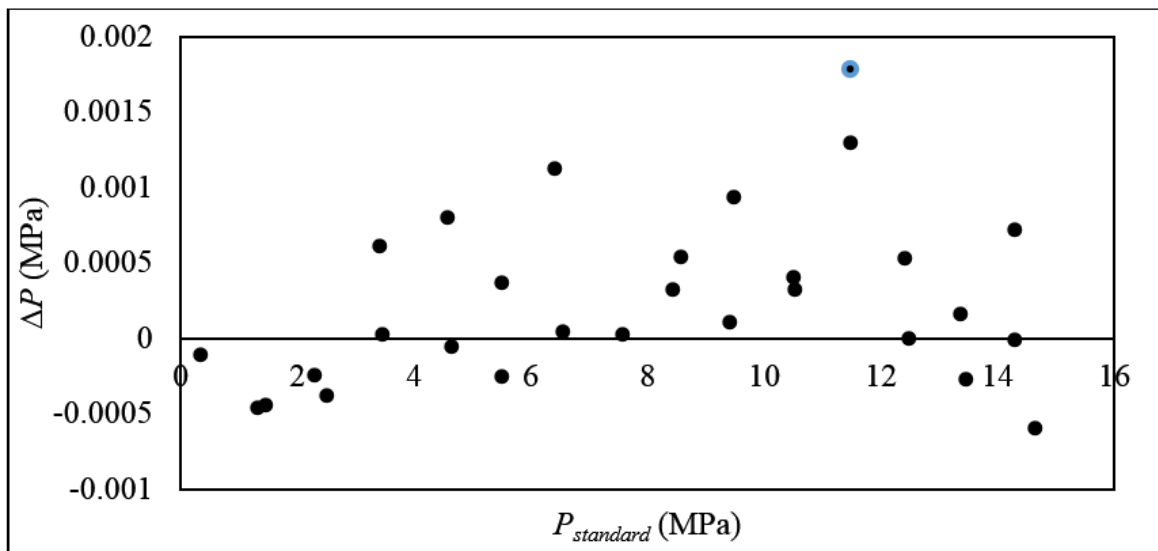


Figure 5.2: Deviations from the standard pressure due to a first-order relation with the maximum deviation of ± 1.8 kPa.

5.3.2 Temperature calibration

The temperature probe was calibrated over the temperature range from 269.15 K to 315.65 K. Figure 5.3 shows the calibration curve that was obtained. A 1st order polynomial was fitted to the data to obtain the calibration curve. Figure 5.4 shows the deviations of the measured temperature values to the calibration polynomial. In the graph, ΔT represents the difference between the temperature recorded by the standard temperature probe and the temperature

measured by the Pt-100 probe. The maximum temperature calibration error is reported as the maximum deviation of the measured values to the calibration polynomial, taken from the highlighted data point shown in Figure 5.4.

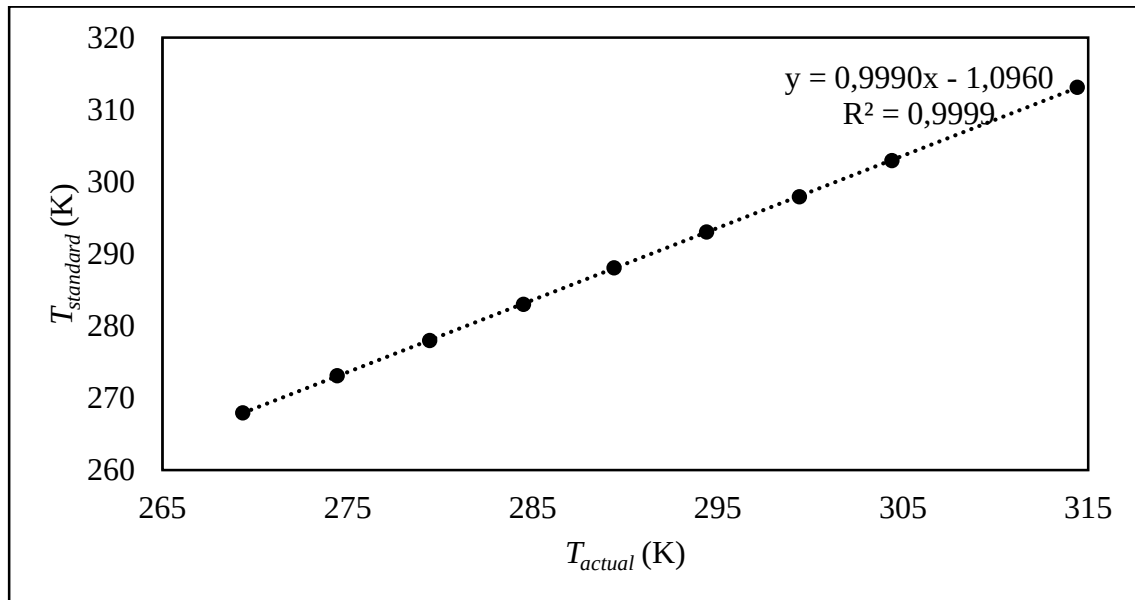


Figure 5.3: Calibration of the Pt-100 thermocouple thermometer probe used in the study.

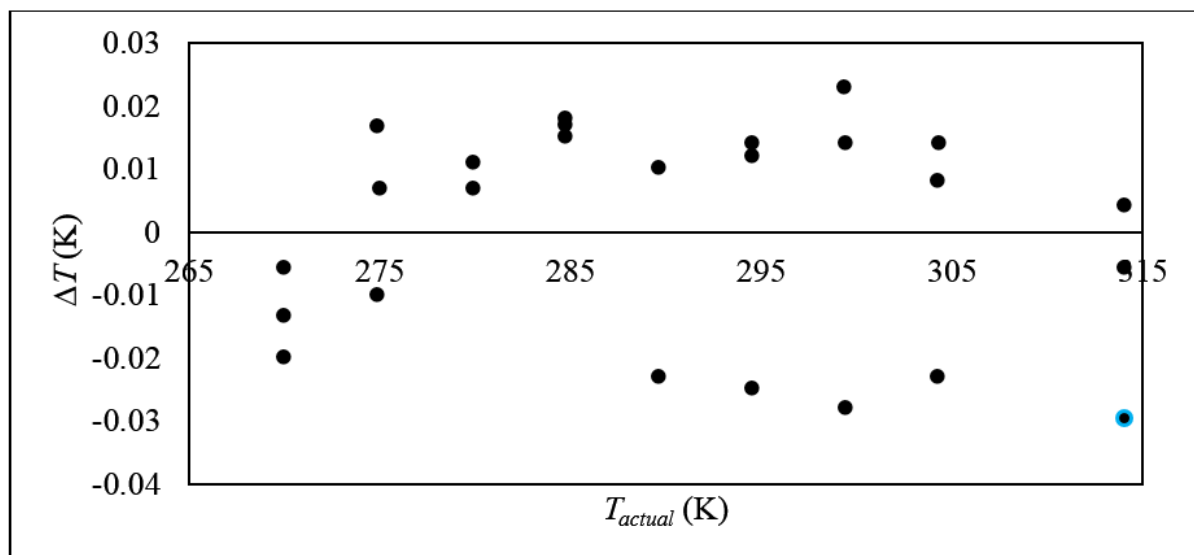


Figure 5.4: Deviations from the temperature due to the first-order relation, with a maximum deviation of ± 0.03 K.

5.3.3 GC detector calibration

The GC Thermal Conductivity Detector (TCD) was calibrated for the gas mixture containing xenon, argon, and krypton. Ternary mixtures of the gases were prepared using the procedure outlined in Section 4.2.8.

Figures 5.5 and 5.6 show the GC calibration curves that were obtained for the ternary mixture. The highlighted data point was not used in the calibration as it showed a notable deviation from the trend. The calibration curves obtained did not pass through zero, this was because of the distortion introduced by the dead volume which was noted to be particularly inherent in gas syringes. As such, only the gradient from the calibration equation was used in the calculation of the number of moles. (Nelson, 2012, Williams-Wyn, 2016). Figures 5.7 and 5.8 show the deviations of the measured values to the calibration polynomials. A maximum deviation of ± 0.01 in molar composition was obtained for compositions of Xe and Ar. First-order polynomials were fitted to the data to obtain the calibration curves.

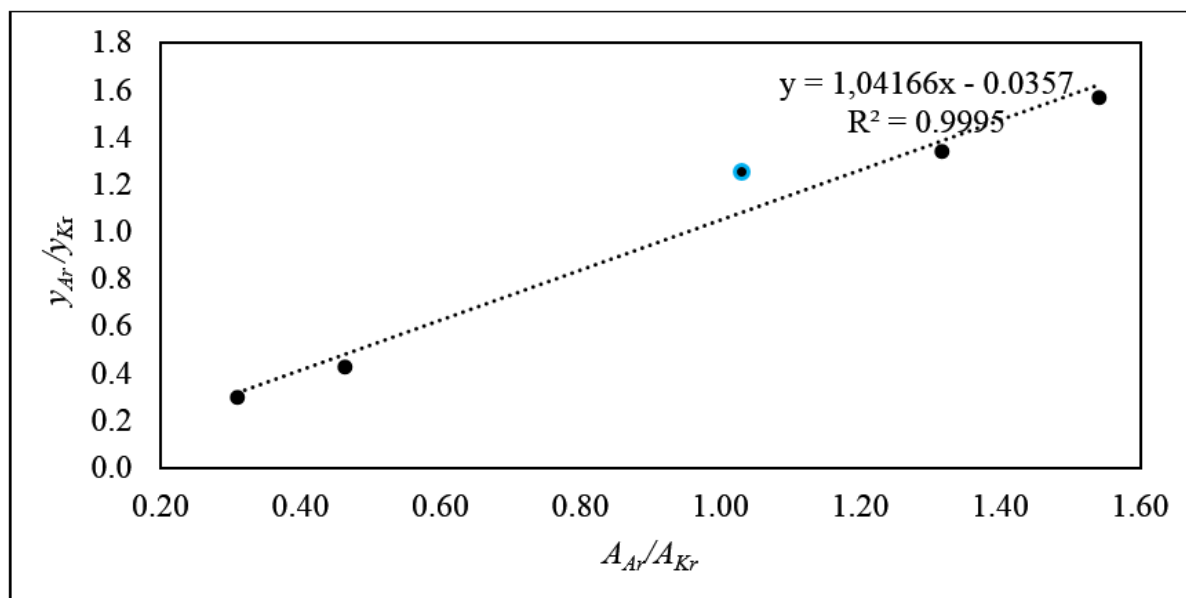


Figure 5.5: GC detector calibration curve for the system Ar + Kr used in the study.

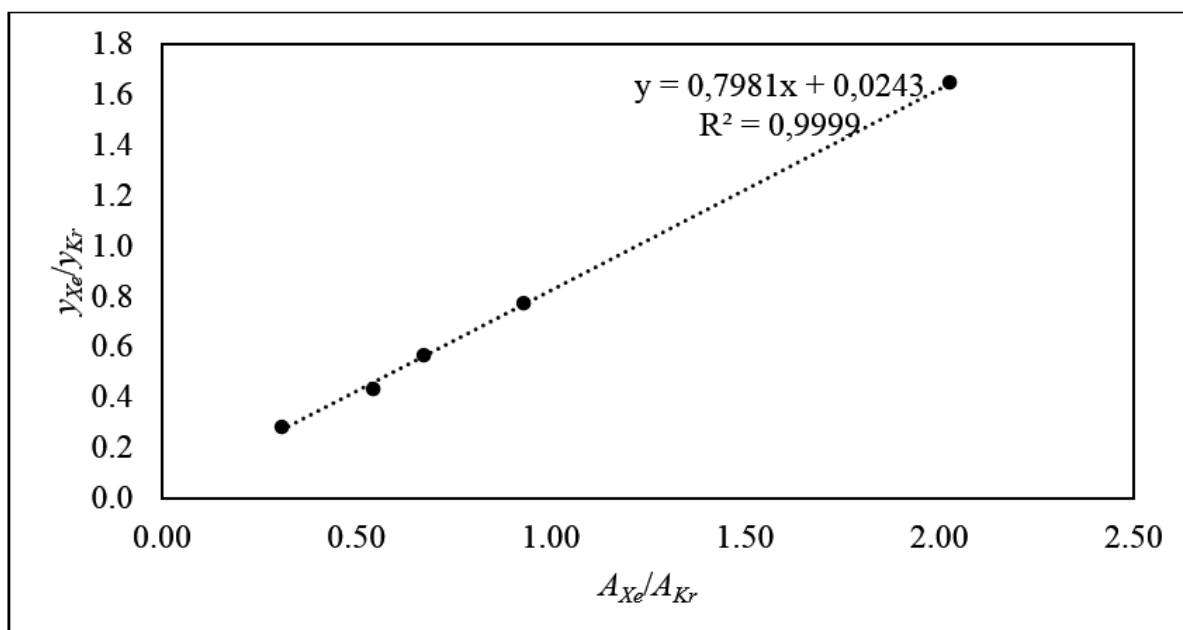


Figure 5.6: GC detector calibration curve for the system Xe + Kr used in the study.

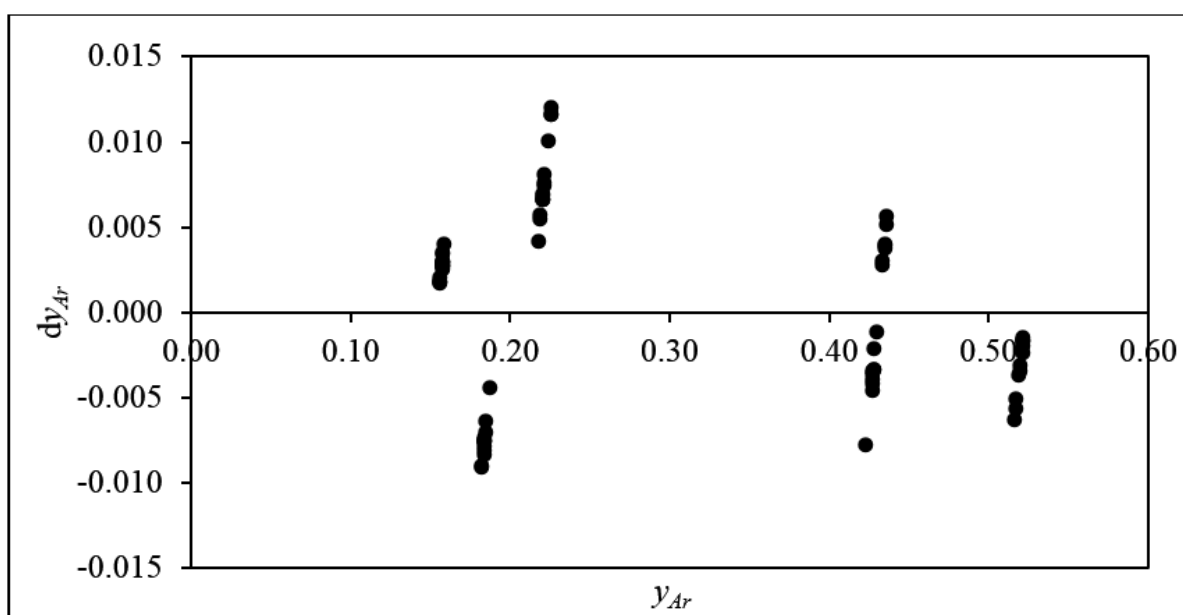


Figure 5.7: Deviations from the measured molar composition of argon (y_{Ar}) due to a first-order relation, with a maximum deviation of ± 0.01 .

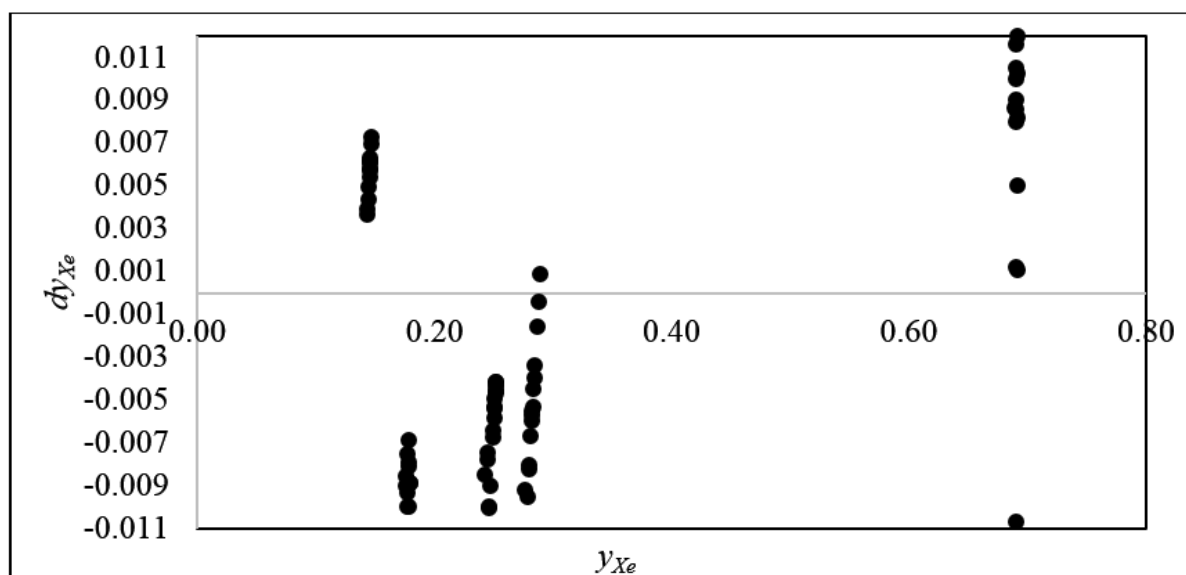


Figure 5.8: Deviations from the measured molar composition of xenon (y_{Xe}) due to a first-order relation, with a maximum deviation of ± 0.01 .

5.4 Uncertainty in measurements

Table 5.3 shows the sources of uncertainty and the combined standard uncertainties for pressure, temperature and composition. Appendix A presents the formulas and procedure that were used in calculating the uncertainties for pressure, temperature presented in Table 5.3. Appendix A also presents a step by step calculation of composition uncertainties.

Table 5.3: Summary of the sources of uncertainty for variables reported in this study.

Property	Source of uncertainty	Deviation estimate
Composition	Mass balance, manufacturer stated instrument error u_{instr} (g)	0.03
	Repeatability of mass, u_{rep}	0.0085
	Correlation error, u_{corr}	0.0135
	Combined standard uncertainty, $u_c(x)$	0.0163
Pressure	0 – 16 MPa WIKA pressure transducer, manufacturer stated instrument error, u_{instr} (MPa)	0.0050
	Repeatability of P , u_{rep} (MPa)	0.0015
	Correlation error, u_{corr}	0.0020
	Combined standard uncertainty, $u_c(x)$	0.0036
Temperature	WIKA model REB Pt-100 thermocouple thermometer, manufacturer stated instrument error, u_{instr} (MPa)	0.03
	Repeatability of T , u_{rep} (K)	0.03
	Correlation error, u_{corr}	0.03
	Combined standard uncertainty, $u_c(x)$	0.05

The general equation that was used for calculating the combined standard uncertainty is:

$$u_c(x) = \pm \sqrt{\sum_i u_i(x)^2} \quad (5.1)$$

Where $u_c(x)$ is defined as the standard uncertainty in quantity x , $u_i(x)$ represents the contributing uncertainties, and i represents component i . Equation 5.1 was expanded into the equation:

$$u_c(x) = \pm \sqrt{u_{calibration}(x_i)^2 + u_{repeatability}(x_i)^2} \quad (5.2)$$

Where $u_{calibration}$ was the error from the calibration polynomial and the uncertainty of the instruments used for calibration. $u_{repeatability}$ was the uncertainty due to random errors. Appendix A presents a more comprehensive explanation. For a 95% level of confidence, the combined standard uncertainties were multiplied by a coverage factor of 2 ($k=2$) to determine the combined

expanded uncertainty values. The calculated combined expanded uncertainty values for temperature, pressure and composition were quoted for all experimental results in this work.

5.5 Experimental measurements of hydrate dissociation conditions

5.5.1 Test system

CO₂ final hydrate dissociation data were measured to validate the experimental technique through a comparison of the measured data with reliable literature sources. Three *H-L_w-V* (Hydrate – Liquid – Vapour) data points were measured for the test system of carbon dioxide + water at three different initial pressures and the results demonstrate good comparison with the literature data. Table 5.4 presents the hydrate phase equilibrium data for the carbon dioxide + water system. Figures 5.9 and 5.10 presents the graphical results of the comparison of the data obtained for the test system with literature data.

Table 5.4: Hydrate dissociation conditions for the system of CO₂ + water.

This work		(Adisasmito et al., 1991)		(Babae, 2015)		(Wang et al., 2017)	
T_{exp} (K)	P_{exp} (MPa)	T_{lit} (K)	P_{lit} (MPa)	T_{lit} (K)	P_{lit} (MPa)	T_{lit} (K)	P_{lit} (MPa)
283.5	4.522	277.5	2.05	274.2	1.31	276.45	1.81
281.8	3.580	282.2	3.84	278.2	2.22	278.15	2.25
278.1	2.211	282.5	4.02	280.2	2.87	279.05	2.51
				281.4	3.34	280.25	2.94
						280.85	3.19
						281.55	3.55
						282.05	3.83

Combined expanded uncertainties U_c , are $U_c(T_{exp}) = \pm 0.1$ K and $U_c(P_{exp}) = \pm 0.007$ MPa.

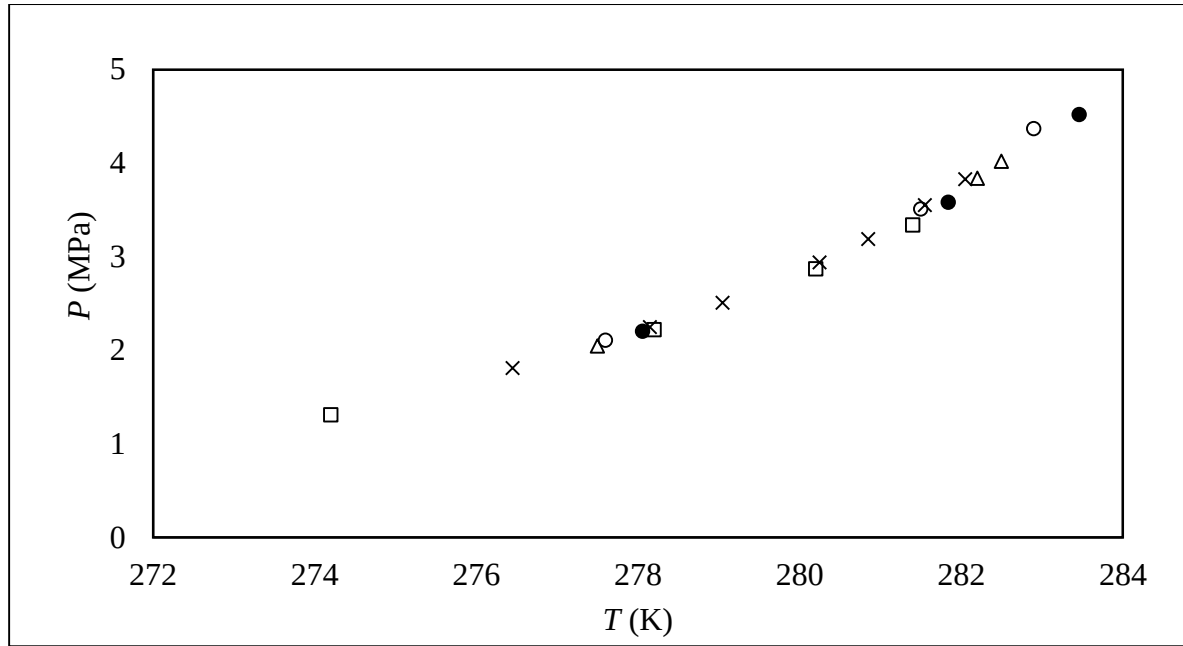


Figure 5.9: Hydrate dissociation data for the system of carbon dioxide + water. ●, exp (this work); Δ, (Mohammadi et al., 2005); ×, (Wang et al., 2017); □, (Babaei, 2015); ○, (Adisasmito et al., 1991).

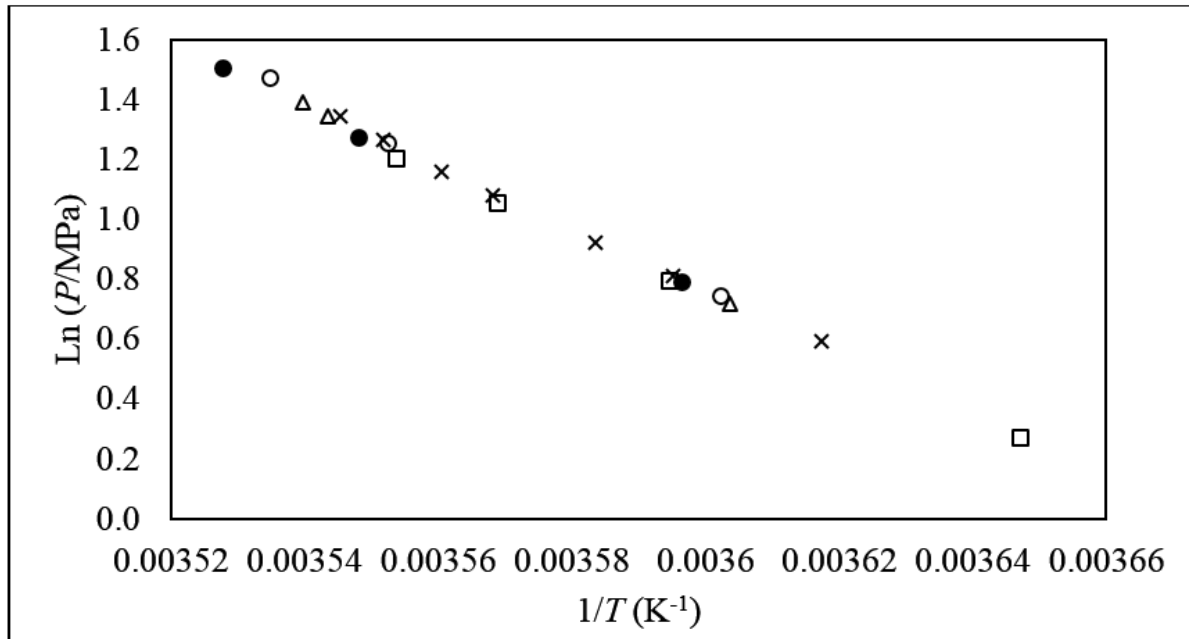


Figure 5.10: Ln P vs $1/T$ correlation for the hydrate dissociation conditions for the system of carbon dioxide + water. The symbols represent experimental data: ●, this work; Δ, (Mohammadi et al., 2005); ×, (Wang et al., 2017); □, (Babaei, 2015); ○, (Adisasmito et al., 1991).

The excellent agreement between the measured and literature data confirmed that the apparatus and procedure for this experiment were reliable.

5.5.2 Hydrate dissociation conditions for the mixtures of Ar + Kr + Xe

Hydrate phase equilibrium conditions for the mixtures of Ar + Kr + Xe were measured in order to determine the conditions at which the hydrate phase dissociates. Table 5.5 reports the experimental hydrate dissociation conditions for the system of Ar + Kr + Xe + water.

Hydrate dissociation data for four data sets were measured over the pressure range of 0.63 to 4.29 MPa and temperature range of 276.6 to 295.6 K. It was intended to measure enough systems to cover a wide range of xenon concentrations between 0 and 1 mole composition to better understand the effect of the different xenon concentrations on the hydrate dissociation conditions. However, due to limitations with of the quantity of xenon gas available for experimentation, the hydrate dissociation conditions were measured for only four Ar + Kr + Xe mixtures.

Table 5.5: Experimental hydrate dissociation conditions for the Ar + Kr + Xe + water system.

System ^a	T_{exp} (K) ^b	P_{exp} (MPa) ^b
argon (0.16) + krypton (0.65) + xenon (0.19)	276.6	0.630
	276.5	0.782
argon (0.40) + krypton (0.34) + xenon (0.26)	283.5	1.424
	286.4	1.950
	279.9	0.823
argon (0.21) + krypton (0.50) + xenon (0.29)	284.8	1.430
	289.9	2.392
	286.9	1.221
argon (0.31) + krypton (0.25) + xenon (0.44)	291.3	2.130
	295.6	4.292

^aMole fractions of the gaseous mixture, ^bCombined expanded uncertainties U_c , are $U_c(T_{exp}) = \pm 0.1$ K and $U_c(P_{exp}) = \pm 0.007$ MPa.

Figure 5.11 shows the data in comparison to hydrate dissociation data for pure components of xenon, argon and krypton.

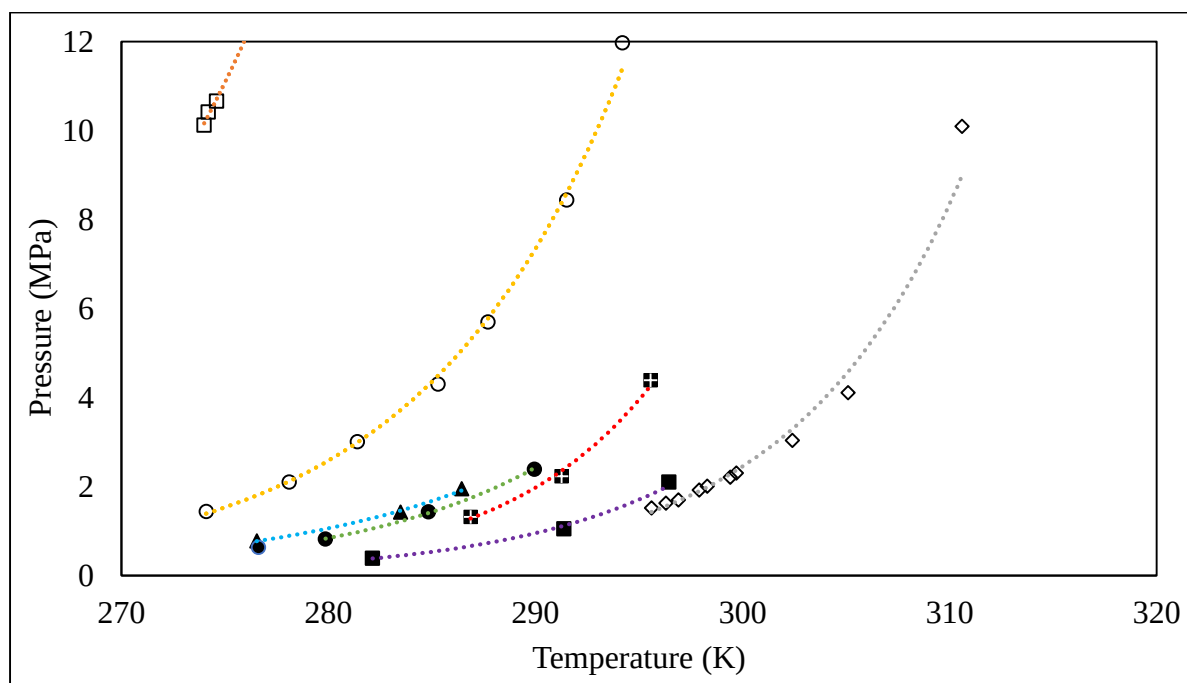


Figure 5.11: Hydrate dissociation data for the system argon + krypton + xenon + water. $\blacktriangle$, exp (this work: $y_{H,Ar} = 0.41$, $y_{H,Kr} = 0.33$, $y_{H,Xe} = 0.26$); $\bullet$, exp (this work: $y_{H,Ar} = 0.16$, $y_{H,Kr} = 0.65$, $y_{H,Xe} = 0.19$); $\blacksquare$, exp (this work $y_{H,Ar} = 0.31$, $y_{H,Kr} = 0.25$, $y_{H,Xe} = 0.44$); $\blacksquare$, exp (this work $y_{H,Ar} = 0.14$, $y_{H,Kr} = 0.16$, $y_{H,Xe} = 0.70$); $\square$, argon + water (Babae, 2015); $\diamond$, xenon + water (Babae, 2015); $\circ$, krypton + water (Babae, 2015).

It can be observed from Figure 5.11 that as the compositions of the gas mixtures change, the dissociation curve also shifts. As the concentration of one component increases, the dissociation curve shifts towards the dissociation curve for the pure component. As the amount of Xe in the mixture of Ar + Kr + Xe is increased, the equilibrium curve for the mixture of Ar + Kr + Xe shifts to the right towards the higher temperatures and lower pressures. As the concentration of argon in the mixture is increased, the hydrate dissociation isotherm shifts towards that of pure argon, and this was because of the effect of the argon on the mixture dissociation conditions increases as the concentration of argon increases and vice versa. The same phenomenon was observed with krypton; as its concentration in the mixture increased, the isotherm shifts towards that of pure krypton.

Additionally, the experimental results indicate that a slight hydrate equilibrium temperature rise results in a considerable rise in the hydrate equilibrium pressure. Hence, in order to prevent incorrect results, the measurement of hydrate dissociation conditions should be performed very slowly and carefully. For this reason, a step change of 0.5 K/h was used until the temperature approached 1-2 K of the final dissociation point, after which a step-change of 0.1 K per hour was used to raise the cell temperature until the final dissociation point. Sufficient interval time (approximately 3 hours) was taken during the heating process at each temperature stage. On average each thermodynamic test lasted for approximately 22 hrs.

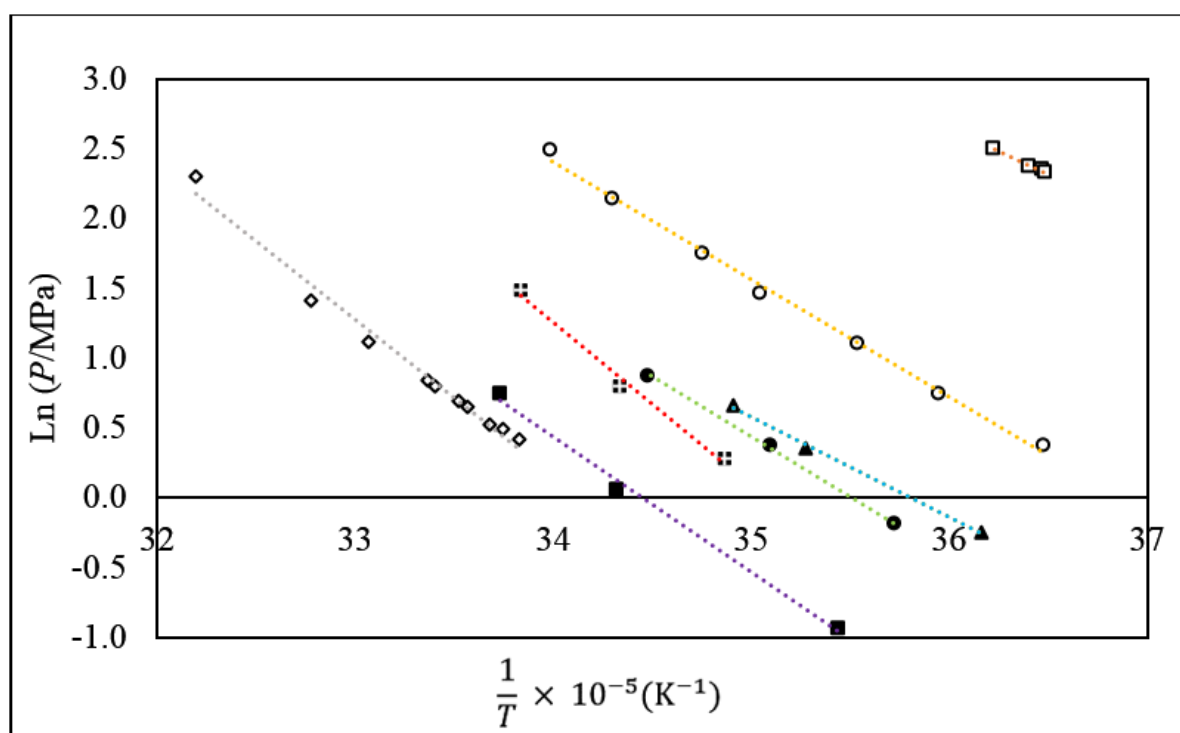


Figure 5.12: $\ln P$ vs $1/T$ correlation for the hydrate dissociation data for the system argon + krypton + xenon + water. $\blacktriangle$, exp (this work: $y_{H,Ar} = 0.40$, $y_{H,Kr} = 0.34$, $y_{H,Xe} = 0.26$); $\bullet$, exp (this work: $y_{H,Ar} = 0.16$, $y_{H,Kr} = 0.65$, $y_{H,Xe} = 0.19$); $\blacksquare$, exp (this work: $y_{H,Ar} = 0.14$, $y_{H,Kr} = 0.16$, $y_{H,Xe} = 0.70$); $\blacksquare$, exp (this work: $y_{H,Ar} = 0.31$, $y_{H,Kr} = 0.25$, $y_{H,Xe} = 0.44$).

Figure 5.12 shows the relation between $\ln P$ and $1/T$ for the hydrate dissociation data obtained for the different mixtures of argon, krypton and xenon. The linearity of the data points showed that the exponential relationship between the pressure and temperature measurement of the data points is true. Additionally, in line with the Clausius-Clapeyron equation, the gradient of the curve was used to determine the enthalpy of dissociation of the hydrates which is a critical

property in the separation of xenon + krypton + argon gas mixture. For hydrate formation reactions, the volume of the hydrate is approximately assumed to be the same as for the liquid water (or ice), thus $\Delta V \approx RT/PZ$, in which Z is the compressibility factor (Proust and Vera, 1989). Inserting this expression into the Clausius–Clapeyron equation (Equation 5.3) yields a more practical form of the equation which is then used to calculate the enthalpy of hydrate dissociation (Equation 5.4).

$$\frac{dP}{dT} = \frac{H_i^\infty - H_i^\psi}{T(V_i^\infty - V_i^\psi)} \cong \frac{\Delta H}{T\Delta V} \quad (5.3)$$

$$\Delta H = -RZ \frac{d \ln(P)}{d \left(\frac{1}{T}\right)} \quad (5.4)$$

The value of ΔH is calculated by multiplying the value of Z (the compressibility factor) with R , the Universal gas constant, and the value of $\frac{d \ln(P)}{d \left(\frac{1}{T}\right)}$, the gradient of the graph of $\ln P$ versus $\frac{1}{T}$, calculated using the hydrate dissociation data obtained by experiment. The compressibility factor, Z , was assumed to be 1 since the gas mixture was assumed to behave ideally. Results from Figure 5.12 were used to calculate the enthalpy of hydrate formation used in evaluating the energy demand for the concentration process of Xe as explained in Section 5.8.2.2.

5.6 Thermodynamic modelling

The objective was to confirm that the experimental results correspond to the predictive model results for the hydrate dissociation conditions. This is necessary when developing calculations for the separation of the mixture to predict thermodynamic conditions for different mixtures of Xe, Ar and Kr. The modelling was not the focus of this study. Rather, Babaei (2020) performed the modelling while the focus of this work was to perform the process calculations for separation and purification. The model approach, relevant equations and the model errors were summarised in Section 2.3. The results for the thermodynamic modelling for the various mixtures of Ar, Kr, and Xe studied in this work are reported in Figure 5.13 and Table 5.6.

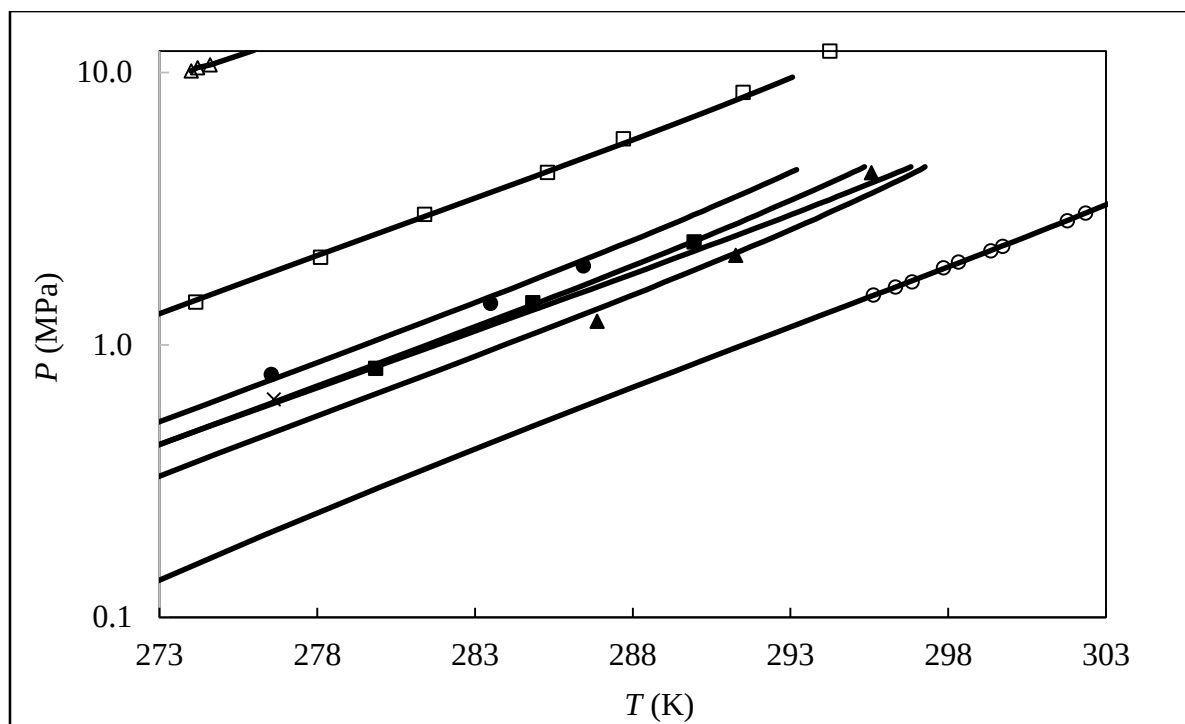


Figure 5.13: Experimental data and modelling results of hydrate dissociation conditions for the system of Ar + Kr + Xe + water for the various mixtures, compositions are in mole fractions. pure Xe hydrates: $\circ$, (Babae, 2015); pure Kr hydrates: $\square$, (Babae, 2015); pure Ar hydrates: $\triangle$, (Babae, 2015); $\bullet$, this work, ($y_{H,Ar} = 0.40$, $y_{H,Kr} = 0.34$, $y_{H,Xe} = 0.26$); $\times$, this work, ($y_{H,Ar} = 0.17$, $y_{H,Kr} = 0.64$, $y_{H,Xe} = 0.19$); $\blacksquare$, this work, ($y_{H,Ar} = 0.21$, $y_{H,Kr} = 0.50$, $y_{H,Xe} = 0.29$); $\blacktriangle$, this work, ($y_{H,Ar} = 0.31$, $y_{H,Kr} = 0.25$, $y_{H,Xe} = 0.44$); Solid lines, model predictions (Babae, 2020).

Table 5.6: Experimental and predicted hydrate dissociation conditions for pure and mixed hydrates of Xe, Kr, and Ar. The mole fractions in the feed are reported on a water-free basis ^a.

System	^b P_{exp} /MPa	^c T_{exp} /K	T_{cal} /K	^d ARD%
Ar (0.17) + Kr (0.64) + Xe (0.19)	0.63	276.6	277.0	1.4
Ar (0.40) + Kr (0.34) + Xe (0.26)	0.78	276.5	277.0	0.2
	1.42	283.5	282.9	0.2
	1.95	286.4	286.0	0.2
Ar (0.21) + Kr (0.50) + Xe (0.29)	0.82	279.9	279.5	0.1
	1.43	284.8	285.0	0.1
	2.39	289.9	289.9	0.0
Ar (0.31) + Kr (0.25) + Xe (0.44)	4.29	295.6	296.9	0.4
	2.13	291.3	291.2	0.0
	1.22	286.9	286.0	0.3
^e Pure Xe	10.09	310.6	310.7	0.0
	4.11	305.1	305.0	0.0
	3.04	302.4	301.8	0.2
	2.86	301.8	302.4	0.2
	2.3	299.7	297.9	0.6
	2.21	299.4	298.4	0.3
	2.01	298.3	299.3	0.3
	1.92	297.9	299.7	0.6
	1.7	296.9	295.7	0.4
	1.63	296.3	296.3	0.0
	1.52	295.6	296.8	0.4
^f Pure Kr	11.97	294.2	295.0	0.3
	8.44	291.5	291.9	0.1
	5.7	287.7	288.1	0.1
	4.3	285.3	285.2	0.0
	3.01	281.4	281.6	0.1
	2.1	278.1	277.8	0.1
	1.44	274.1	274.0	0.0
^g Pure Ar	12.08	276.0	275.7	0.1
	10.66	274.6	274.4	0.1
	10.42	274.2	274.2	0.0
	10.12	274.0	273.9	0.0

^a Combined expanded uncertainties U_c are $U_c(T_{exp}) = 0.1$ K, $U_c(P) = 0.01$ MPa. $U_c(\text{Composition}) = \pm 3.2$ mol %. ^b Pressure; ^c Temperature; ^d $ARD\% = (|T_{exp} - T_{cal}| / T_{exp}) \times 100$, absolute relative deviation; ^e Pure xenon hydrate experimental data (Babae et al., 2015). ^f Pure krypton hydrate experimental data (Babae et al., 2014). ^g Pure argon hydrate experimental data (Babae et al., 2014).

As Table 5.6 shows, the maximum absolute relative deviation between the predicted and experimental temperatures is 1.4%. This demonstrates a reasonable agreement between the experimental data and the model predictions.

5.7 Concentration measurements

Composition analysis was performed using the procedure outlined in Section 4.2.11. Figure 5.14 shows an overview of the method and the results obtained for one set of measurements, increasing the concentration of xenon from 25.7 mol% to 86.1 mol% in 3 hydrate formation and dissociation stages. The gas product from each hydrate stage was fed into the following stage. The 1st hydrate stage finished when the composition of the dissociated gas from the hydrate phase was measured. The 2nd stage commenced by starting the cooling process on the same gas in the cell from the 1st stage (the gas from dissociated hydrate phase from the 1st stage was taken as feed for the 2nd hydrate formation and dissociation stage). The 2nd hydrate stage finished when the composition of the dissociated gas from the hydrate phase was measured and the 3rd stage commenced by starting the cooling process on the same gas in the cell from the 2nd stage, as such the composition of the 2nd stage hydrate phase was taken as the composition of the feed for the 3rd stage. The water that was used in each preceding hydrate formation and dissociation stage was used for the successive separation stage. To increase the cell pressure, more water was added into the cell to the maximum water capacity of the cell using the syringe pump. These results demonstrate that hydrate technology can be considered as an alternative for the separation of noble gas mixtures.

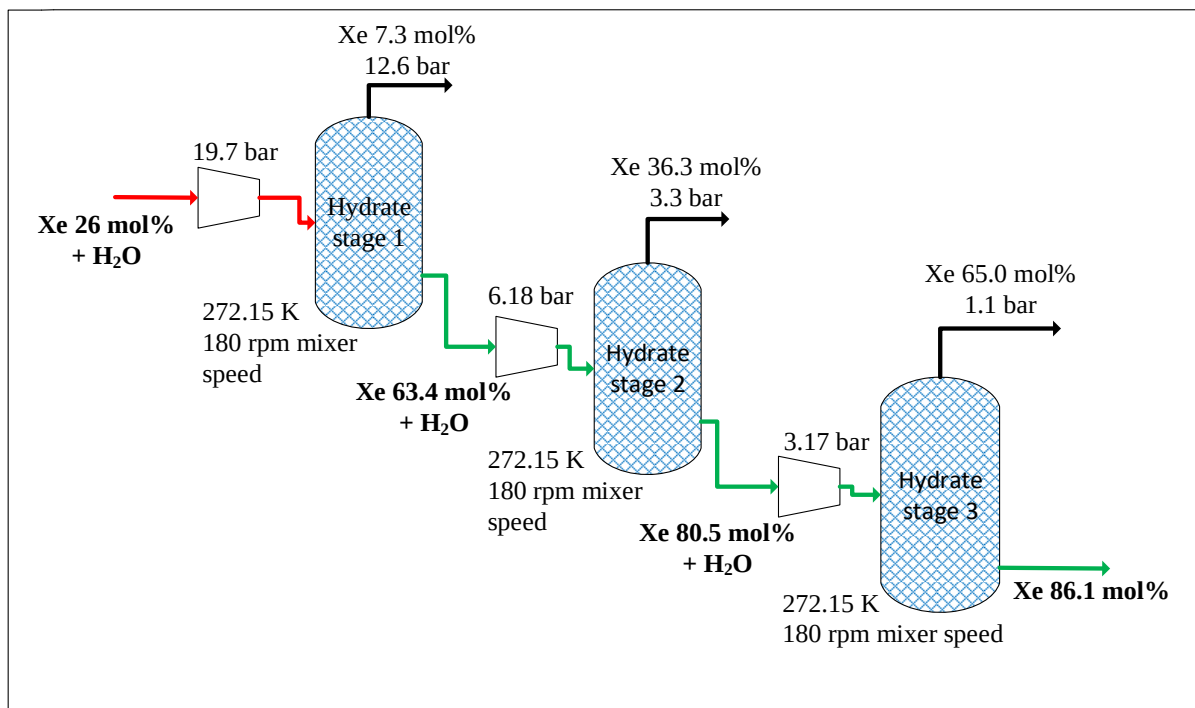


Figure 5.14: Schematic of the stage-wise separation process for the feed mixture (41 mol% Ar + 33 mol% Kr + 26 mol% Xe).

Table 5.7 presents detailed results of the compositional analysis at each separation stage, and the corresponding temperature and pressures. Experimental values presented are averages of more than one measurement for each.

Table 5.7: Stage-wise compositional data for the hydrate-based gas separation of the argon + krypton + xenon + water system.

^a System	Feed	P_{feed} / MPa	Hydrate stage	Stage feed composition			Equilibrium conditions		Gas phase mole fraction, water free basis			Hydrate phase mole fraction, water free basis		
				Ar	Kr	Xe	T / K	P / MPa	Ar	Kr	Xe	Ar	Kr	Xe
argon (0.16) + krypton (0.65) + xenon (0.19) + water	1	0.840	1 st	0.16	0.65	0.19	272.1	0.78	0.18	0.68	0.14	0.07	0.58	0.36
argon (0.41) + krypton (0.33) + xenon (0.26) + water	1	0.714	1 st	0.41	0.34	0.26	272.2	0.58	0.45	0.35	0.20	0.17	0.22	0.61
	2	1.581	1 st	0.41	0.34	0.26	272.2	1.09	0.52	0.37	0.10	0.11	0.26	0.63
		0.652	2 nd	0.11	0.26	0.63	272.2	0.33	0.23	0.36	0.40	0.06	0.17	0.77
	3	2.062	1 st	0.41	0.34	0.26	272.2	1.34	0.56	0.37	0.07	0.10	0.27	0.63
		0.714	2 nd	0.10	0.27	0.63	272.2	0.42	0.20	0.44	0.36	0.04	0.16	0.80
		0.590	3 rd	0.04	0.16	0.80	272.2	0.20	0.07	0.28	0.65	0.02	0.12	0.86
argon (0.21) + krypton (0.50) + xenon (0.29) + water	1	2.174	1 st	0.21	0.51	0.29	272.1	1.91	0.21	0.52	0.27	0.14	0.42	0.44
	2	1.520	1 st	0.21	0.51	0.29	272.2	1.31	0.22	0.52	0.27	0.17	0.38	0.45
argon (0.52) + krypton (0.34) + xenon (0.14) + water	1	1.522	1 st	0.52	0.34	0.14	272.2	1.32	0.22	0.52	0.27	0.17	0.38	0.45
argon (0.18) + krypton (0.16) + xenon (0.66) + water	1	0.780	1 st	0.18	0.17	0.65	272.0	0.66	0.36	0.28	0.35	0.07	0.10	0.83
		0.552	2 nd	0.07	0.10	0.83	272.0	0.21	0.17	0.21	0.62	0.04	0.07	0.89
argon (0.14) + krypton (0.16) + xenon (0.70) + water	1	2.170	1 st	0.14	0.16	0.70	272.0	0.59	0.45	0.35	0.20	0.03	0.11	0.86
		1.640	2 nd	0.03	0.11	0.86	272.1	0.29	0.19	0.37	0.44	0.00	0.05	0.95
		1.204	3 rd	0.00	0.05	0.95	272.1	0.19	0.02	0.23	0.74	0.00	0.03	0.97
argon (0.31) + krypton (0.25) + xenon (0.44) + water	1	4.443	1 st	0.31	0.25	0.44	272.1	1.85	0.60	0.30	0.10	0.07	0.20	0.73
		2.578	2 nd	0.07	0.20	0.73	272.1	1.14	0.15	0.34	0.51	0.02	0.10	0.88
		1.852	3 rd	0.02	0.10	0.88	272.1	0.52	0.19	0.37	0.44	0.00	0.05	0.95
	2	2.279	1 st	0.31	0.25	0.44	272.1	1.03	0.29	0.23	0.48	0.05	0.15	0.80

^aMole fractions, ^b Combined expanded uncertainties (U_c) are $U_c(T_{exp}) = 0.1$ K, $U_c(P) = 0.007$ MPa, $U_c(\text{Composition}) = \pm 3.2$ mol %.

It can be seen in Table 5.7 that the concentration of xenon increased after each hydrate stage. It also can be seen that the reactor pressure drastically reduces after each hydrate stage. For further purification of the gas, the pressure in the equilibrium cell for the succeeding hydrate stage needed to be above hydrate forming pressures. The inability to manually increase the pressure inside the equilibrium cell affected the number of possible hydrate separation stages for each experimental run. Thus, it can be observed from Table 5.7 that the maximum number of hydrate separation stages was 3. These were for experimental runs which had high initial pressures of 2.06 MPa, 2.17 MPa and 4.44 MPa.

Table 5.8 shows a summary of the concentration measurements for the systems studied, over single or several stages. The corresponding initial pressures for the measurements and the initial feed compositions are also reported.

Table 5.8: Summary of concentration measurements in the hydrate-based gas separation for systems of argon + krypton + xenon + water.

System ^a	$P_{feed} /$ MPa ^b	Final hydrate concentration ^b				Number of stages
		Ar	Kr	Xe	Xe+Kr	
Ar (0.16) + Kr (0.65) + Xe (0.19) + H ₂ O	0.840	0.07	0.58	0.36	0.93	1
Ar (0.41) + Kr (0.33) + Xe (0.26) + H ₂ O	0.714	0.13	0.23	0.61	0.84	1
	1.581	0.06	0.17	0.77	0.94	2
	2.060	0.02	0.12	0.86	0.98	3
Ar (0.21) + Kr (0.50) + Xe (0.29) + H ₂ O	2.174	0.14	0.42	0.44	0.86	1
	1.520	0.17	0.38	0.45	0.83	1
Ar (0.52) + Kr (0.34) + Xe (0.14) + H ₂ O	1.522	0.17	0.38	0.45	0.83	1
Ar (0.18) + Kr (0.16) + Xe (0.66) + H ₂ O	0.780	0.04	0.07	0.89	0.96	2
Ar (0.14) + Kr (0.16) + Xe (0.70) + H ₂ O	2.170	0.00	0.03	0.97	1.00	3
Ar (0.31) + Kr (0.25) + Xe (0.44) + H ₂ O	4.443	0.00	0.05	0.95	1.00	3

^aMole compositions are reported as mole fractions.

^bCombined expanded uncertainty, $U_c(\text{Composition}) = \pm 3.2\%$, $U_c(P_{exp}) = \pm 0.007$ MPa.

Notable results that were obtained, as shown in Table 5.8, where the increase of xenon concentration in the argon (0.14) + krypton (0.16) + xenon (0.70) mixture, from 70 mol% Xe

to 97 mol% Xe in 3 hydrate stages. Also, the increase of xenon concentration in the argon (0.31) + krypton (0.25) + xenon (0.44) mixture, from 44 mol% Xe to 95 mol% Xe in 3 hydrate stages. These results demonstrate a high degree of purification of the feed gas mixture after using the hydrate process.

The results presented in Tables 5.7 and 5.8 show that the concentration effect over a single hydrate separation stage decreased with an increasing number of separation stages. The highest concentration effect over a single hydrate stage, occurred for the argon (0.41) + krypton (0.34) + xenon (0.26) mixture from 26 mol% Xe to 63 mol% Xe at equilibrium temperature and pressure conditions of 272.2 K and 1.09 MPa. The composition data for this mixture were used in performing the economic evaluation of the hydrate process. The results presented in Tables 5.7 and 5.8 demonstrate that it is possible to concentrate and purify xenon from a gaseous mixture of xenon + argon + krypton mixture using the hydrate-based separation method.

5.8 Comparison of energy costs for distillation versus hydrate process

In order to assess the viability of a technology for industrial application, it is fundamentally important to perform an economic analysis of the proposed technology versus the current technology/ technologies used in the industry. This section presents a comparison of the heating and cooling utilities of a proposed hybrid-hydrate process with the conventional distillation process. The same feed conditions and final product specifications which were based on experimental measurements were used for comparison. This economic analysis only focuses on the heating and cooling requirements of the proposed and conventional processes. The capital and mechanical costs are not included as these can be assumed to be the same as that for the distillation process, based on the column and fittings required.

5.8.1 Heating and cooling energy requirement for the distillation process

A simulation of the conventional process for the separation and purification of xenon was done using Aspen Plus® V10. Figure 5.15 shows a process flow diagram for the distillation column. The Aspen Plus® V10 DSTWU column was used to obtain the initial column

specifications for the desired feed and product specifications. The DSTWU column has 16 trays with approx. 35 cm tray spacing. The tray pressure drop is assumed to be 0.0068 atm. The column specifications from the DSTWU simulation were then be applied for the initial settings when using the rigorous column design RADFRAC which calculates the temperature (T), pressure (P), liquid composition (x), vapour composition (y), vapour flow (V) and liquid flow (L) on every stage, thus giving a temperature, pressure and composition profile for the column. The total condenser was used so that a liquid product is obtained from the condenser. The design specification was to achieve a product composition of 99.995% Xe (Advanced Specialty Gases, 2018). The feed stage was set to be varied until the design purity is obtained. Tables 5.9 and 5.10 detail the initial design specifications for the simulated distillation column. Bubble cap trays were used as they allow low liquid flow rates which are applicable in this kind of column. The sections which follow explain the method in designing this purification column, from the selection of the property method to the final design specifications.

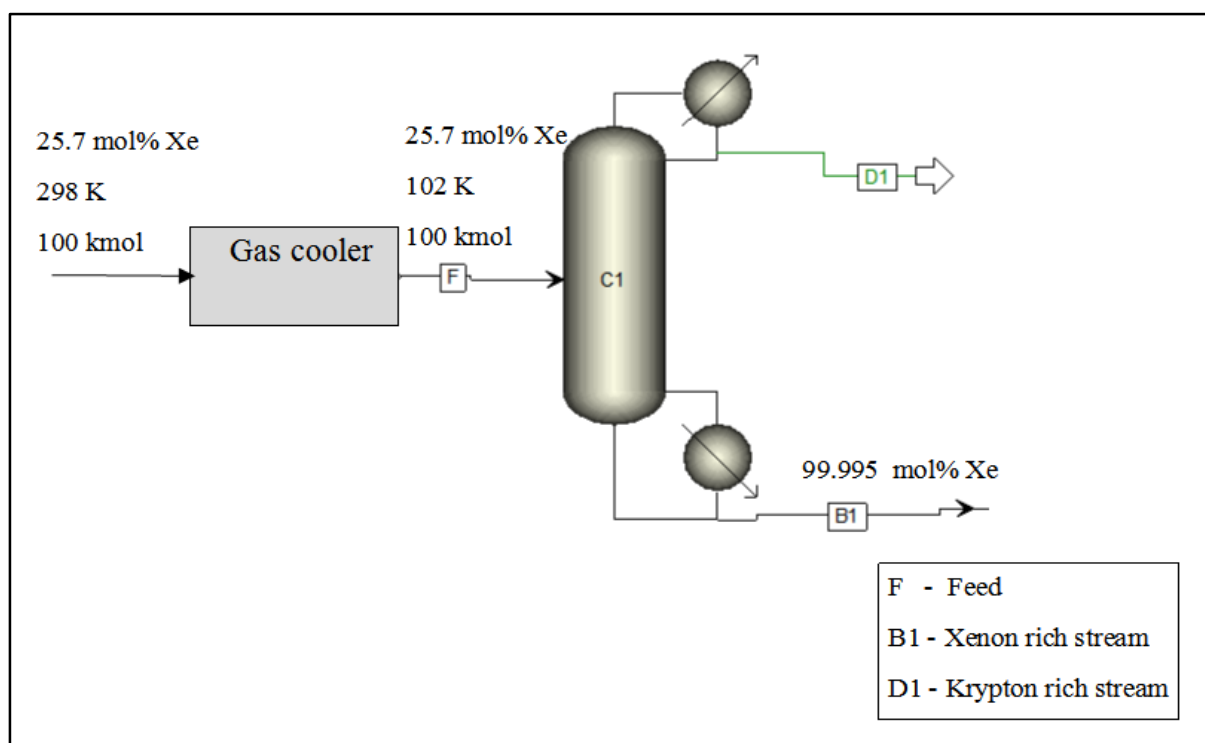


Figure 5.15: Aspen Plus® V10 steady-state simulation for the concentration of Xe from 25.7 mol% to 99.995 mol%.

Table 5.9: Initial RADFRAC distillation column specifications.

Specifications	Details
No. of trays	16
Feed stage	Variable
Type of tray	Bubble cap tray
Material of construction	Stainless steel

Table 5.10: Initial RADFRAC feed conditions and other design specifications.

Specifications	Details
Temperature (K)	102
Pressure (bar)	1.5
Molar flow (kmol/hr)	100
Xe mole fraction	25.7
Ar mole fraction	40.7
Kr mole fraction	33.6
Reflux ratio	1.5
Design specification	99.999 Xe

The initial column specifications and conditions were obtained from the initial DSTW simulation, which was used to input into the more rigorous RADFRAC simulation.

5.8.1.1 Property method selection

Selection of the appropriate property method for estimating properties is a vital stage in the design. The Peng-Robinson Equation of State (PENG-ROB) (Grady, 2012) property method was utilized in simulating an air separation processes by Bhunya (2014), Bose (2012) and Bian et al. (2005), and was used in this simulation. Xu et al., (2014) used the PRMHV2 (a modified Peng – Robinson equation) equations in simulating the distillation process when separating and concentrating carbon dioxide from a carbon dioxide laden gas stream with other gases such as H₂, N₂, O₂, Ar, and CH₄ from a purity of 80.0% to a purity of 99.9%. The PENG-ROB, PRWS (Peng Robinson Equation of State with the mixing rules of Wong and Sandler) and PSRK (Predictive Soave-Redlich-Kwong) models in ASPEN Plus® V10.0 were tested against the VLE experimental data (Allister, 1963) of the Kr + Xe and Ar + Kr systems to

evaluate and choose the best fitting model. Figure 5.16 shows the comparison of experimental and property method data for the Xe/Kr system.

The best-fitting model was chosen based on the percentage average absolute deviation (AAD%) from the VLE experimental data, calculated using the equation,

$$AAD\% = \frac{1}{N} \sum \frac{n_{exp} - n_{calc}}{n_{exp}} \times 100\% \quad (5.5)$$

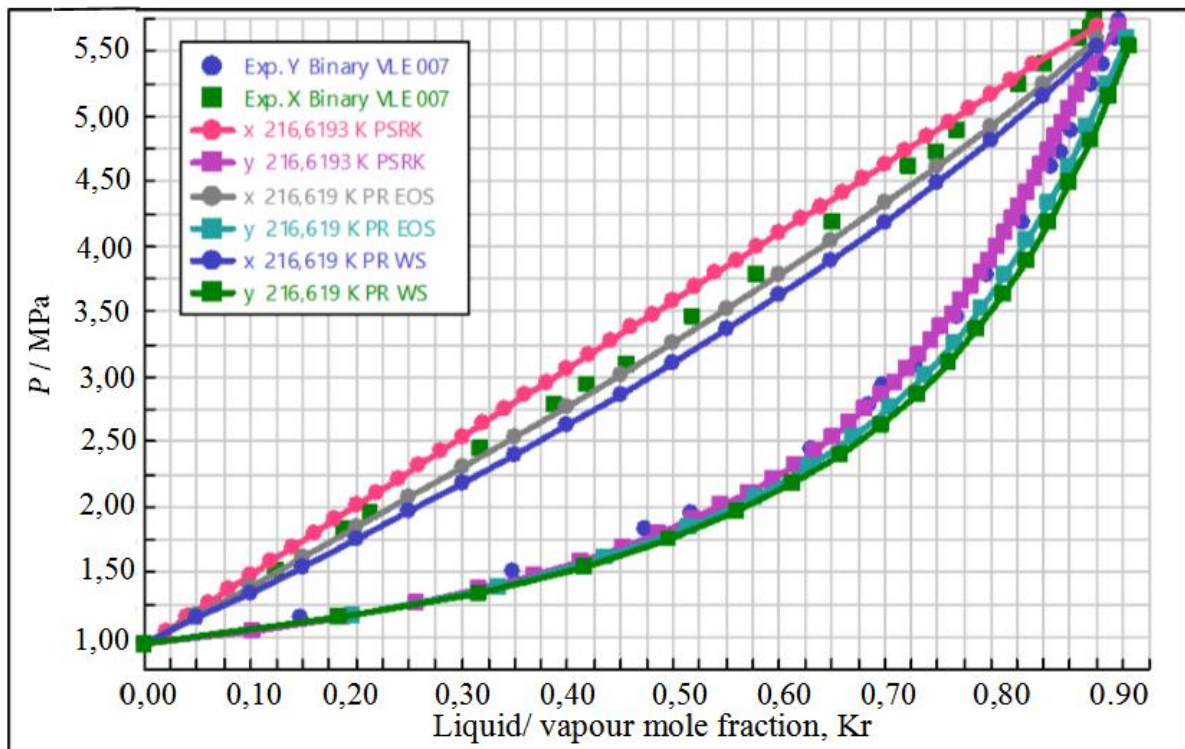


Figure 5.16: Comparison of experimental and property method data for the Xe/Kr system at 216.6 K using Aspen Plus® V10 to VLE - 007 data (Mastera, 1976).

Comparing the model results to the VLE-007 data set, the PR-EOS property method had the lowest combined % AAD of 2.65% compared to 3.77% for PRWS and 4.54% for the PSRK. Thus it was concluded that the PR-EOS was the most suitable property method to model the simulated system.

5.8.1.2 Column optimization

Selecting optimum column operating conditions is key to maximizing column operation and minimizing operational cost. In most distillation columns, the reboiler duty accounts for the major operating costs of the distillation column (Taqvi et al., 2016). The reboiler duty was optimized by varying the column feed stage, the minimum number of trays and the minimum reflux ratio whilst maintaining the design specification of 99.99% Xe (Luyben, 1999). Tables 5.11, 5.12 and 5.13 show the optimization for the minimum reflux ratio, minimum number of stages, condenser and reboiler duty.

Table 5.11: Optimization of minimum reflux ratio, R_{min} .

Total number of stages, N	Feed stage, N_{feed}	Reflux ratio, R	
9	5	0.666	
14	7	0.068	
16	8	0.056	
18	10	0.0457	$R_{min} = 0.457$
22	12	error	

Therefore Reflux ratio, $R = R_{min} \times 1.2 = 0.055$.

When optimizing for the minimum reflux ratio, the total number of stages and feed stage were varied until the smallest possible reflux ratio was achieved. The composition of Xe was set as the design specification, so that the quality of the product does not change. Using a common distillation economic heuristic, the minimum reflux ratio was then multiplied by 1.2 to obtain the design reflux ratio (Luyben, 1999). When optimizing for the minimum number of stages (N_{min}), the number of stages (N), and feed stage (N_{feed}), were lowered until the highest possible reflux ratio to determine the minimum number of stages. Using a common distillation economic heuristic, the minimum number of stages was then multiplied by 2 to obtain the design number of stages, N (Luyben, 1999).

Table 5.12: Optimization of the minimum number of stages, N_{min} .

Number of stages, N	Feed stage, N_{feed}	Reflux ratio, R	
15	9	0,122	
10	5	0.217	
9	4	0.996	
9	4	15.20	
8	3	390.2	$N_{min} = 8$
7	3	error	

Therefore, number of stages, $N = N_{min} \times 2 = 16$.

Table 5.13: Optimization of the reboiler (Q_R) and condenser (Q_C) duties.

Feed stage	Q_C / kW	Q_R / kW	Reflux ratio, R
3	2763.72	-2524.72	13.920
4	326.21	-289.22	0.606
5	250.76	-213.77	0.159
6	239.24	-202.25	0.091
7	235.20	-198.20	0.067
8	233.27	-196.28	0.056
9	232.22	-195.23	0.050
10	231.77	-194.77	0.047
11	233.05	-202.05	0.060
12	260.96	-228.96	0.226
13	450.46	-412.47	1.348
14	2206.22	-2103.23	10.859

According to the results in Table 5.11 and Table 5.12, the optimized value for the minimum reflux ratio and the minimum number of stages are obtained 0.457 and 8, respectively. As it can be observed in Table 5.13, feed stage 10 had the lowest reboiler duty, lowest condenser duty and lowest reflux ratio; thus, the optimum feed stage used for the column is stage 10.

Without considering heat integration, which is usually applied in industry, the utility load for the distillation column, as computed by Aspen Plus® V10 are shown in Table 5.14. These values shown are purely for assessing the utilities.

Table 5.14: Utility load for the distillation process based on a 100 kmol feed (25.7 to 99.995 mol %).

Duties	Utility load (kW)
Heating duty	231.0
Cooling duty	194.2
Total cooling + heating duty	425.2

The basis of calculation for this distillation process is 1 hour. Thus, from Table 5.14, the total energy load for a 100 kmol feed in 1 hour is,

$$Q_{distillation\ column} = \frac{425.2 \times 3600}{1000} \text{ MJ} \quad (5.6)$$

$$Q_{distillation\ column} = 1530.72 \text{ MJ}$$

5.8.1.2.1 Energy for gas cooler

The energy to cool the feed gas entering the column from 298 K to 102 K, to the required feed temperature, was calculated using the equation below for each gas mixture constituent. The coefficients for gas heat capacity that were used in the calculation are presented in Table 5.15.

$$Q_{gas\ cooler}(gas) = \Delta H = n_i \int_{272.25K}^{297.61K} C_p dT = n_i \left[aT + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4} - \frac{e}{T} \right]_{102.15}^{298.15} \quad (5.7)$$

where $C_p = a + bT + cT^2 + dT^3 + e/T^2$

n_i = number of moles of individual gas mixture constituent

C_p = heat capacity (J/mol*K)

T = Temperature in Kelvins / 1000

Table 5.15: Coefficients for the gas heat capacity (Chase, 1998)

Coefficient	Krypton	Argon	Xenon
<i>A</i>	20.78603	20.78603	20.78603
<i>B</i>	4.850638×10^{-10}	2.825911×10^{-7}	7.449320×10^{-7}
<i>C</i>	$-1.582816 \times 10^{-10}$	-1.494191×10^{-7}	-2.049401×10^{-7}
<i>d</i>	1.525102×10^{-11}	1.092131×10^{-8}	1.066661×10^{-8}
<i>e</i>	3.196347×10^{-11}	-3.661371×10^{-8}	2.500261×10^{-8}

The energy requirement for the gas cooler was calculated using the following equation:

$$Q_{gas\ cooler}(gas) = Q_{gas\ cooler}(Xe) + Q_{gas\ cooler}(Ar) + Q_{gas\ cooler}(Kr) \quad (5.8)$$

where, $n_{Xe} = 25720.1$ moles, $n_{Kr} = 33616.7$ moles and $n_{Ar} = 40663.2$ moles.

$$\begin{aligned} Q_{gas\ cooler}(gas) &= [(-104.6) + (-165.3) + (-136.7)] \text{ kJ} \\ &= -0.41 \text{ MJ} \end{aligned}$$

5.8.1.2.2 Total heating and cooling requirement for the conventional distillation process

Without considering heat integration, which is usually applied in industry, the heating and cooling load for the distillation process was calculated as follows:

$$\begin{aligned} Q_{distillation\ process} &= Q_{gas\ cooler} + Q_{distillation\ column} \quad (5.9) \\ Q_{distillation\ process} &= 0.41 \text{ MJ} + 1530.72 \text{ MJ} \\ &= 1530.4 \text{ MJ} \end{aligned}$$

Based on the simulation using Aspen Plus® V10, the heating and cooling energy required to increase the concentration of a 100 kmol feed with composition 25.7 mol% to 99.995 mol% using the distillation process is 1530.4 MJ. Capital costs for the precooler and the distillation column are not included in this calculation.

5.8.2 Energy requirement for the hydrate-hybrid process

The hybrid process consists of the hydrate reactor, a gas cooler and a distillation column. The feed conditions for the process and calculations were chosen based on the experimental measurements. In the experimental measurements, the highest concentration effect occurred for the argon (0.41) + krypton (0.34) + xenon (0.26) mixture from 25.7 mol% Xe to 63.3 mol% Xe over one hydrate stage. The conditions at which this concentration effect were achieved, were used when performing the energy analysis calculations, including the Aspen Plus® V10 simulation for the distillation process presented in Section 5.8.1 above.

The hybrid process was chosen as an alternative process based on the results obtained in Section 5.7 above. It was observed that as the number of hydrate stages increased, the concentration effect over one hydrate stage, drastically decreased. More hydrate stages would increase the concentration but at a higher cost, because of the much-reduced concentration effect as concentration increases. It was then proposed to use the distillation column to further increase the concentration of the product from the one hydrate reactor stage to the desired value. This would drastically reduce the energy load for the distillation process since the feed, the product from the 1 stage hydrate process, would have a very high xenon concentration. In the proposed hybrid process, the hydrate reactor increases the concentration of xenon from 25.7 to 63.3 mol%, the gas cooler decreases the temperature of the feed gas from 298 K to 102 K (the required feed temperature for the distillation column) and the distillation column then concentrates the xenon to 99.99%. Figure 5.17 shows the block diagram for the hybrid process, and Figure 5.18 shows the conceptual design for the hybrid process.

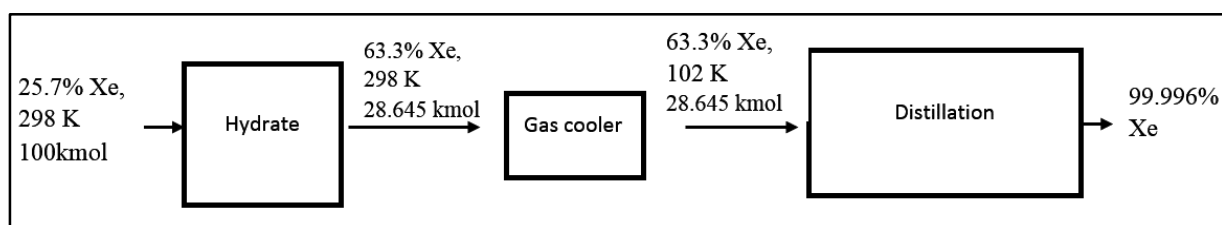


Figure 5.17: Block diagram for the proposed hybrid hydrate process.

From the experimental results, it was decided to select the data set showing the largest concentration-effect over one hydrate stage. As already stated, it was assumed that the capital costs for a hydrate reactor and distillation column is similar, thus the economic evaluation is based on heating and cooling loads only. The ideal gas behaviour was used to model the gas phase. The energy required for this hybrid process was calculated using energy balances, and the calculation only considers the heating and cooling requirements for hydrate formation and dissociation.

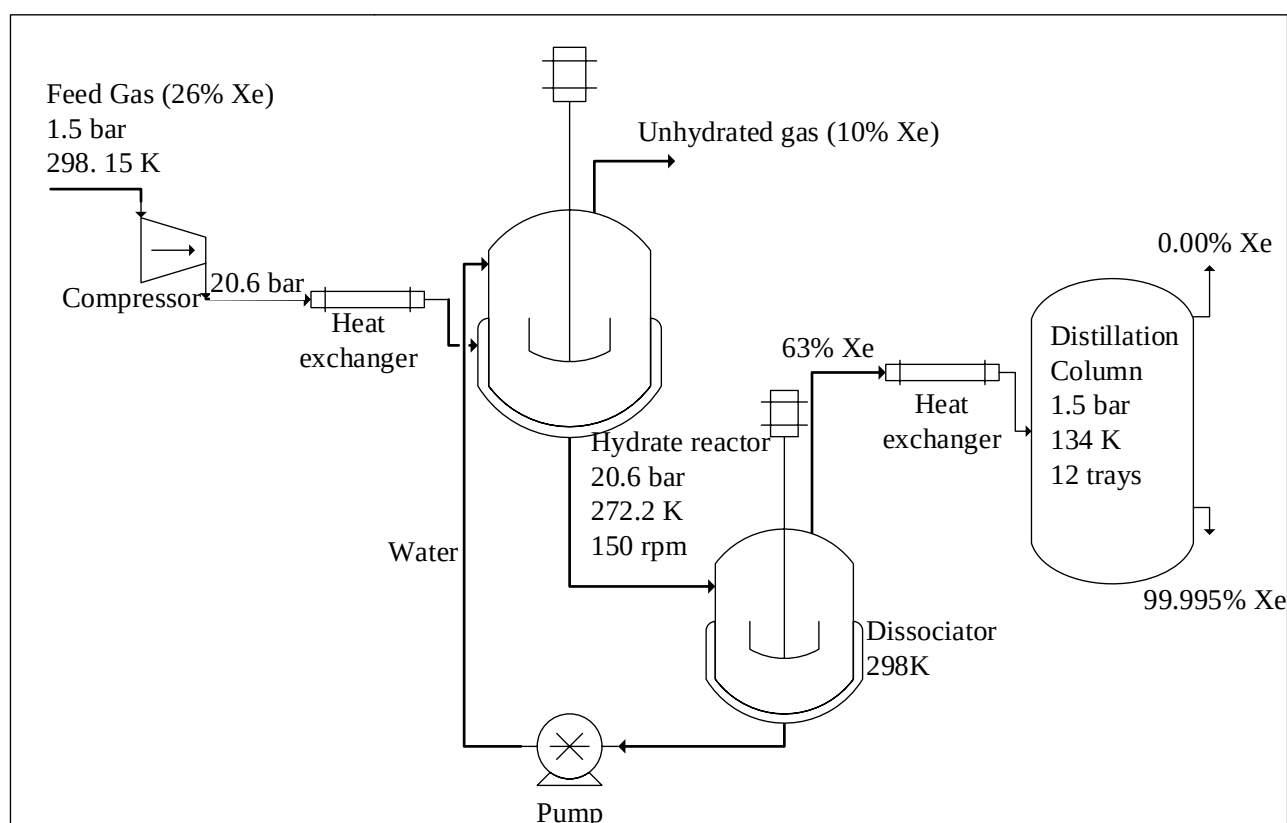


Figure 5.18: Conceptual design for the hydrate hybrid process for concentrating xenon from 25.7 to 99.995 mol %.

5.8.2.1 Process description

The preliminary energy calculations presented in this sub-section are based on the laboratory scale experiments. The energy requirement for the lab-scale hydrate cell was evaluated before scaling up the calculation to feed conditions similar to the simulated distillation column in Section 5.8.1 above.

For the laboratory scale hydrate reactor, the feed gas was at a temperature and pressure of 298.15 K and 1.5 bar, respectively and the hydrate reactor operated at a pressure of 2.06 MPa and temperature 272.16 K. Thus, the feed gas mixture (0.028 mol) of composition 26 mol% Xe, 41 mol% Ar and 33 mol% Kr, was pressurized to the hydrate reactor operating pressure. There was also need to cool the feed gas and water to the operating conditions as well as maintain an operating temperature of 272 K. The hydrate crystals formed in the hydrate reactor were heated in the dissociator to dissociate the hydrate and release the product gas. For the calculations and in estimating the energy usage, a chiller and temperature bath with a 50% water and 50% ethyl glycol mixture were used to cool and maintain cell conditions. The following equation was used to compute the energy requirement for the hydrate process:

$$Q_{total} = Q_{heat\ exchange} + Q_{hydrate\ formation} - Q_{dissociator} + Q_{chilling\ unit} \quad (5.10)$$

The heat exchanger cools the feed gas mixture from ambient temperature (298.1 K) to the operating temperature of 272.15 K. When calculating the energy for cooling this feed mixture, coefficients for gas heat capacity stated in Table 5.15 were used with Equation 5.7 where:

$$Q_{heat\ exchange}(gas) = \Delta H = n_i \int_{272.25K}^{297.61K} C_p dT = n_i \left[aT + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4} - \frac{e}{T} \right]_{272.15}^{298.15}$$

where $C_p = a + bT + cT^2 + dT^3 + e/T^2$

n_i = number of moles of individual gas mixture constituent

C_p = heat capacity (J/mol*K)

T = Temperature in Kelvins /1000

The number of moles (n_i) of each gas in the cell was calculated using the ideal gas equation, and the gas mixture was composed 0.007 moles of xenon, 0.009 moles of krypton and 0.011 moles of argon. The heating and cooling energy requirement for the heat exchanger was calculated for each gas mixture constituent and summed up using the following equation:

$$Q_{\text{heat exchanger}} = Q_{\text{heat exchanger}}(\text{Xe}) + Q_{\text{heat exchanger}}(\text{Ar}) + Q_{\text{heat exchanger}}(\text{Kr}) \quad (5.11)$$

$$\begin{aligned} Q_{\text{heat exchanger}} &= [(-3.78) + (-5.98) + (-4.94)] \times 10^{-6} \text{ kJ} \\ &= -14.69 \times 10^{-5} \text{ kJ} \end{aligned}$$

5.8.2.2 Calculating energy for hydrate formation

Hydrate formation is an exothermic reaction. The heat energy generated at hydrate formation needs to be accounted for, and it is calculated using the following equation:

$$Q_{\text{hydrate formation}} = \text{mass of hydrate formed} \times \Delta H_{\text{hydrate formation}} \quad (5.12)$$

The enthalpy of hydrate formation was only calculated for the argon (0.40) + krypton (0.34) + xenon (0.25) mixture as the experimental results from this mixture were chosen for energy evaluation since the results for this mixture showed the highest concentration-effect over one hydrate stage. The compressibility factor, Z , was assumed to be 1 since the gas mixture was assumed to behave ideally. The gradient, $\frac{d \ln(P)}{d \left(\frac{1}{T}\right)}$, of the curve of $\ln(P/\text{MPa})$ vs $\frac{1}{T}$, presented in Figure 5.12 for the argon (0.40) + krypton (0.34) + xenon (0.25) mixture was calculated to be -7216.3. The equation below was then used to calculate the enthalpy of hydrate formation as follows:

$$\begin{aligned} \Delta H_{\text{hydrate formation}} &= -RZ \frac{d \ln(P)}{d \left(\frac{1}{T}\right)} \quad (5.13) \\ &= -8.314 \times 1 \times -7216.3 \\ &= 59.996 \text{ kJ/mol} \end{aligned}$$

The mass of hydrate formed was determined from the model (refer to Section 2.3), which was developed by Dr. S. Babaei. According to the model calculation, the number of water molecule in the hydrate phase, $n_{w,H}$, is 0.0478, which is equal 0.859 cm³ or 0.0477 moles of water.

Equation 5.12 was used to calculate the energy required for hydrate formation as follows:

$$Q_{hydrate\ formation} = mass\ of\ hydrate\ formed \times \Delta H_{hydrate\ formation}$$

$$\begin{aligned} Q_{hydrate\ formation} &= 0.0477\ mol \times 59.996\ kJ.\ mol^{-1} \\ &= 2.86\ kJ \end{aligned}$$

5.8.2.3 Heat in chiller

The temperature bath that houses the hydrate reactor has to be cooled from ambient temperature to the reactor operating temperature and also maintained at that temperature for the duration of the experiment. The water bath (SS 316L dimensions 43 cm x 35 cm x 26 cm) which was filled to 70% of capacity was used (25.30 litres) in the experiment; this bath was used to maintain the temperature of the hydrate cell of dimensions. To determine the energy required for the chiller, the following equation was used.

$$Q_{chiller} = Q_{liquid\ bath} - Q_{heat\ flux} \quad (5.14)$$

The specific heat capacity (C_p) of the liquid bath was assumed to be 4.158 kJ/kg as the ethyl glycol was only used to prevent the freezing of the water. The energy required to cool the bath from ambient temperature to operating temperature was calculated as follows:

$$\begin{aligned} Q_{liquid\ bath} &= m \times C_p \times \Delta T \\ &= 25\ kg \times \left(\frac{4.158\ kJ}{kg} \right) \times (-1 - 25) \\ &= -2636.2\ kJ \end{aligned} \quad (5.15)$$

To calculate the energy requirement for maintaining the temperature of the bath at -1 °C, the heat transfer coefficient for the SS 316L reactor walls was determined as shown below. The conduction heat transfer coefficient (K) for SS 316L is 0.023 W.m⁻¹.K⁻¹.

$$\begin{aligned} U &= \frac{K}{L} \\ &= \frac{0.023}{0.01} = 2.3\ W.\ m^{-2}.\ K^{-1} \end{aligned} \quad (5.16)$$

where L and K are the thickness and conduction heat transfer coefficient, respectively.

$$\begin{aligned}
 Q_{heat\ flux} &= UA\Delta T \\
 &= 2.3\ \text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1} \times 0.0239\ \text{m}^2 \\
 &\quad \times (298.15 - 272.15)\ \text{K} \\
 &= 1.39 \times 10^{-6}\ \text{kW}
 \end{aligned} \tag{5.17}$$

The hydrate formation process took approximately 3 hrs; thus, using Equation 5.14, the energy required by the chiller to reduce the temperature to operating conditions and maintain the bath temperature is:

$$\begin{aligned}
 Q_{chiller} &= (-2636.2 - 3 \times 3600 \times 1.39 \times 10^{-6})\ \text{kJ} \\
 &= -2636.19\ \text{kJ}
 \end{aligned}$$

It is assumed that the amount of energy needed for hydrate dissociation is the same as the amount of energy consumed at hydrate formation as the mass of hydrate formed is the same as the mass of hydrate dissociated. Thus, the heating and cooling energy requirement of the experimental hydrate process is then calculated as follows:

$$\begin{aligned}
 Q_{total} &= Q_{heat\ exchanger} + Q_{hydrate\ formation} - Q_{dissociator} + Q_{chiller} \\
 &= -14.69 \times 10^{-5}\ \text{kJ} + 2.86\ \text{kJ} - 2.86\ \text{kJ} - 2636.19\ \text{kJ} \\
 &= -2636\ \text{kJ}
 \end{aligned} \tag{5.18}$$

5.8.2.4 Scale-up of the hybrid hydrate process

5.8.2.4.1 Hydrate reactor

As stated earlier, the calculations presented above are for a laboratory-scale experiment with a feed gas of 0.028 mol of feed gas. For comparison purposes, the calculation was scaled up to match the 100 kmol feed flowrate for the distillation process. The ratio of moles of feed gas to moles of water that formed hydrate was used as a basis for the scale-up. This ratio was 0.028 moles of feed gas: 0.0477 moles of hydrate formed (see Section 2.3). For a feed of 100 kmol:

$$\begin{aligned}
 \text{Number of moles of hydrate forming water} &= \frac{100\ 000 \times 0.048}{0.028} \\
 &= 171\ 189.5\ \text{mol}
 \end{aligned} \tag{5.19}$$

The procedure and calculations used in evaluating the energy requirement for the experimental hydrate process were used to evaluate the energy requirement for the scaled-up process.

For the scaled-up process, the total heat energy requirement for the hydrate process is:

$$\begin{aligned}
 Q_{total} &= Q_{heat\ exchanger} + Q_{hydrate\ formation} - Q_{dissociator} + Q_{chiller} \quad (5.20) \\
 &= -53\ \text{kJ} + 10\ 270\ 738\ \text{kJ} - 10\ 270\ 738\ \text{kJ} - 332\ 928.7\ \text{kJ} \\
 &= -333.0\ \text{MJ}
 \end{aligned}$$

5.8.2.4.2 Gas cooler

The energy required to cool the product from the hydrate reactor to the operating conditions for the distillation column was calculated as shown below. The initial temperature was 298.15 K, and the final temperature was 102 K. The feed (the product from the hydrate reactor with a xenon concentration of 63.3 mol%) for the gas cooler had 28.645 kmol of gas.

$$\begin{aligned}
 Q_{gas\ cooler}(gas) &= Q_{gas\ cooler}(Xe) + Q_{gas\ cooler}(Ar) + Q_{gas\ cooler}(Kr) \quad (5.21) \\
 Q_{gas\ cooler}(gas) &= 74\ \text{kJ} + 11\ \text{kJ} + 31\ \text{kJ} \\
 &= 0.12\ \text{MJ}
 \end{aligned}$$

5.8.2.4.3 Distillation column used in the hybrid-hydrate process

Another component of the hybrid process is the distillation column for purifying the product from the hydrate process from a concentration of 63.3 mol% Xe to 99.995 mol% Xe. The column used here was designed as outlined in Section 5.8.1 above. The reboiler and condenser utilities for this distillation column was computed using Aspen Plus® V10 simulation software and Table 5.17 shows the computed energy values for this column.

Table 5.16: Energy requirements for the distillation column (63 to 99.995 mol %).

Duties	Utility load (kW)
Heating duty	153.59
Cooling duty	104.73
Total cooling + heating duty	258.3

Feed quantity = 28.645 kmol, feed temperature = 298 K.

The basis of calculation for this distillation process is 1 hour. Thus, from Table 5.16, the total energy load for a 28.645 kmol feed in 1 hour is,

$$Q_{distillation\ column} = \frac{258.3 \times 3600}{1000} \text{ MJ} \quad (5.22)$$

$$Q_{distillation\ column} = 929.88 \text{ MJ}$$

The heating and cooling energy consumption for the hybrid process was then calculated as follows:

$$\begin{aligned}
 Q_{total, hybrid\ process} &= Q_{hydrate\ reactor} + Q_{cooler} + Q_{distillation\ column} \quad (5.23) \\
 &= 333 \text{ MJ} + 0.12 \text{ MJ} + 929.88 \text{ MJ} \\
 &= 1263.1 \text{ MJ}
 \end{aligned}$$

In summary, the heating and cooling energy required to increase the concentration of a 100 kmol feed gas with a xenon concentration of 25.7 mol% to 99.99 mol% using the proposed hybrid process is 1263.1 MJ. The energy required for the hybrid process is 17.5 % less than the energy required by the conventional distillation process (1530.4 MJ). These energy values are based on preliminary utility calculations that did not account for capital costs, but they provide an important demonstration of the possible use of the proposed hybrid process as an alternative to distillation. Moreover, the operating pressure for the proposed process hybrid is high, therefore the cost for design of the reactor(s) and the operation would be high, thus increasing the cost. In this calculation, these were not factored in the calculation as this work is a preliminary design and based on cooling and heating utilities. It is assumed that the capital costs for the distillation columns, internals, reboiler and condenser would be comparable to a high pressure reactor operating as a hydrate formation unit. A more rigorous evaluation would

be needed for further scrutiny into industrial applications. A summary of the assessment is presented in Table 5.18.

A basis of 1 hour was chosen based on the design feed rate of the distillation column. For a logical comparison, the same feed quantities were used as the basis for both the distillation and the hybrid hydrate process. As such, a basis of 1 hour for the distillation column ensured that the amount of feed gas separated by distillation is 100 kmol, the same quantity to be separated using the hybrid process calculation.

Table 5.17: Overview of the distillation and hydrate processes.

Technology	Components	Concentration (mol%)	Energy input (MJ)	<i>P</i> (MPa)	<i>T</i> (K)
Distillation process	Gas cooler +distillation column	25.7% Xe to 99.99% Xe	1530.4	0.15	102
Hydrate hybrid process	Hydrate + gas cooler + distillation column	25.7% Xe to 99.99% Xe	1263.1	2.06	272

The energy calculations done for the proposed hybrid process are preliminary, no pinch analysis or energy integration processes were applied. In contrast, the conventional distillation process has been in existence for a long time and has undergone a lot of improvement and is highly optimized, thus resulting in lower energy requirements. The primary consumer of energy with the hydrate process is the cooling of the hydrate reactor. With a more rigorous, optimized and effective energy integration system, the energy needed to cool the hydrate reactor may reduce drastically. This would result in a further reduction of the energy required for the proposed hybrid process. Furthermore, the calculations were based on unoptimized lab-scale experiments with various simplifications and assumptions. Other factors such as the use of hydrate promoters and optimized operating conditions of pressure and temperature can further improve the efficiency of the system.

In summary, the proposed hybrid hydrate process demonstrates potential as an alternative to the distillation process, but more research is needed.

6

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

This study aimed to determine the feasibility of separating xenon from the ternary mixtures of (Xe + Kr + Ar) using gas hydrate technology as an alternative technology to the energy-intensive distillation process. Thermodynamics plays an essential role in the development of economical and sustainable technology. The non-visual isochoric pressure search method was used in the experimental work carried out in this study because of its reliability and accuracy.

A test system of carbon dioxide + water system was used to test the reliability of the equipment that was used and show the consistency of the results obtained using the equipment. Hydrate phase equilibrium data at three pressures of 2.21 MPa, 3.58 MPa and 4.52 MPa were obtained for the system of carbon dioxide + water and compared against thermodynamic dissociation data reported in the literature. The excellent agreement between the measured and literature data confirmed that the apparatus and procedure for this experiment were reliable. The instruments that were used to measure temperature, pressure and composition were calibrated and the calibrations were verified.

Novel hydrate phase equilibrium data are reported for the gas mixture of argon + krypton + xenon. The standard uncertainty in temperature and pressure values were ± 0.1 K and ± 0.01 MPa, respectively. As the amount of Xe in the mixture of Ar + Kr + Xe was increased, the

equilibrium curve for the mixture of Ar + Kr + Xe shifted towards the higher temperatures and lower pressures, indicating the higher dissociation conditions needed for mixtures with high xenon composition.

The experimental hydrate data was modelled to confirm that the experimental results corresponded to the model that was generated. A maximum absolute relative deviation of 1.4% between experimental results and model predictions was obtained, thereby demonstrating a reasonable agreement.

Novel compositional analysis data was also obtained for the system of argon + krypton + xenon. The standard uncertainty in composition was $\pm 3.2\%$. Data obtained for the argon (0.14) + krypton (0.16) + xenon (0.70) mixture showed a xenon concentration increase from 70 mol% Xe to 97 mol% Xe in 3 hydrate stages. Data obtained for the argon (0.31) + krypton (0.25) + xenon (0.44) mixture also showed a xenon concentration increase from 44 mol% Xe to 95 mol% Xe. An increase in the number of hydrate stages decreased the concentration effect, and the highest concentration effect was for the mixture argon (0.41) + krypton (0.34) + xenon (0.26) where the molar concentration of xenon increased from 26% to 63% in one hydrate stage.

To assess the applicability of gas hydrate technology as an alternative for noble gas separation to the conventional distillation process, an economic analysis of a proposed gas hydrate process was done in comparison to the conventional distillation process using the same initial conditions of pressure and temperature and composition, mixture argon (0.41) + krypton (0.34) + xenon (0.26). Simulation of a distillation column was performed using the PR EOS. The economic analysis was only based on energy requirements. The hybrid process was evaluated to use 1263.1 MJ, whereas the distillation process was evaluated to use 1530.4 MJ thereby showing that the hybrid process used 17.5% less energy. This study demonstrated that the proposed hydrate based process is a viable alternative to the distillation process.

6.2 Recommendations

As a continuation of this work, various measurements can be considered.

- i. Further experimental work to determine the hydrate formation and dissociation conditions for a broader range of xenon concentrations in the Ar + Kr + Xe mixtures to have a better understanding of the thermodynamic behaviour of the mixture.
- ii. Further experimental work to determine the effect of pressure, temperature, mixing speed, and hydrate promoters as TBAB and SDSS on the kinetics of hydrate formation and dissociation conditions and/or induction time, as these factors are useful when scaling up to pilot scale and ultimately industrial scale. Optimisation of these factors may possibly further reduce the energy costs of the process

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APPENDIX A

A. Estimation of experimental uncertainties

For a measured value to be considered as accurate, it has to be accompanied by the respective uncertainty. The uncertainty in a measurand is caused by the error in the instruments used and random errors caused by the experimenter. A measured variable should be quoted with the respective uncertainty so that when the measurement is repeated, the data point obtained should be within the acceptable stated interval (Taylor, 2009). In this work, uncertainties for temperature, pressure and composition were computed as per the National Institute of Standards and Technology (NIST) guidelines. The approach recognises the uncertainty of non-negligible possible components of uncertainty which are grouped into Type A and Type B (Taylor and Kuyatt, 1994). The contributing factors to the combined standard uncertainty are the standard uncertainty in the measuring instrument (temperature probe, pressure transducer, and mass balance), the uncertainty of the calibration curves and the deviations due to repeated measurements. The method followed in this work utilises the procedure of Raal and Mühlbauer (Raal and Mühlbauer, 1998), where the combined uncertainty is the root-sum square of the individual contributing uncertainties.

The equation used for calculating the combined standard uncertainty is

$$u_c(x_i) = \pm \sqrt{\sum_i u_c(x_i)^2} \quad (\text{A.1})$$

Where $u_c(x)$ is defined as the standard uncertainty in (x) , $u_c(x_i)$ represents contributing uncertainties, and i represents component i .

Equation A.1 is expanded into the equation:

$$u_c(x_i) = \pm \sqrt{u_{\text{calibration}}(x_i)^2 + u_{\text{repeatability}}(x_i)^2} \quad (\text{A.2})$$

In Equation A2, the uncertainty due to the random errors, $u_{\text{repeatability}}(x)$ (Type A) is determined using the equation:

$$u_c(x_i) = \pm \frac{\sigma}{\sqrt{N_{rp}}} \quad (\text{A.3})$$

Where σ and N_{rp} represent the standard deviation and represents the number of repeated data points, respectively.

When the combined standard uncertainty components are classified as Type B, they will be considered to have an equal likelihood of residing anywhere within the distribution and are evaluated as follows:

$$u_i(x) = \frac{b}{\sqrt{3}} \quad (\text{A.4})$$

In this work, the value of b was set to be the maximum error in the polynomial.

A.1 Temperature and pressure uncertainty

The following equation was used to determine the combined standard uncertainty in temperature:

$$u_c(T) = \pm \sqrt{u_{\text{correlation}}(T)^2 + u_{\text{repeatability}}(T)^2 + u_{\text{standard}}(T)^2} \quad (\text{A.5})$$

Where $u_{\text{correlation}}(T)$ is the standard uncertainty due to the calibration polynomial and $u_{\text{standard}}(T)$ is the standard uncertainty of the standard temperature probe. Both uncertainties are classified as Type B. Values of the instrument error on the temperature and pressure probes used were 0.03 K and 0.05% of the full range of the pressure sensor, respectively as stated by WIKA.

The standard uncertainty in pressure was also evaluated in a similar manner, using the correlation:

$$u_c(P) = \pm \sqrt{u_{correlation}(P)^2 + u_{repeatability}(P)^2 + u_{standard}(P)^2 + u_{atm}(P)^2} \quad (A.6)$$

Where the standard uncertainties in (i) calibration polynomial, (ii) standard pressure transducer, (iii) barometer and (iv) repeatability are represented by $u_{correlation}(P)$, $u_{standard}(P)$, $u_{atm}(P)$, $u_{repeatability}(P)$ respectively.

All the uncertainty components were classified as Type B, with the exception of the standard uncertainty in repeatability.

Composition uncertainty

The contributing factors to the combined standard uncertainty in molar composition are the errors arising from the TCD calibration and from averaging values of repeated measurements. The combined standard uncertainty is given by Equation A.2:

In this study, $\sigma = 0.0189$; therefore:

$$\begin{aligned} u_{repeatability}(x) &= \pm \frac{0.0189}{\sqrt{5}} \\ &= 0.0085 \end{aligned}$$

In calculating, $u_{calib}(x_i)$, the use of the mass balance results in uncertainties in the preparation of the gas mixtures. Calibration of the TCD using Equation 4.1 results in errors (u_{corr}) in the correlations generated to link the ratio of areas generated by the GC ($\frac{A_i}{A_j}$) to the ratio of molar composition ($\frac{x_i}{x_j}$). Thus, the calibration error is determined using the equation;

$$u_c(x_i) = \pm \sqrt{u_{repeatability}(x_i^2) + u_{correlation}(x_i^2)} \quad (A.7)$$

Where $u_{correlation}(x_i)$ is given by:

$$u_{correlation}(x_i) = x_i \frac{\left| \frac{x_{iTrue} - x_{icalculated}}{x_{iTrue}} \right|_{maximum}}{\sqrt{3}} \quad (A.8)$$

$$u_{correlation}(x_i) = \frac{\left(\frac{0.22453 - 0.21927}{0.22453} \right)}{\sqrt{3}} = 0.01353 \quad (A.9)$$

This method for estimation of $u_{correlation} x_i$ was adopted from the work of (Nelson, 2012) and the values for determining $u_{correlation} x_i$ were obtained from the work presented in Figure 5.7.

$u_{balance}(x_i)$ is determined using the equation;

$$u_{balance}(x_i) = \sqrt{\left[\left(\frac{dx_i}{dm_1} \right) \cdot u(m_1) \right]^2 + \left[\left(\frac{dx_i}{dm_2} \right) \cdot u(m_2) \right]^2 + \left[\left(\frac{dx_i}{dm_3} \right) \cdot u(m_3) \right]^2} \quad (A.10)$$

Where,

$$x_1 = \frac{\frac{m_1}{M_1}}{\left(\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3} \right)} \quad (A.11)$$

$$\frac{dx_1}{dm_1} = \frac{1}{M_1 \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3} \right)} - \frac{m_1}{M_1^2 \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3} \right)^2} \quad (A.12)$$

$$\frac{dx_1}{dm_2} = - \frac{m_1}{M_1 M_2 \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3} \right)^2} \quad (A.13)$$

$$\frac{dx_1}{dm_3} = - \frac{m_1}{M_1 M_3 \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3} \right)^2} \quad (\text{A.14})$$

As a consequence of that, the masses of the gases added to make the mixture were measured using the same balance, $u(m_1) = u(m_2) = u(m_3)$.

$$u(m_i) = \frac{b}{\sqrt{3}} \quad (\text{A.15})$$

Where b is the width of the interval. In this work $b = 0.03\text{g}$ (the precision of the mass balance as stated by the manufacturer).

Thus, $u(m_i) = \frac{0.03}{\sqrt{3}} = 0.0173$

Solutions to Equations A.11, A.12, A.13, A.14 and A.15, are then substituted into Equation A.10 to determine $u_{bal}(x_i)$. Equation A.2 was then used to determine the combined standard uncertainty, $u_c(x_i)$.

The sources of uncertainties (instrument, repeatability, correlation) and the deviation estimates for each source that contributed to the combined standard uncertainty for temperature, pressure and composition were reported in Table 5.3.

Reporting the uncertainties

The overall uncertainty in the pressure, temperature and composition were reported in this study in terms of expanded uncertainty $U(x)$, which is expressed as:

$$U(x) = k \cdot u_c(x) \quad (\text{A.15})$$

Where k is the coverage factor and $u_c(x)$ is the combined standard uncertainty, $u_c(x)$ incorporates all sources of uncertainty/deviation in the values. A confidence interval of 95% was used, and this corresponds with using a coverage factor = 2 for all measurements.

Table A.1: Compositional uncertainty calculation

	Component	Mass (m_i)	Moles (n_i)	Mole frac (x_i)	dx₁ /dm₁	dx₁ /dm₂	dx₁ /dm₃	u_{mi}	u_{bal}	u_{corr}	u_{calib}	u_{rep}	u_c(x)	U(x)
Mix 1	Ar (1)	1.010	0.012	0.101	0.166	-0.021	-0.014	0.017	0.0029	0.0135	0.0138	0.0085	0.0162	0.0323
	Kr (2)	7.007	0.084	0.703				0.017						
	Xe (3)	3.055	0.023	0.196				0.017						
Mix 2	Ar (1)	3.225	0.081	0.431	0.076	-0.027	-0.017	0.017	0.0014	0.0135	0.0136	0.0085	0.0160	0.0321
	Kr (2)	5.045	0.060	0.321				0.017						
	Xe (3)	6.110	0.047	0.248				0.017						
Mix 3	Ar (1)	1.753	0.044	0.213	0.096	-0.012	-0.008	0.017	0.0017	0.0135	0.0136	0.0085	0.0161	0.0321
	Kr (2)	8.622	0.103	0.500				0.017						
	Xe (3)	7.760	0.059	0.287				0.017						
Mix 4	Ar (1)	2.313	0.058	0.523	0.108	-0.056	-0.036	0.017	0.0022	0.0135	0.0137	0.0085	0.0161	0.0322
	Kr (2)	3.100	0.037	0.333				0.017						
	Xe (3)	2.098	0.016	0.144				0.017						
Mix 5	Ar (1)	0.680	0.017	0.154	0.192	-0.017	-0.011	0.017	0.0033	0.0135	0.0139	0.0085	0.0162	0.0324
	Kr (2)	1.410	0.017	0.152				0.017						
	Xe (3)	10.075	0.077	0.694				0.017						

A combined expanded uncertainty of 3.2% for composition was obtained from mixture 5 (15.4%Ar + 15.2%Kr + 69.4% Xe). This value of uncertainty was used when quoting compositions as it was the highest possible composition uncertainty obtained

APPENDIX B

B. Validation of the TCD calibrations

The initial calibrations for gas mixtures were validated by performing calibrations using pure gases. The direct injection technique was used to calibrate the TCD of the Shimadzu GC-2014. The 50 μl and 250 μl gas tight syringes were used to inject known volumes of pure gases into the GC and the peak areas produced by the GC were used to produce calibration polynomials. The micro-litre syringes are open systems, it then is assumed that the ambient conditions recorded at the exit nozzle of the gas cylinder are representative of the pressure and temperature of the syringe contents (Nelson, 2012, Williams-Wynn, 2016). The ambient temperature at the gas sampling point was measured via a thermometer while the ambient atmospheric pressure was measured by the internal barometer of a Mensor CPC 3000 pneumatic high-speed pressure controller. The ideal gas equation was used to calculate the number of moles of gas in the syringe that were injected into the GC. The peak areas obtained as a response from the GC were used with the actual number of moles were used to calculate values of $\frac{A_i}{A_j}$ and $\frac{y_i}{y_j}$. $\frac{y_i}{y_j}$ was calculated using the equation;

$$\frac{y_i}{y_j} = \frac{n_i}{n_j} \quad (\text{B.1})$$

Graphs of $\frac{A_i}{A_j}$ vs $\frac{y_i}{y_j}$ for pure gases were drawn and compared to the graphs of $\frac{A_i}{A_j}$ vs $\frac{y_i}{y_j}$ for gas mixtures.

Figure B.1 and Figure B.2 show the superimposed calibration polynomials for pure gas calibrations and for gas mixtures calibrations. The linear plots for gas mixture calibrations were extrapolated to cover the range of values produced by the pure gases. The calibrations curves show a reasonable agreement between each other; thus, it was concluded that the gas mixture calibrations, that were used, were valid.

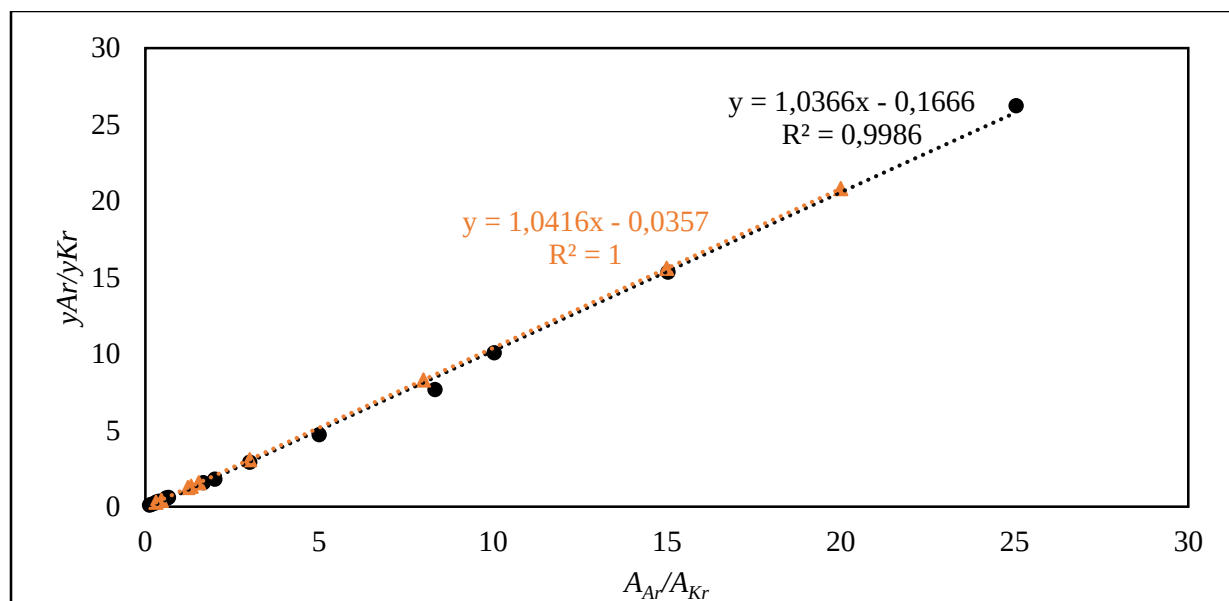


Figure B.1: GC detector calibration curve for the system Ar + Kr: ●, using mixtures; ▲, using pure gases.

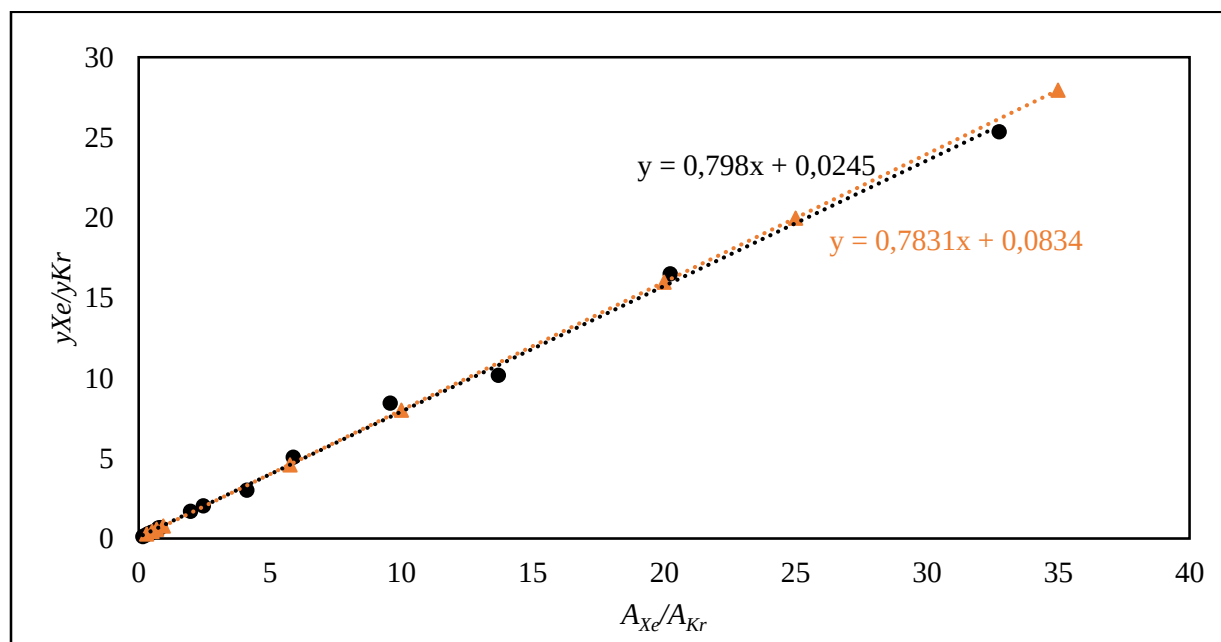


Figure B.2: GC detector calibration curve for the system Xe + Kr: ●, using mixtures; ▲, using pure gases.

As was outlined in Section 5.3.3 for calibrating using gas mixtures, the polynomials obtained when calibrating by injecting pure gases, were used to obtain composition data and these calculated compositions were compared to the compositions that were obtained gravimetrically. Figure B.3 and Figure B.4 show a comparison of the deviations of calculated compositions from the measured molar compositions. It can be noted that the calculated compositions obtained using gas mixture calibrations had the least deviation from from the measured molar compositions. The maximum deviation of the gas mixture calibration was then used in computing the combined uncertainty in composition.

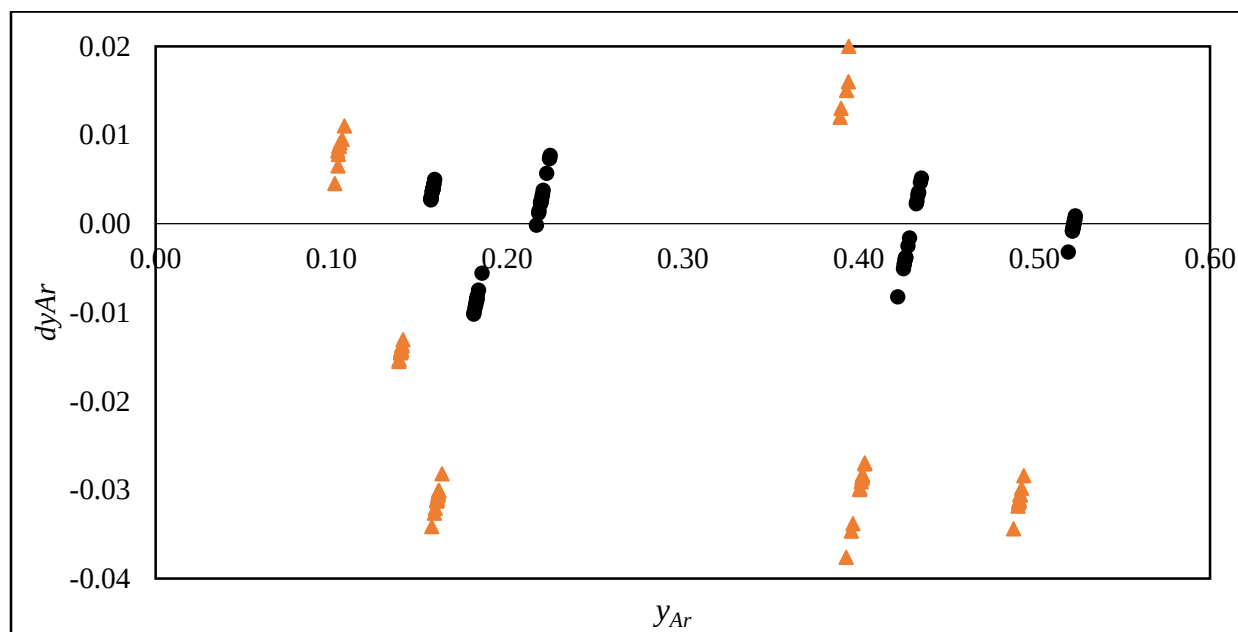


Figure B.3: Deviations from the measured molar composition of argon (y_{Ar}) due to a first-order relation: ●, using mixtures, with a maximum molar deviation of $\pm 0,01$; ▲, using pure gases, with a molar deviation of $\pm 0,04$.

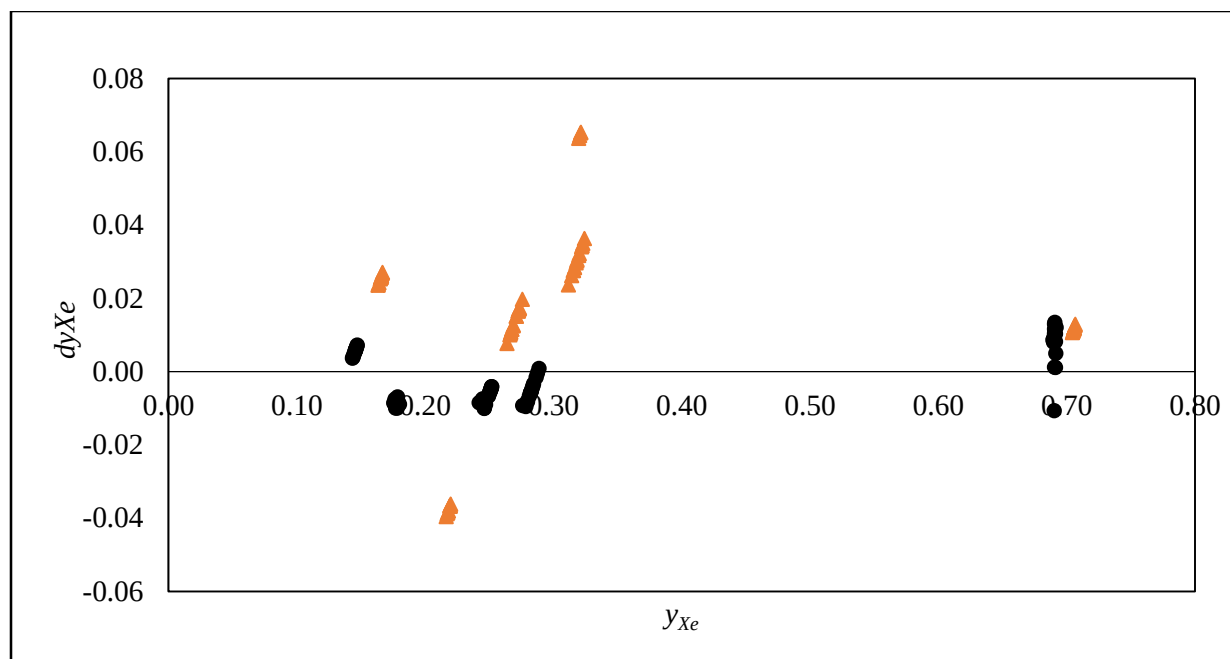


Figure B.4: Deviations from the measured molar composition of argon (y_{Xe}) due to a first-order relation: ●, using mixtures, with a maximum molar deviation of ± 0.01 ; ▲, using pure gases, with a molar deviation of ± 0.06 .