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Dehydration and Compression of Contaminated CO_2-rich Gas

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Preface

This master thesis is written during spring of 2011. The thesis is mandatory for Master of Science students graduating at the Department of Chemical Engineering at the Norwegian University of Science and Technology. The title of this thesis is *Dehydration and Compression of Contaminated* CO_2*-rich Gas*. The thesis is an individual work, and has been done in collaboration with Statoil ASA.

I would like to express my gratitude towards my educational advisor Professor Magne Hillestad, and my external advisors Eivind Johannessen and Even Solbraa at Statoil ASA. Thank you for giving valuable directions and knowledge.

Trondheim, 30 June 2011

Vidar Graff

Abstract

The use and demand of energy by exploiting fossil fuels is increasing. Carbon Capture and Storage (CCS) may be the solution to achieve decreased emissions, from various emitters of climate gases such as carbon dioxide. By permanent storage, the emissions of carbon dioxide will not reach the atmosphere, avoiding the greenhouse effect. The CO_2-rich streams resulting from carbon capture need to be processed before transport and storage. Typical CO_2 processing systems consist of compression, free-water removal and dehydration. The focus of this thesis is on the processing of captured CO_2 from natural gas.

Most often, the captured CO_2-rich streams from natural gas are not 100% pure, and may contain several impurities in addition to water. The presence of impurities like methane and nitrogen may have a noticeable effect on the choice of design and process operability of the CO_2 processing system.

The effect of impurities on the phase behaviour of CO_2-rich mixtures has been analysed. Predictions from different thermodynamic models have been evaluated and compared with experimental data from literature. Regression of binary interaction parameters has been done based on the assembled empirical data. Aspen Properties has been used to perform the regressions.

The following cases were found relevant for design and process operability; four-stage system with reservoir pump, three-stage system with reservoir pump, effect of high level of impurities, effect of type of impurity, effect of impurity concentration, compression-only system (no pump), maximum free-water removal and handling of impurities.

Technical solutions for dehydration of CO_2 have been discussed. Basic concepts of absorption and adsorption are given together with relevant block diagrams and other key information.

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1 Introduction

Energy is of global importance. The energy use across the world is rising, and it is expected that increased population and welfare in developing countries will raise the demand of energy, even more. The generation of electricity in power plants based on coal, petroleum or other fossil fuels, is a significant contributor to the increase of climate gases in the atmosphere. Other main contributors of climate gases are from oil and gas, steel and cement production. The international treaty United Nations Framework Convention on Climate Change and its Kyoto Protocol has the objective of ensuring stabilisation of greenhouse gas concentrations in the atmosphere to prevent dangerous interference with the climate system (UNFCCC 1992). In order to achieve the goal set by the UNFCCC, emission of carbon dioxide must be reduced. The Norwegian Government has since 1993 had tax on offshore CO_2 emissions, making Statoil's storage of CO_2 in the Sleipner field (since 1996) economical (Kongsnes 2008). The UK is the first country in the world to introduce a guaranteed minimum price for carbon under the emission trading scheme of the European Union, a so-called floor-price (Webb 2011). Recently, the Government in Australia has proposed tax on CO_2 emissions (Hovland 2011). Carbon Capture and Storage (CCS) is considered to becoming even more important in the future.

Simply put, the concept of CCS is to capture and concentrate the carbon dioxide (CO_2), and store it in a sink that prohibits the gas of entering the atmosphere. In that way, the environmental impact due to emissions from exploitation of fossil fuels can be diminished.

Several options for permanent storage of carbon dioxide are economical feasible, some are in demonstration phase or in research phase (IPCC 2005). The options are geological storage, ocean storage, mineral carbonation or for industrial usage. As of today, geological storage technology are generally more mature than ocean storage and mineral carbonation (IPCC 2005). Examples of forms of geological storage are in aquifers (e.g. Sleipner field), in depleted oil and gas reservoirs or in saline formations (IPCC 2005). Additional geological options are Enhanced Coal Bed Methane recovery (ECBM), which is currently in the demonstration phase (IPCC 2005), or Enhanced Oil Recovery (CO_2 promotes swelling and decreases oil viscosity), which is applied in USA and Canada. Both options will give a commercial product value of CO_2.

In general, there are three main carbon capture categories for industrial and power plant usage (IPCC 2005). These are pre-combustion, oxy-fuel combustion and post-combustion. For pre-combustion, primary fuels (coal, natural gas, oil or biomass) are processed in a reactor, producing one waste-stream of CO_2 and one fuel-stream of hydrogen. With a post-combustion system, CO_2 is separated from flue gas produced by burning primary fuels in air. For oxy-fuel combustion, primary fuels are burnt in oxygen instead of air, producing a flue gas of mainly CO_2

and water. For each category there exist different CO_2 separation technologies, such as membranes, physical and chemical solvents, solid sorbents, distillation, and more (IPCC 2005). Transportation of CO_2 is the CCS stage that links capture and storage. Long-distance transport in large quantities is currently done by pipelines (IPCC 2005). The longest CO_2 pipeline in the USA stretches as far as 808 km and has a capacity of 19.3 $MtCO_2$ yr^{-1} [a](IPCC 2005). That capacity is similar to the CO_2 emissions of three 1-GW coal-fired power stations (IPCC 2005). For transportation of large amounts of gas, it is advantageous to compress the gas in order to reduce its volume. Further reductions can be obtained by liquefaction, solidification or hydrate formation. Ship transport is practical and economical for small volumes and/or long distances for liquefied CO_2. Contrary to pipeline CO_2 transport, non-continuous transport of CO_2 requires intermediate storage facilities. Experience from LNG and LPG[b] can be transferred to CO_2 ship transport (IPCC 2005). Solidification (dry ice) is inferior from a cost and energy viewpoint (IPCC 2005). Transporting natural gas as hydrates is intended to compete with LNG in the future, hence, hydrate transport may become applicable for CO_2 ship transport (IPCC 2005).

Prior to industrial usage or permanent storage, the CO_2 needs to be processed. Figure 1-1 is a process tree of Carbon Capture and Storage, origination from fossil fuels and biomass. The tree shows the location of CO_2 compression and gas treatment (CO_2 processing).

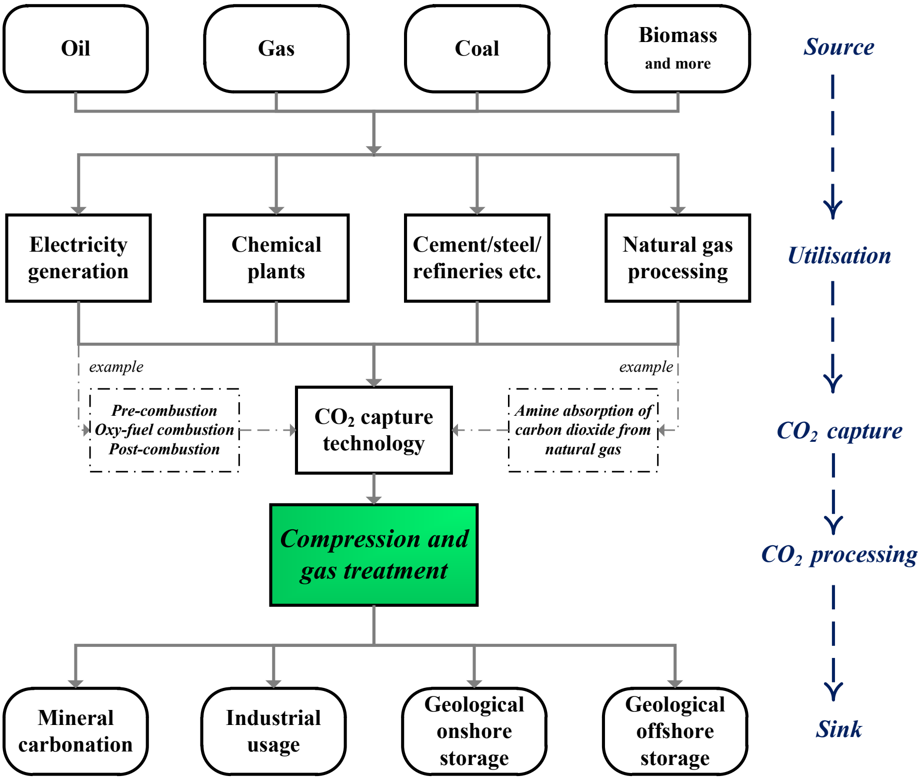

Figure 1-1 – Process tree of CCS (Carbon Capture and Storage/Sequencing) locating CO_2 processing

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[a] Million metric tonnes CO_2 per year

[b] Liquefied Natural Gas and Liquefied Petroleum Gas

In general, CO_2-rich streams resulting from capturing processes are not 100% pure, and may contain several impurities. Depending on the source of carbon and capture process, those may be hydrogen, nitrogen, nitrogen-containing gases, carbon monoxide, sulfur-containing gases, water and more (Chapoy et al. 2009). Methane and nitrogen is likely to be present for capture in association with natural gas processing. The presence of these impurities may have a noticeable effect on the choice of design and process operability of CO_2 compression and processing. For instance, non-considered presence of free-water can result in corrosion or ice/gas hydrate formation, leading to equipment/pipe rupture or blockage. There exists little information on dehydration requirements/water specifications (Chapoy et al. 2009).

Carbon dioxide is commonly transported in subsea pipelines in either dense-phase or liquid phase for offshore storage (Chapoy et al. 2009). For flow-assurance purposes, it is highly desirable to avoid two-phase flow. During most feasibility studies of CO_2 injection, the effect of the impurities (other than water) have been considered as insignificant or been completely ignored (Chapoy et al. 2009). Analogous with the work of Chapoy et al., this work tries to reveal that ignoring effects of impurities could lead to operating difficulties (such as material or mechanical failure), e.g. with respect to level of compression to ensure single-phase flow.

To reveal the significance of impurities, the effect of impurities on the phase behaviour of CO_2-rich mixtures will be analysed. Predictions from different thermodynamic models will be evaluated and compared with experimental data from literature. Regression of binary interaction parameters will be done based on assembled empirical data, by use of Aspen Properties.

Upon regression, multiple case studies will be performed on the CO_2 compression system. Key results and discussion will be on design margins and modification of designs. The results and discussion will be based on the effect of impurities and saturated water content within stated design objectives and possible constraints. In addition, technical solutions for dehydration of carbon dioxide will be discussed with key information.

1.1 Carbon dioxide and hydrate formation

Based on theory given by Helbæk and Kjelstrup, an illustrative phase diagram (Figure 1-2) was made for pure carbon dioxide (Helbæk and Kjelstrup 2006). The pressure-temperature diagram shows the characteristic behaviour of CO_2; dry ice (solid CO_2) sublimes to carbon dioxide gas when exposed to ambient temperature at ambient pressure. The triple point is at about 5.1 bar and –56.4°C (Helbæk and Kjelstrup 2006), hence, below 5.1 bar there exist only two stable phases; either solid or vapour. The critical point is at about 72.9 bar and 31°C (Helbæk and Kjelstrup 2006), hence, supercritical conditions exist above 72.9 bar when temperature is higher than 31°C. At supercritical conditions, the CO_2 is a fluid of dense phase, wherein a higher density than vapour/gas and lower than liquid.

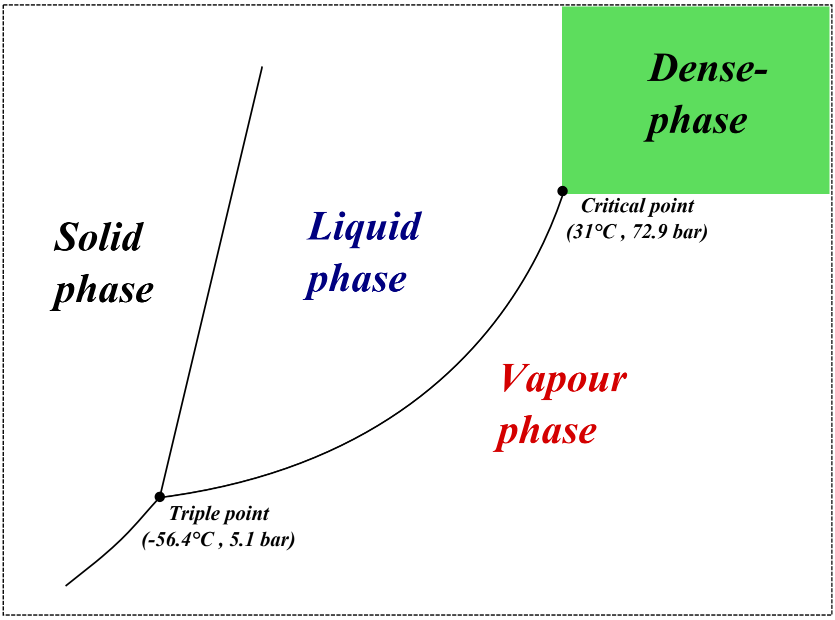

Figure 1-2 – Illustrative pressure-temperature diagram for CO_2 (Helbæk and Kjelstrup 2006)

The part between liquid and vapour phase in Figure 1-2 is further studied in Figure 1-3 and Figure 1-4, which are generated pressure-temperature diagrams for a CO_2-rich system with either pure CO_2, 1 or 5 mol% methane. The diagrams are generated by the use of simulator model Aspen HYSYS, SRK. The curve representing 95 mol% CO_2 and 5 mol% CH_4 (blue, Figure 1-3) shows a clear two-phase vapour-liquid envelope, marked by "V-L phase". In addition, three-phase vapour-liquid-liquid envelopes exist (for 1 and 5 mol% methane system), in the lower left corner without marked borders/transitions. The two and three-phase areas become more pronounced as the concentration of methane increases, which is shown by comparing Figure 1-4 (1 mol% CH_4, red curve) with Figure 1-3 (5 mol% CH_4, blue curve).

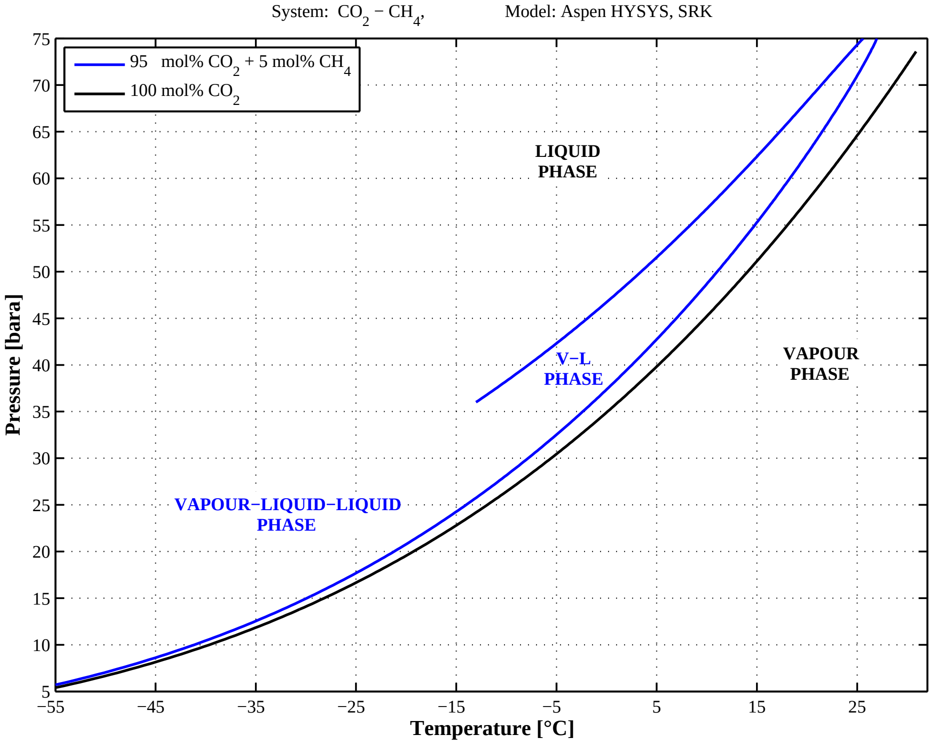

Figure 1-3 – Generated pressure-temperature diagram for CO_2-rich system, either pure or with 5 mol% CH_4

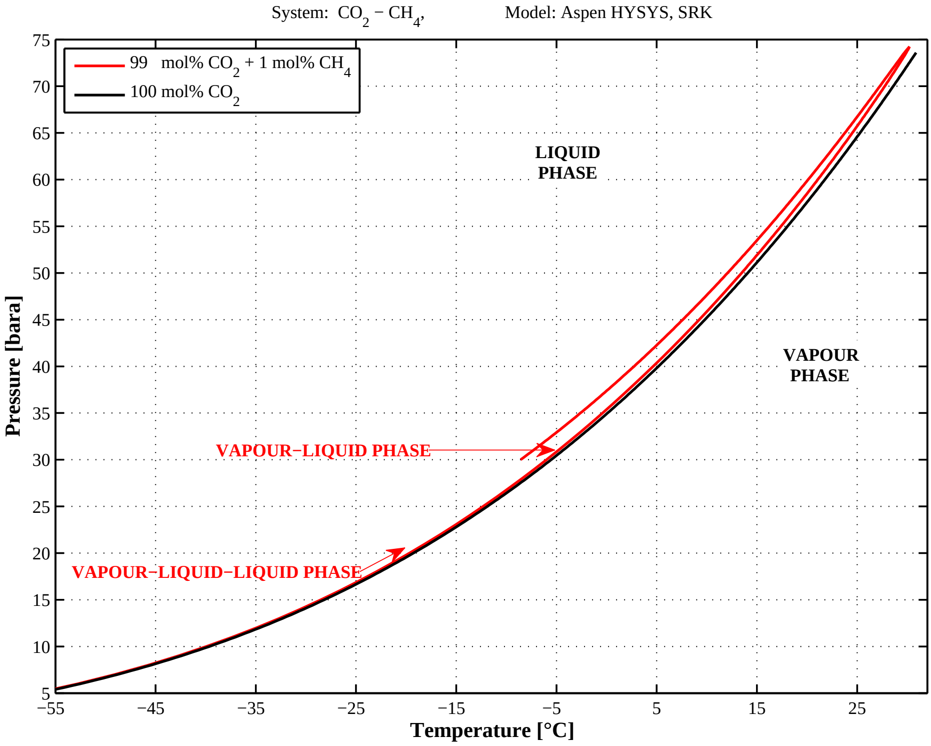

Figure 1-4 – Generated pressure-temperature diagram for CO_2-rich system, either pure or with 1 mol% CH_4

Corrosion

Carbon dioxide dissolves in water as carbonic acid (carbonates and bicarbonates). Corrosion can occur in piping and equipment exposed to acidic water. Corrosive solutions can tear down the layers of iron by oxidation, resulting in weak points or even rupture. Corrosion occurs over time and some parts of equipment and piping may be more exposed.

A recent article by Cole et al. (2011) addresses the phenomenon of corrosion in pipelines used for Carbon Capture and Storage (CCS). The authors remark that articles reviewing experimental testing under conditions directly relating to CCS are very limited, and that significant work needs to be done to explain relevant fundamental corrosion mechanisms (Cole et al. 2011). They address the “urgent and critical” need to benchmark corrosion levels, thereof estimation of service life.

Dehydration of the carbon dioxide results in lower level of corrosion. Sufficient dehydration by adsorption or absorption processes will limit the level, granting use of less expensive materials (e.g. carbon steel), (Campbell 2005). Before dehydration occurs, it may be required to use the more expensive stainless steel piping and equipment (Campbell 2005).

Hydrate formation

Figure 1-5 is a pressure-temperature diagram showing measurement points verifying different phases for a carbon dioxide with free-water system (Austegard et al. 2006). The figure shows that CO_2 and water can form hydrates at temperatures around and below 10°C, depending on pressure. CO_2-water hydrates are similar to snow in texture, and may exist in co-existence/equilibrium with CO_2, where CO_2 is in either liquid or vapour phase. The hydrate formation temperatures are not exact and hydrates may form (or not) above (or below) the formation line (GPSA 2004). Hydrates can cause plugging in pipes and equipment, leading to blockage or even rupture. Precautions should be taken regarding design of systems containing water and carbon dioxide, since hydrates formation in high-pressure systems may occur when exposed to sudden pressure drop with an accompanying temperature drop. Water removal or dehydration may prevent hydrate formations.

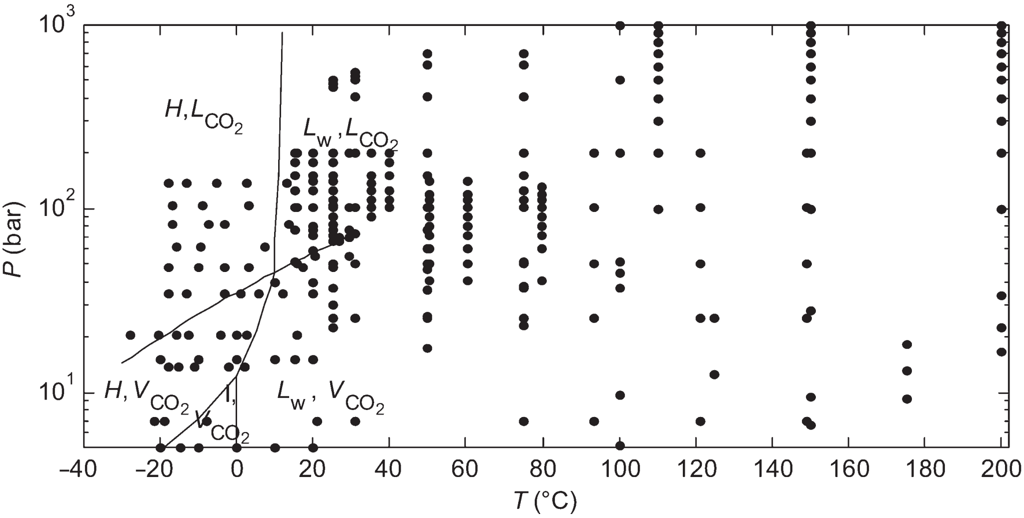

Figure 1-5 – Measurements from several sources indicating different phases (**V**apour, **L**iquid, **H**ydrate and **I**ce), System: CO_2–H_2O with free-water (Austegard et al. 2006).

2 Experimental data and model fitting

2.1 Theory

2.1.1 Thermodynamic properties

A gas can be characterised as ideal if (Helbæk and Kjelstrup 2006):

- the gas molecules occupy no appreciable volume,
- continuous movement of molecules exists (in possession of kinetic energy), and
- that there exists no intermolecular forces (neither attraction nor repulsion).

The ideal gas law is an equation of state (EOS), which describes the nature of an ideal gas. The pressure is a function of temperature, volume and number of moles, which can be expressed according to Eq. 1.1.1,

$$P = \frac{RT}{v} \tag{1.1.1}$$

where P is pressure [N/m^2], R is the universal gas constant [J/(mol K)], v is the molar volume of the gas [m^3/mol] and T is the temperature [K] (Helbæk and Kjelstrup 2006).

Certain type of gases (small molecules) at certain conditions (low pressure and high temperature) can be accurately described by the ideal gas law. More advanced theoretical equations are needed in order to describe larger and more complex molecules (dipole moment etc.). The effect of high pressure on the accuracy can be significant. Application of fugacity coefficients to liquid and vapour phase can describe high-pressure vapour-liquid equilibria well, also for multicomponent mixtures (Prausnitz et al. 1999). The general thermodynamic relationship of fugacity and pressure are given by Eq. 1.1.2,

$$\ln\frac{f}{P} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P}\right) dP \tag{1.1.2}$$

where f is the fugacity of a pure component (Soave 1972). At a given condition (temperature, pressure and total composition), the following saturation condition can be satisfied (Soave 1972):

$$f_i^{liquid} = f_i^{vapour} \tag{1.1.3}$$

An appropriate EOS can be used to calculate fugacity coefficients. A perfect single EOS can in theory, meet the requirements for both liquid and vapour. As of today, there exist no such perfect equation (Helbæk and Kjelstrup 2006; Prausnitz et al. 1999). Nonetheless, EOS of approximate results are available for many mixtures (Prausnitz et al. 1999). Prausnitz et al. state that the simplest procedure for calculating the fugacity coefficients is to choose an EOS that holds for pure fluid 1 and for pure fluid 2, and to assume that the same equation holds for all mixtures of 1 and 2 by interpolation (Prausnitz et al. 1999).

Soave-Redlich-Kwong

The Soave-Redlich-Kwong (SRK) equation is a modification of the Redlich-Kwong equation of state (Soave 1972):

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{1.1.4}$$

The term co-volume is used for variable *b* in the SRK EOS (Eq. 1.1.4.). The molar volume *v* in the ideal gas law is the third dimensional space, where the gas molecules can move freely (per number of moles). In contrary to ideal gas, the molecules in real gases do occupy space, thus, limiting the available space for movement. Hence, the co-volume is subtracted in Eq. 1.1.4. In contrary to ideal gas, the molecules in real gases do experience intermolecular forces. The last term in Eq. 1.1.4, thereof variable *a*, tries to account for that effect. The pressure of a gas is dependent on how often the molecules collide with the wall of the container and also the force equivalent to each collision (Helbæk and Kjelstrup 2006). Attraction between the molecules reduces the collision frequency and the force of impact, thus, reducing the pressure.

The Soave-Redlich-Kwong is a cubic equation of state, and can therefore be written on this polynomial form,

$$Z^3 - Z^2 + Z\left(A - B - B^2\right) - A \cdot B = 0 \tag{1.1.5}$$

where the compressibility factor *Z*, and parameters *A* and *B* are given by Eq. 1.1.6-1.1.8 (Soave 1972).

$$Z = Pv/RT \tag{1.1.6}$$

$$A = aP/R^2T^2 \tag{1.1.7}$$

$$B = bP/RT \tag{1.1.8}$$

The fugacity can be calculated by the following equation,

$$\ln\frac{f}{P}=Z-1-\ln\left(Z-B\right)-\frac{A}{B}\cdot\ln\left(\frac{Z+B}{Z}\right) \tag{1.1.9}$$

which is derived by applying Eq. 1.1.2 to Eq. 1.1.4 (Soave 1972).

The mixing rules applied to parameters *a* and *b* in the SRK EOS are shown by Eq. 1.1.10 and 1.1.11, respectively (Soave 1972).

$$a=\sum_i\sum_j x_i\, x_j\sqrt{a_i\, a_j}\left(1-k_{ij}\right) \tag{1.1.10}$$

$$b=\sum_i x_i b_i \tag{1.1.11}$$

Parameter k_{ij} is an empirical correction factor, which is determined from experimental data for each binary present in the mixture (Soave 1972). Hence, this factor is often called a binary interaction parameter. In addition, for general SRK computations;

$$k_{ij}=k_{ji}. \tag{1.1.12}$$

The parameters a_i and b_i are dependent on the critical temperature and critical pressure of component *i*:

$$a_i=\alpha_i\cdot 0.42747\cdot R^2\cdot T_{ci}^2\big/p_{ci} \tag{1.1.13}$$

$$b_i=0.08664\cdot R\cdot T_{ci}\big/p_{ci} \tag{1.1.14}$$

Soave modification

As shown by Eq. 1.1.13, the parameter a_i is also dependent on another parameter α_i, which can be represented by temperature dependent alpha functions. For the Soave modification, the alpha function is written as followed,

$$\alpha_i^{1/2}=1+m_i\left(1-\sqrt{T/T_{ci}}\right) \tag{1.1.15}$$

where m_i is expressed by an acentric factor ω_i for pure components (Soave 1972):

$$m_i=0.480+1.574\cdot\omega_i-0.176\cdot\omega_i^2 \tag{1.1.16}$$

Mathias-Copeman alpha function

Mathias-Copeman alpha function is another method for estimating the alpha parameters. The equation is given below (Mathias and Copeman 1983). This method drives to provide a more accurate fit of vapour pressure for polar components (AspenTech 2010b).

$$\alpha_i^{1/2} = 1 + c_{1,i}\left(1 - \sqrt{T/T_{ci}}\right) + c_{2,i}\left(1 - \sqrt{T/T_{ci}}\right)^2 + c_{3,i}\left(1 - \sqrt{T/T_{ci}}\right)^3 \tag{1.1.17}$$

Mathias alpha function

Mathias alpha function is also a method for estimating the alpha parameters. The equations are given below. This method also drives to provide a more accurate fit of vapour pressure for polar components (AspenTech 2010b). The parameter η is for polarity and parameter m_i is calculated by Eq. 1.1.16. For below critical temperature (AspenTech 2010b):

$$\alpha_i^{1/2} = 1 + m_i\left(1 - \sqrt{T/T_{ci}}\right) - \eta_i\left(1 - T/T_{ci}\right)\left(0.7 - T/T_{ci}\right) \tag{1.1.18}$$

For above critical temperature (AspenTech 2010b):

$$\alpha_i^{1/2} = \exp\left(c_i\left(1 - \left(T/T_{ci}\right)^d\right)\right) \tag{1.1.19}$$

$$d_i = 1 + \frac{m_i}{2} + 0.3 \cdot \eta_i \tag{1.1.20}$$

$$c_i = 1 - \frac{1}{d_i} \tag{1.1.21}$$

2.1.2 Regression of binary interaction parameter (BIP)

Phase equilibria are important in most chemical processes (Seider et al. 2008). Thus, process design teams spend significant time assembling data, e.g. vapour-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) data (Seider et al. 2008). Obviously, only assembling data is not adequate. Proper processing of the data is crucial in order to obtain reliable predictions, e.g. for phase conditions and separation of specific components. For specific systems and conditions, the accuracy of different property methods within and between process simulators can be evaluated by comparison with experimental data. Furthermore, improvement can be done by parameter regression. Moreover, implementing more complex EOSs for better predictions, such as an association model, are becoming increasingly important (Yan et al. 2009).

Interaction parameters are usually regressed from binary VLE data (Englezos et al. 1990). The data is normally obtained from experimental studies, wherein temperature, pressure, and vapour and liquid mole fractions are measured (TPxy data). Traditionally, the regression is often done by simple least-squares estimations (Englezos et al. 1990). Seider et al. suggest a regression method by the use of Aspen Properties (Seider et al. 2008), which by default use a maximum-likelihood objective function and Britt-Luecke algorithm (AspenTech 2010c).

Seider et al. showed an example of regression for a CH_4-H_2S system with Soave-Redlich-Kwong EOS by use of Aspen Properties. They adjusted three parameters, a binary interaction parameter ($k_{CH4,H2S}$) and two acentric factors, ω, by regression (Seider et al. 2008). Generally, pure component parameters (e.g. ω) should not be adjusted based on binary component data. That adjustment could erroneously change the pure component properties (e.g. vapour pressure). Seider et al. should have limited the regression to the binary parameter.

2.1.2.1 Proposed procedure of BIP regression in Aspen Properties

RK-Soave and RK-Aspen were found to be relevant thermodynamic property packages after evaluation of the Aspen Properties Help manual (AspenTech 2010b). The relevancy stems from using standard Soave-Redlich-Kwong equations. The RK-Aspen was included in the evaluation, since it was suggested in the manual that the package, with its the Mathias function, could improve predictions of pure component vapour pressures (AspenTech 2010b).

According to the manual, the standard Soave-Redlich-Kwong equations with Soave's modification will be used for default RK-Soave as described in Section 2.1.1. According to the manual, the standard Soave-Redlich-Kwong equations with Mathias alpha function will be used for default RK-Aspen as described in Section 2.1.1. However, both packages also have these minor differences:

(AspenTech 2010b) versus (Soave 1972)

$$a_i = \alpha_i \cdot 0.42748 \cdot R^2 \cdot T_{ci}^2 / p_{ci} \quad \text{instead of} \quad a_i = \alpha_i \cdot 0.42747 \cdot R^2 \cdot T_{ci}^2 / p_{ci}$$

$$m_i = 0.48508 + 1.55171 \cdot \omega_i - 0.15613 \cdot \omega_i^2 \quad \text{instead of} \quad m_i = 0.480 + 1.574 \cdot \omega_i - 0.176 \cdot \omega_i^2$$

These key specifications were done in order to regress one binary interaction parameter (BIP) for two different property packages, namely RK-Soave and RK-Aspen:

- SI-CBAR as Unit of Measurements,
- RK-Soave or RK-Aspen as Property Package,
- CO_2, CH_4, N_2, H_2O as Components,
- TPXY as type of data set with default standard deviations for measurement data,
  (0.1°C, 0.1% (bar), 0.1% and 1% for T, P, liquid mole fraction and vapour mole fraction, respectively)
- entered data from each reference as individual data sets,
- each set were equally weighted,
- regression of temperature independent BIP (= k_{ij}),
  parameter RKSKBV/1 for RK-Soave,
  parameter RKAKA0 for RK-Aspen,
- Maximum-likelihood as Objective Function (default),
- Britt-Luecke as Algorithm (default), and
- Deming as Initialisation Method (default).

2.1.3 Pure component parameters of Aspen HYSYS and Aspen Properties

Pure component parameters for Aspen HYSYS and Aspen Properties are given in Table 2-1 and Table 2-2, respectively. The parameters are critical temperatures (T_c), critical pressures (P_c) and acentric factors (ω) for components H_2O, CO_2, CH_4 and N_2. The parameters do not differ much between the programmes, and they are considered as valid.

Table 2-1 – Pure component parameters (AspenTech 2010a)

Simulator:				Aspen HYSYS
	H_2O	CO_2	CH_4	N_2
T_c	374.149	30.9500	- 82.4510	-146.9560
P_c	221.200	73.7000	46.4068	33.9437
ω	0.34400	0.23894	0.01150	0.04000

Table 2-2 – Pure component parameters (AspenTech 2010c)

Simulator:				Aspen Properties
	H_2O	CO_2	CH_4	N_2
T_c	373.946	31.0600	-82.5860	-146.9500
P_c	220.640	73.8300	45.9900	34.0000
ω	0.34486	0.22362	0.01155	0.03772

2.2 Gathering of solubility data and Vapour-Liquid Equilibrium data

Water solubility data and vapour-liquid equilibrium (VLE) data from 56 sources were assembled from literature. The data comprises of measurements for five binary systems, i.e. H_2O in CO_2, H_2O in CH_4, H_2O in N_2, CH_4-CO_2 and N_2-CO_2. The first three sets are gathered in effort to improve prediction of water content in a CO_2-rich system, with methane and nitrogen as minor impurities. The latter two sets are gathered in effort to improve prediction of interaction between carbon dioxide and methane/nitrogen. It was conceived that the interaction between methane and nitrogen was less significant, hence, the data assembly of the CH_4-N_2 system was excluded.

A total of 1011 points were found, analysed and categorised. Table 2-3 shows the total number of points and sources for each binary system. Measurements above about 100°C were excluded due to irrelevancy.

Table 2-3 – Experimental measurements used in data regression

	No. of points / (No. of references)		
	CO_2	CH_4	N_2
H_2O	202 / (12)	158 / (13)	169 / (10)
CO_2		310 / (12)	172 / (9)

Table 2-4, Table 2-5 and Table 2-6 show the temperature range and number of experimental points for each reference found for systems H_2O-CO_2, H_2O-CH_4 and H_2O-N_2, respectively.

Table 2-4 – Solubility of H_2O in CO_2

Reference	Temp. range [°C]	No. of exp. points below 100°C
(Tödheide and Franck 1963)	[50 , 200]	8
(King and Coan 1971)	[25 , 100]	22
(Gillespie and Wilson 1982)	[15 , 260]	16
(Song and Kobayashi 1990)	[-22 , 30]	11
(Briones et al. 1987)	50	8
(Nakayama et al. 1987)	[25]	3
(Müller et al. 1988)	[100 , 200]	7
(King et al. 1992)	[15 , 40]	41
(Dohrn et al. 1993)	[50]	3
(Bamberger et al. 2000)	[50 , 80]	29
(Frøyna 2004)	[-20 , 20]	24
(Valtz et al. 2004)	[5 , 45]	30

Table 2-5 – Solubility of H_2O in CH_4

Reference	Temp. range [°C]	No. of exp. points below 100°C
(Olds et al. 1942)	[38 , 104]	35 (incl. 104°C)
(Culberson and McKetta 1951)	38	15
(Rigby and Prausnitz 1968)	[25 , 100]	12
(Sharma 1969)	[38 , 71]	15
(Kosyakov et al. 1982)	0 & 10	5
(Gillespie and Wilson 1982)	50 & 75	6
(Yarym-Agaev et al. 1985)	40 & 65	10
(Yokoyama et al. 1988)	25 & 50	5
(Bogoya et al. 1993)	[5 , 15]	5
(Althaus 1999)	[5 , 20]	15
(Chapoy et al. 2003)	[30 , 45]	21
(Mohammadi et al. 2004)	[10 , 40]	17
(Frøyna 2004)	[10 , 20]	8

Table 2-6 – Solubility of H_2O in N_2

Reference	Temp. range [°C]	No. of exp. points below 100°C
(Saddington and Krase 1934)	[50 , 230]	8
(Rigby and Prausnitz 1968)	[25 , 100]	13
(Gillespie and Wilson 1980)	[38 , 316]	10
(Kosyakov et al. 1982)	[0 , 20]	18
(Bogoya et al. 1993)	[0 , 15]	8
(Althaus 1999)	[0 , 20]	22
(Blanco et al. 1999)	[1 , 11]	24
(Chapoy et al. 2004)	38 & 93	10
(Frøyna 2004)	[0 , 20]	21
(Mohammadi et al. 2005)	[10 , 90]	35

Table 2-7 and Table 2-8 show the temperature range and the number of experimental points for each reference found for systems CO_2-CH_4 and CO_2-N_2, respectively.

Table 2-7 – VLE, binary CO_2-CH_4 system

Reference	Temp. range [°C]	No. of exp. points below 100°C
(Donnelly and Katz 1954)	[-73, -2]	53
(Kaminishi et al. 1968)	[-40, 10]	14
(Neumann and Walch 1968)	[-100, -87]	36
(Arai et al. 1971)	[-20, 15]	2
(Davalos et al. 1976)	[-43,-3]	36
(Mraw et al. 1978)	[-120, -54]	8
(Somait and Kidnay 1978)	-3	10
(Al-Sahhaf et al. 1983)	[-53, -3]	30
(Xu et al. 1992)	15 & 20	23
(Bian et al. 1993)	28	7
(Wei et al. 1995)	[-43, -3]	52
(Webster and Kidnay 2001)	-43 & -3	39

Table 2-8 – VLE, binary CO_2-N_2 system

Reference	Temp. range [°C]	No. of exp. points below 100°C
(Yorizane et al. 1970)	0	12
(Arai et al. 1971)	[0, 15]	4
(Somait and Kidnay 1978)	-3	34
(Al-Sahhaf et al. 1983)	-53 & -33	29
(Yorizane et al. 1985)	[0, 25]	34
(Brown et al. 1989)	-23 & -3	17
(Xu et al. 1992)	15 & 20	20
(Bian et al. 1993)	28 & 30	14
(Yucelen and Kidnay 1999)	[-33, -3]	8

All the collected measurements mentioned above, which were used for the data regression, are given in Appendix A – Appendix F. In order to show how each set of measurements from each reference were categorised, one set for the CO_2-CH_4 system is given by Table 2-9. T is temperature in degrees Celsius, P is total pressure in bar (absolute), x is liquid mole fraction and y is vapour mole fraction.

Table 2-9 – Example of measured VLE data (Kaminishi et al. 1968)

T [°C]	P [bara]	x CH_4	x CO_2	y CH_4	y CO_2
-40	52.7	0.251	0.749	0.717	0.283
-40	62.0	0.360	0.640	0.727	0.273
-40	71.9	0.519	0.481	0.703	0.297
-20	52.7	0.150	0.850	0.515	0.485
-20	62.0	0.213	0.787	0.556	0.444
-20	71.9	0.294	0.706	0.566	0.434
-20	78.0	0.357	0.643	0.563	0.437
-20	81.1	0.400	0.600	0.540	0.460
0	52.7	0.070	0.930	0.254	0.746
0	77.0	0.204	0.796	0.370	0.630
0	81.9	0.246	0.754	0.367	0.633
10	62.0	0.069	0.931	0.188	0.812
10	71.9	0.115	0.885	0.240	0.760
10	81.9	0.177	0.823	0.250	0.750

2.3 Evaluation of regression results and model predictions

The gathered experimental data sets were entered in Aspen Properties (Section 2.2). Regressions on temperature independent binary interaction parameters k_{ij} were preformed according to the procedure given in Section 2.1.2.1. It was intended to carry out regression on binary interaction parameters in the SRK property package of Aspen HYSYS. However, Aspen Properties lack the possibility of performing regression on the Aspen HYSYS packages. Instead, two similar Aspen Properties packages (in terms of EOS), the RK-Soave and the RK-Aspen, were investigated. RK-Aspen due to its allegedly improved vapour pressure predictions (AspenTech 2010b). Both packages can be used in Aspen HYSYS simulations.

The results of regressions of k_{ij} for the RK-Soave and RK-Aspen property method are given in Table 2-10 and Table 2-12, respectively. The standard deviations of the parameters are given in Table 2-11 and Table 2-13 for each interaction parameters. Please note that since the CH_4-N_2 data set has not been investigated, the values marked in *italic* were retrieved from the property packages.

Table 2-10 – Regressed binary interaction parameters

Model: RK-SOAVE				(Aspen Properties)
	CO_2	H_2O	CH_4	N_2
CO_2		0.01392	0.09782	-0.03841
H_2O	0.01392		0.44645	0.02416
CH_4	0.09782	0.44645		*0.02780*
N_2	-0.03841	0.02416	*0.02780*	

Table 2-11 – Standard deviation of regressed binary interaction parameters

Model: RK-SOAVE				(Aspen Properties)
	CO_2	H_2O	CH_4	N_2
CO_2		0.01488	0.00097	0.00198
H_2O	0.01488		0.01159	0.02839
CH_4	0.00097	0.01159		
N_2	0.00198	0.02839		

Table 2-12 – Regressed binary interaction parameters

Model: RK-ASPEN				(Aspen Properties)
	CO_2	H_2O	CH_4	N_2
CO_2		0.08070	0.09274	-0.07444
H_2O	0.08070		0.45058	0.01057
CH_4	0.09274	0.45058		*0.00000*
N_2	-0.07444	0.01057	*0.00000*	

Table 2-13 – Standard deviation of regressed binary interaction parameters

Model: RK-ASPEN				(Aspen Properties)
	CO_2	H_2O	CH_4	N_2
CO_2		0.01275	0.00096	0.00327
H_2O	0.01275		0.01115	0.02860
CH_4	0.00096	0.01115		
N_2	0.00327	0.02860		

Standard values for k_{ij}, retrieved from the SRK model in Aspen HYSYS, are given in Table 2-14.

Table 2-14 – Binary interaction parameter, standard values

Model: SRK				(Aspen HYSYS)
	CO_2	H_2O	CH_4	N_2
CO_2		*0.03920*	*0.09560*	*-0.01710*
H_2O	*0.03920*		*0.50000*	*-0.49070*
CH_4	*0.09560*	*0.50000*		*0.03120*
N_2	*-0.01710*	*-0.49070*	*0.03120*	

Due to the operating conditions for the systems in this thesis, the water solubility data is considered more important than gas solubility in water. The regressed interaction parameters should be positive (above zero) when the data was water solubility in CO_2, CH_4 and N_2. The k_{ij} resulting from regression of water solubility data in CO_2, CH_4 and N_2 were all positive values (e.g. 0.01392, 0.44645, 0.02416 for RK-Soave, respectively). The N_2-H_2O interaction parameter for SRK in Aspen HYSYS is –0.49070, which can indicate that regression on data for nitrogen solubility in water (the opposite) was done by Aspen.

Water solubility predictions

The binary interaction parameters do only have significance for high pressure or relative low temperature (non-ideality). It does not have significant effect on low pressure and high temperature, since the SRK EOS (Eq. 1.1.4) then reduces to the ideal gas law (Eq. 1.1.1). Thus, for low-pressure systems, adjustment of the interaction parameters will not have any relevant effect. However, the alpha functions are relevant for prediction of the pure vapour pressures, e.g. Soave modification (classical SRK) vs. Mathias-Copeman. To analyse the accuracy at low pressure, some simulation results were compared between the predictions of SRK (Aspen HYSYS), RK-Soave (Aspen Properties) and RK-Aspen (Aspen Properties), and a known well-predicting model SRK of the programme NeqSim (Solbraa 2003). Water solubility in methane at 25°C and one bar was investigated. The results are given in Table 2-15. To eliminate the possibility of effect caused by different interaction parameters k_{ij} or pure component parameters, the same parameters were used for the NeqSim model, according to Table 2-15, Table 2-1 and Table 2-2.

Table 2-15 – Prediction of water in methane, 25°C and 1 bar

Model **Alpha function** **Interaction parameter**	NeqSim – SRK Classic (k_{ij} = 0.5)	Aspen HYSYS – SRK “Classic” (k_{ij} = 0.5)
Mole fraction of methane	0.976361	0.968953
Mole fraction of water	0.023639	0.031047

Model **Alpha function** **Interaction parameter**	NeqSim – SRK Classic (k_{ij} = 0.44645)	Aspen Properties- RK-SOAVE Classic (k_{ij} = 0.44645)
Mole fraction of methane	0.976434	0.977109
Mole fraction of water	0.023566	0.022891

Model **Alpha function** **Interaction parameter**	NeqSim – SRK Mathias-Copeman (k_{ij} = 0. 45058)	Aspen Properties - RK-ASPEN Mathias function (k_{ij} = 0.45058)
Mole fraction of methane	0.967823	0.976387
Mole fraction of water	0.032177	0.023613

The results show that the classical SRK alpha function (Soave modification) fails to predict the molar fraction of water in methane that should be close to 0.03. The RK-Soave and the RK-Aspen fail, however, the HYSYS - SRK prediction is good. According to the help file in Aspen HYSYS, the SRK should have a classical alpha function (AspenTech 2010a), however the good prediction suggests otherwise. Based on the results and the limitations of the Soave modification and Mathias function, the Aspen Properties packages predictions of water content at low pressure were questionable (also for the CO_2 and N_2). The package options in Aspen Properties were further looked at, however, Mathias-Copeman equations and parameters were not managed to be included in the models. Hence, further model improvements were not successfully made. The accuracy of the models for water content prediction is investigated further in Section 3.1.4 and Section 3.2.7.

Binary interaction predictions

The binary interaction parameters affect properties for operating conditions deviating from ideal state. To show different predictions for a CO_2-N_2 mixture, a pressure-liquid/vapour mole fraction (*Pxy*) diagram was made for temperature of -3.15°C with experimental measurements (references according to Table 2-8). For comparison and in addition to the standard value, the interaction parameter for SRK (Aspen HYSYS) has been changed to represent the same values as the RK-Soave regression and RK-Aspen regression. The result is shown in Figure 2-1.

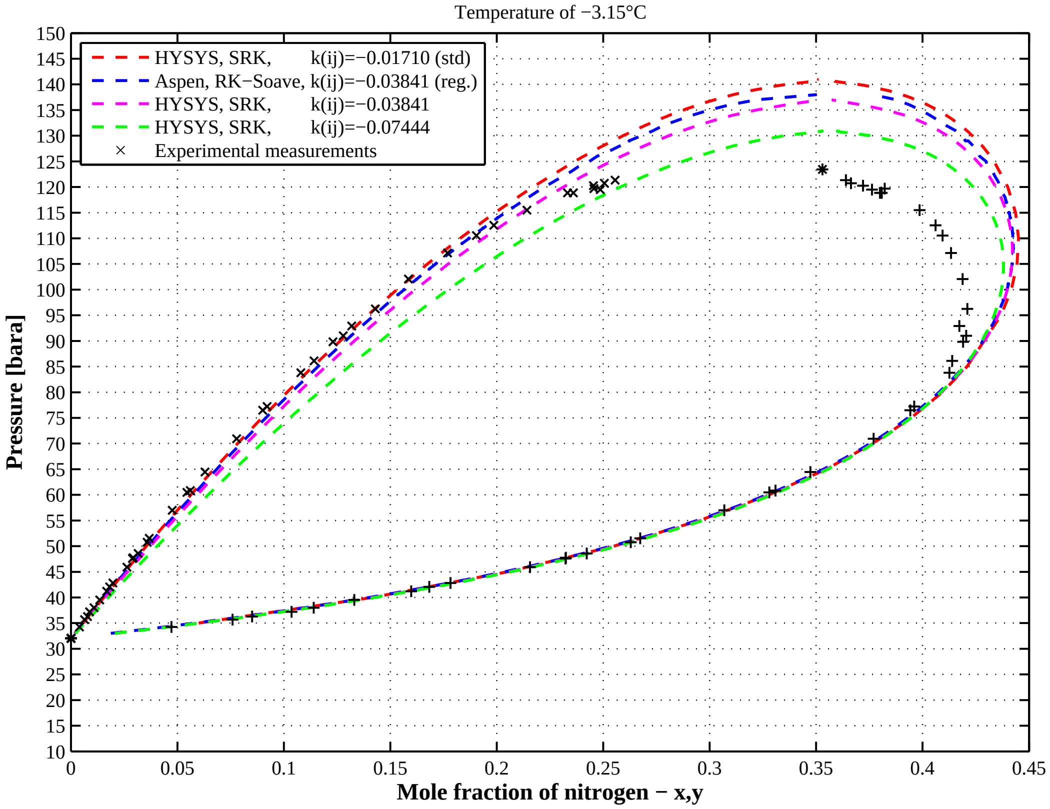

Figure 2-1 – *P-xy* diagram for CO_2-N_2 at -3.15°C with experimental measurements

The regressed RK-Soave (Aspen Properties) and standard SRK (Aspen HYSYS) give very similar predictions. All the models seem to predict well at the lowest pressures and lowest concentration (richest system). However, as the concentration of nitrogen increases the accuracy seems to decrease. At the highest concentrations in this diagram, the interactions parameters do also have the largest effect, which can be recognised by Eq. 1.1.10. Shown by the red, magenta and green curves, the two-phase area decrease when the absolute value of the interaction parameters increases.

Further comparisons with *P-xy* diagrams have not been made. The system investigated in this thesis is considered to have a concentration of impurities nitrogen and methane of maximum 5% on molar basis. The difference between fair and excellent binary interaction parameters and its effect on the CO_2-rich system is questionable.

3 Design and simulation results

3.1 Design considerations

3.1.1 Basic concept

The overall concept of the CO_2 compression process is to make the carbon dioxide denser (compact) and to remove water (corrosion/ice/hydrate); making it transportable and/or fit for storage. Contrary to methane, carbon dioxide is easier to liquefy, since the critical temperature of CO_2 is roughly 113°C higher (-82°C vs. 31°C, Table 2-1), hence, pumping the liquid to reservoir pressure is a possibility. Figure 1-5 shows that temperatures below around 0 and 10°C for pressurised CO_2, may lead to dry ice or hydrate formation, which is undesirable for fluid transport and storage. In addition, supercritical carbon dioxide is also easier to obtain than for methane, which is a possible option for transport and storage.

The most fit-for-purpose process design depends on the source/origin of the CO_2 (concentration, impurities), capture process and potential pre-existing transportation systems. According to The Times existing natural gas pipelines can be used to transport CO_2 from UK power stations to geological storage formations in the North Sea (Pagnamenta 2009). In Lacq (France), existing pipeline limit the transport to 30 bar (Total 2007).

3.1.2 Conventional process designs

Carbon dioxide can be absorbed from natural gas by an amine solvent, e.g. by activated methyl diethanolamine (a-MDEA) solution. The CO_2 gas will then be stripped off the amine solution in a stripper column by heat addition at slightly above atmospheric pressure. Conventionally, excess water is returned to the stripper by cooling the gas at e.g. 20°C. Thus, the gas exits the capture process saturated with water.

A flowsheet for a general CO_2 compression and gas treatment (dehydration) system is shown in Figure 3-1.

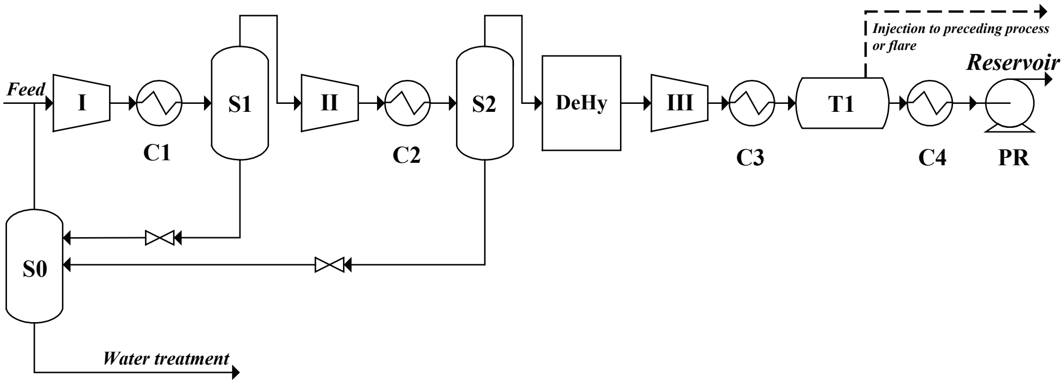

Figure 3-1 – CO_2 compression system; three-stage compression (I, II and III), intermediate coolers (C1, C2 and C3), gas-liquid separators (S0, S1 and S2), dehydration unit (DeHy), tank (T1), cooler (C4) and reservoir pump (PR).

The flowsheet (Figure 3-1) shows a system containing three-stage compression with intermediate cooling, gas-liquid separation, one dehydration unit, a tank and a reservoir pump. Detailed information regarding stage pressures and temperature is given in Section 3.2 (Case studies of CO_2 processing systems).

Water-saturated CO_2-rich gas enters the first compressor stage. At the higher discharge pressures after stage I and II, the equilibrium water-contents are lower. Thus, upon cooling, water is condensed in gas-liquid separators. The water contains small amounts of soluble carbon dioxide. The liquid streams from the separators are depressurised prior to entering a third separator, which ensures that the gas soluble at higher pressure is freed from the liquid streams, and re-enter the compression system. Water is sent to treatment.

A dehydration unit (DeHy), which is a treatment process that removes water soluble in the gas, is placed before the last compression step. The unit can provide a water content of as low as 50 ppm (Maldal and Tappel 2004). Process alternatives can be adsorption (e.g. molecular sieve), absorption (treatment with glycol, etc.), and other.

The discharge pressure of the last compression step must be of a certain high pressure. That is, after condensation the resulting liquid must be dense enough to be further processed by a pump. Also, hydrate formation must be avoided.

A tank with top outlet and a controlled liquid level could possibly reduce the chances of two-phase flow in an effluent liquid pump. The NPSH (net positive suction head) of the pump could be secured by sufficient static head, to prevent cavitation (as pressure increases the bubbles implode) and/or vibrations (efficiency loss). The discharged gas could be sent to an earlier stage of the plant and/or to flare. Whether the static head is big enough to secure NPSH is questionable, and further pre-cooling can have larger effect.

For a given bottom hole pressure (BHP) of 285 bar (Snøhvit reservoir), a CO_2 pump pressure of between 80 and 150 bar can ensure flow, depending on the CO_2 injection rate (Maldal and Tappel 2004). The lower pump pressure than BHP can be explained by the hydrostatic CO_2 column that exists between the pump and the bottom hole. The increase of pressure across the vertical column is dependent on the density of the liquid and the height of the column. Thereof, the required CO_2 pump pressure is also dependent on the change in density due to change in temperature. Change in temperature can occur during injection and maintenance (Maldal and Tappel 2004). Impurities like CH_4 and N_2 will also affect the density of the column. To which extent the effect will have on the required pump pressure, has not been investigated during this thesis.

Compression-only

A flowsheet for another CO_2 compression and gas treatment (dehydration) system is shown in Figure 3-2. This system does not contain a reservoir pump, and the total pressure increase is obtained by compressors, only.

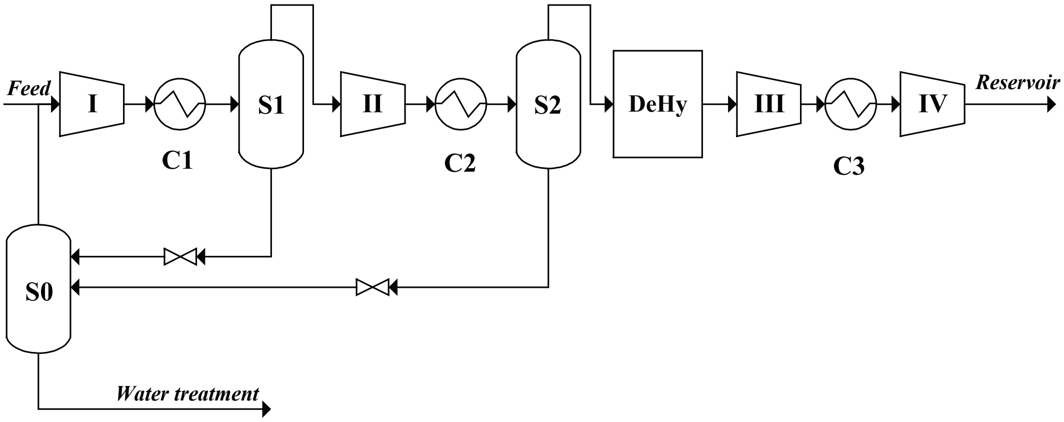

Figure 3-2 – CO_2 full compression system; four-stage compression (I, II, III, IV), intermediate coolers (C1, C2 and C3), gas-liquid separators (S0, S1 and S2) and dehydration unit (DeHy).

This compression system has four-stage compression with intermediate cooling and gas-liquid separation. A dehydration unit is placed after the second gas-liquid separator (S2) and compression stage (IV) ensure required pressure for flow to reservoir. A fifth stage may be required.

3.1.3 Compressor design

In general, during design of multi-stage compression, equal ratios of compression per stage are used (GPSA 2004). If necessary, an allowance for piping and cooler losses is granted (GPSA 2004). Thus, the outlet pressure should be set as,

$$P_{outlet,i} = P_{inlet,i} \cdot \left(\frac{P_{outlet,n}}{P_{inlet,1}} \right)^{1/n} \tag{2.1.1}$$

where n is the number of stages and stage i is an element of [1, n]. In practise for high-pressure work, a lower compression ratio for the higher stages is used to reduce excessive rod loading (heavier and more expensive frame) (GPSA 2004).

Since packing life may be considerably reduced when sealing gas of high pressure and high temperature, a discharge temperature of 125°C and 135°C may be a practical limit (GPSA 2004). It is economically unfavourable to have an excessive compression ratio. That is, since a high compression ratio leads to a low volumetric efficiency; thus, requiring a large cylinder to produce the same capacity (GPSA 2004).

3.1.4 Water content of CO_2-rich gases

Figure 3-3 show how the water content varies for water saturated carbon dioxide. The figure has a pressure range of 10 to 180 bara for temperatures 12, 20, 25 and 50°C. Carbon dioxide is in vapour phase at the lowest pressures and liquid phase at the highest pressures. The phase transition can be observed by a sudden high increment in water content. The water contents have been estimated with an SRK model in Aspen HYSYS. For comparison, experimental data has also been given for temperatures 20, 25 and 50°C (references according to Table 2-4).

The water content of gases depends on pressure, temperature and composition. Generally, the water content of a gas increases with temperature, which is in agreement with Figure 3-3. For a given temperature, the content decreases until a local minimum is reached. After the minimum point, it increases again until a sudden relatively high increment occurs. The sudden increase in solubility occurs after phase transition to either liquid (e.g. at about 65 bar for a temperature of 25°C) or dense-phase. The standard SRK model in Aspen HYSYS fails to predict the water content at higher pressures, which can be seen by the large vertical distance between the predictive curves and the experimental points. The failure is in agreement with the foresight given by the authors of the GPSA, which also strongly recommend experimental data comparison, especially for acid gas purposes (GPSA 2004). Similar model imperfections has been found for one adapted SRK-HV Pedersen model (Austegard et al. 2006). The sudden increase of water content is less pronounced at higher temperatures, which can be seen by the experimental points for 50°C.

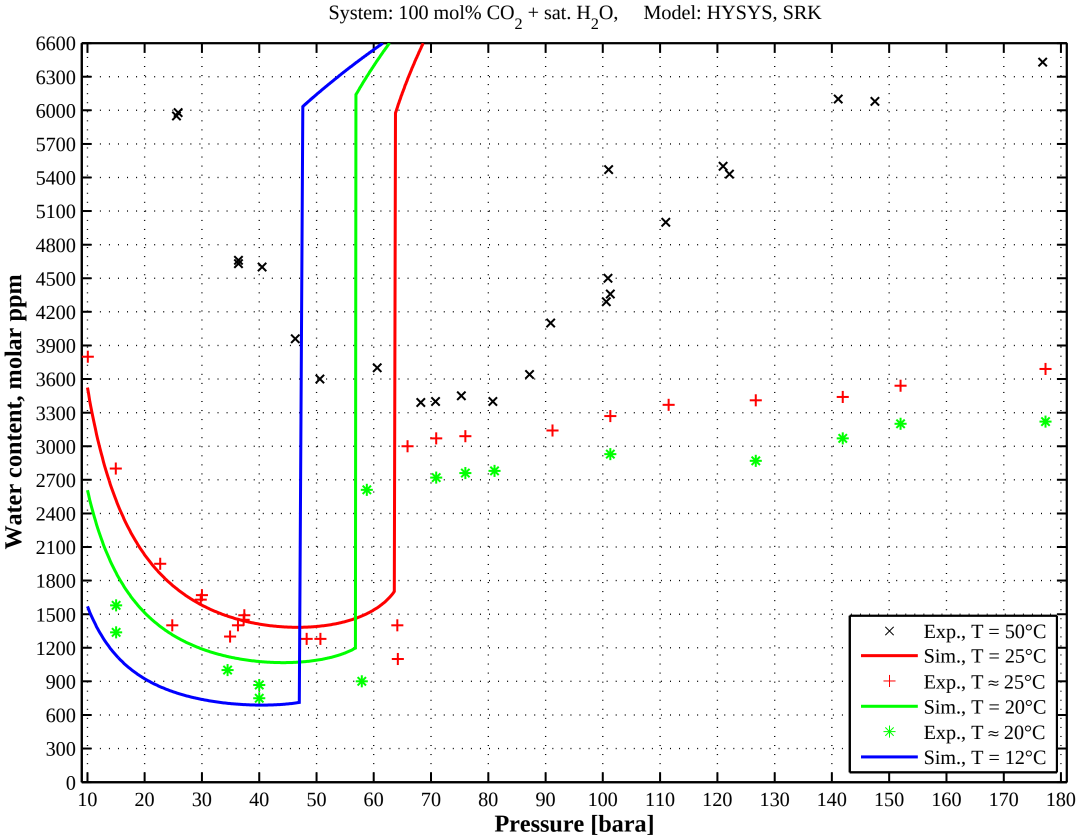

Figure 3-3 – Solubility of water in CO_2, model prediction and experimental points (references cf. Table 2-4)

In general, water is more soluble in carbon dioxide than methane or sweet natural gas mixtures (GPSA 2004). In accordance, this is shown by Figure 3-4 for a temperature of 25°C. The water solubility in CO_2 is higher throughout the pressure range, and especially at higher pressures, where the carbon dioxide condenses to liquid phase. Methane is in liquid phase only at temperatures below its critical temperature of below -82°C (Table 2-1), thus, no phase transition occurs for methane for this range. The model predictions of water content seem to be much better for CH_4 than CO_2. It is considered that a mixture of the two components will have intermediate contents of water. Based on the experimental points, it is considered that a trend similar to CO_2 will occur for systems rich in CO_2 and lean in CH_4 (Song and Kobayashi 1990). Very few articles were found for CO_2-rich mixtures.

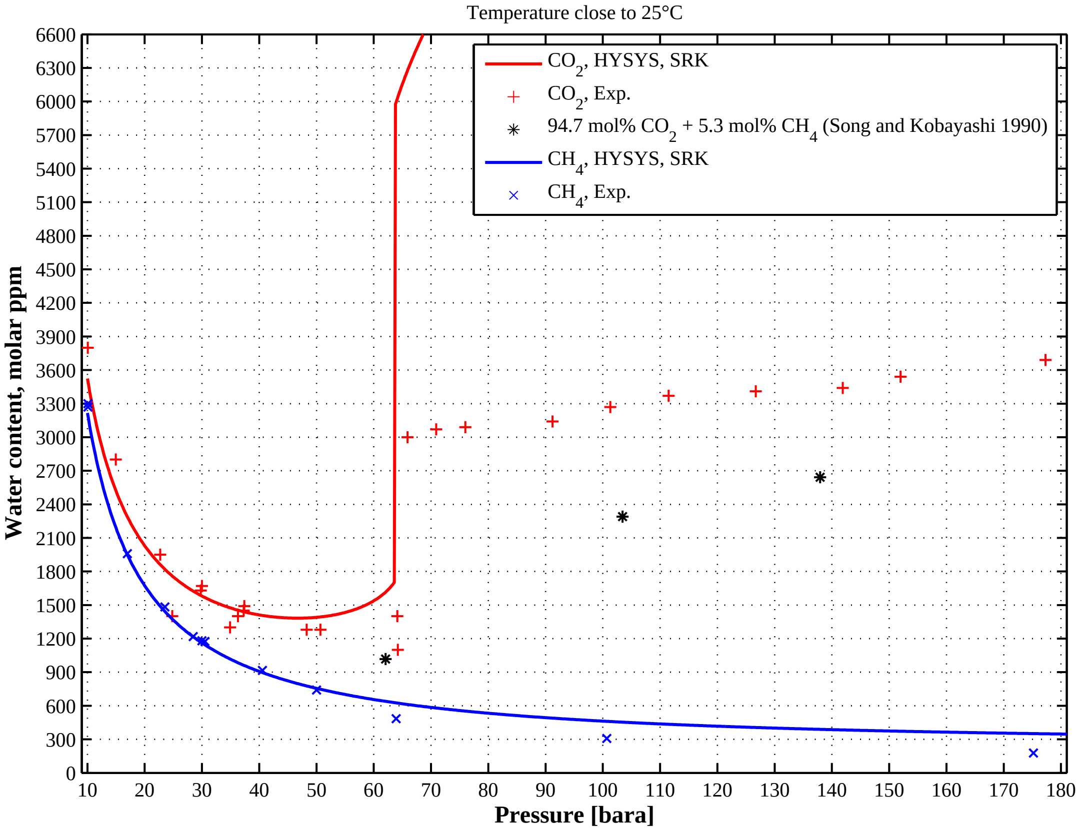

Figure 3-4 – Solubility of water in carbon dioxide or methane, model predictions and experimental points (references cf. Table 2-4 and Table 2-5)

3.1.5 Design objectives and constraints

The design of a CO_2 compression system should be tailored to meet certain objectives within given constraints. One can specify the number of compression stages, discharge pressures and intermediate cooling temperature to reach certain goals. The objectives could be:

- minimising overall compressor duty (lower operating costs),
- ideal pressure ratios (as mentioned),
- maximum condensation of water, and
- no dehydration/gas treatment (if possible).

Moreover, the relevant constraints could be due to:

- maximum discharge temperature of each stage (as mentioned),
- maximum compression ratio (as mentioned)
- available cooling medium (temperature and flow rate),
- corrosion in equipment and piping, and
- cavitation and vibration in effluent liquid CO_2 pump (two-phase).

3.2 Case studies of CO_2 processing systems

Several case studies have been done in order to investigate sensitivity of key properties of the CO_2 compression system. Subsequent sections highlight the main results and give brief discussions. The following cases were found relevant:

- 3.2.1 Four-stage system
- 3.2.2 Three-stage system
- 3.2.3 Effect of high level of impurities
- 3.2.4 Effect of type of impurity
- 3.2.5 Effect of impurity concentration
- 3.2.6 Compression, only
- 3.2.7 Maximum free-water removal (without dehydration)
- 3.2.8 Handling of impurities

3.2.1 Four-stage system without impurities (water saturated pure CO_2)

A simple and illustrative four-stage compression system is shown by a flowsheet (Figure 3-5) and by a pressure-enthalpy diagram for pure CO_2 (Figure 3-6).

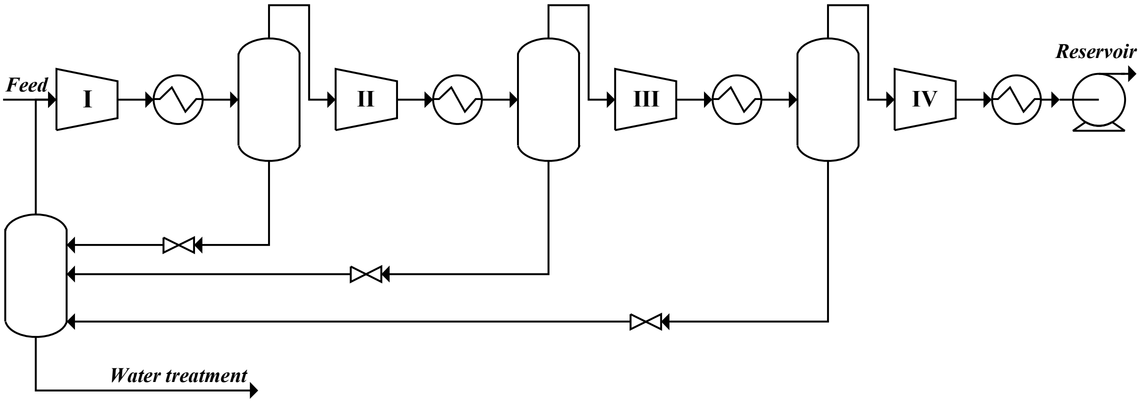

Figure 3-5 – CO_2 four-stage compression system without dehydration/gas treatment

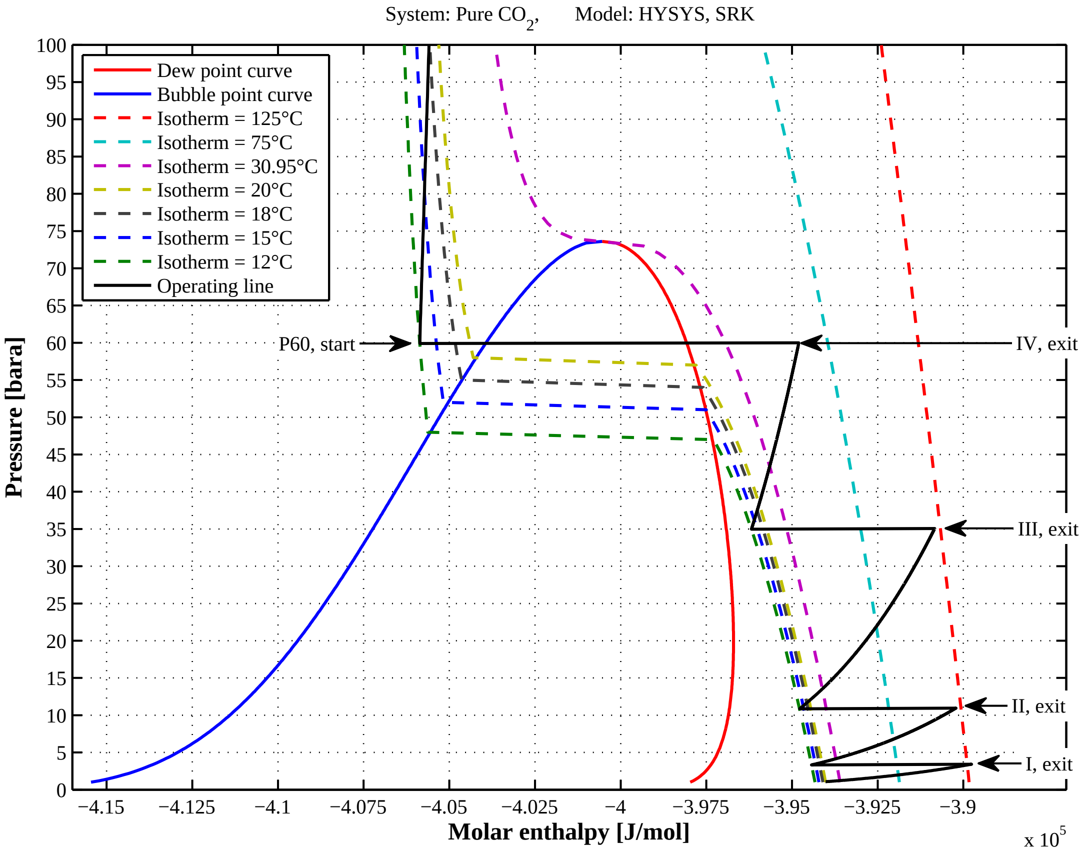

Figure 3-6 – *P-h* diagram for pure CO_2 with four stages, basis: Aspen HYSYS and SRK

The pressure-enthalpy diagram (Figure 3-6) shows one operation option in agreement with the flowsheet (Figure 3-5). The diagram represents carbon dioxide without any contaminants/impurities. The effect of water content on this diagram (also Figure 3-8, Figure 3-9 and Figure 3-11) is considered negligible. The diagram (also Figure 3-8, Figure 3-9, Figure 3-10, Figure 3-11 and Figure 3-13) are calculated by use of the standard SRK model in Aspen HYSYS (AspenTech 2010a).

CO_2-rich gas from the capturing process enters the compression system at the first compression stage, indicated by I in Figure 3-5. The gas is compressed to 3.4 bara (arrow I, Figure 3-6) and cooled to 12°C. Subsequently, condensed water exits the bottom of a gas-liquid separator, and the gas exits at top. It is further compressed by a 2nd compression stage to 11 bara (II, Figure 3-6). The gas heats up during compression and exits at 125°C before cooling to 12°C. Further compression at stage III to 35 bara (III, Figure 3-6) and stage IV to 60 bara (IV, Figure 3-6). After reaching 60 bara, the gas is condensed to liquid CO_2 at 12°C (P, Figure 3-6). After condensation, the liquid CO_2 is pumped to a high enough pressure to ensure flow to the reservoir (Section 3.1.2).

Prioritised objectives/limitations for this case

1. Cooling to 12°C
2. Gas condensation of 60 bara
3. Maximum compressor discharge temperatures of 125°C
4. Gas/liquid separation (water removal) at 35 bara
5. Equal compressor pressure ratios

The compressor ratios are set equal to about 3.2 for the first 3 stages and about 1.7 for the last stage. The last ratio is much lower than the previous three, since gas condensation at 60 bara was set. Using ratio of 3.2 on the first three stages lead to maximum discharge temperatures of 125°C, this is within the limits suggested in Section 3.1.3. Setting discharge pressure of stage III at 35 bara, can be beneficial in terms of removing as much water as possible (cf. Section 3.2.7).

3.2.2 Three-stage system without impurities (water saturated pure CO_2)

A simple and illustrative three-stage compression system is shown by a flowsheet (Figure 3-7) and by a pressure-enthalpy diagram for pure CO_2 (Figure 3-8).

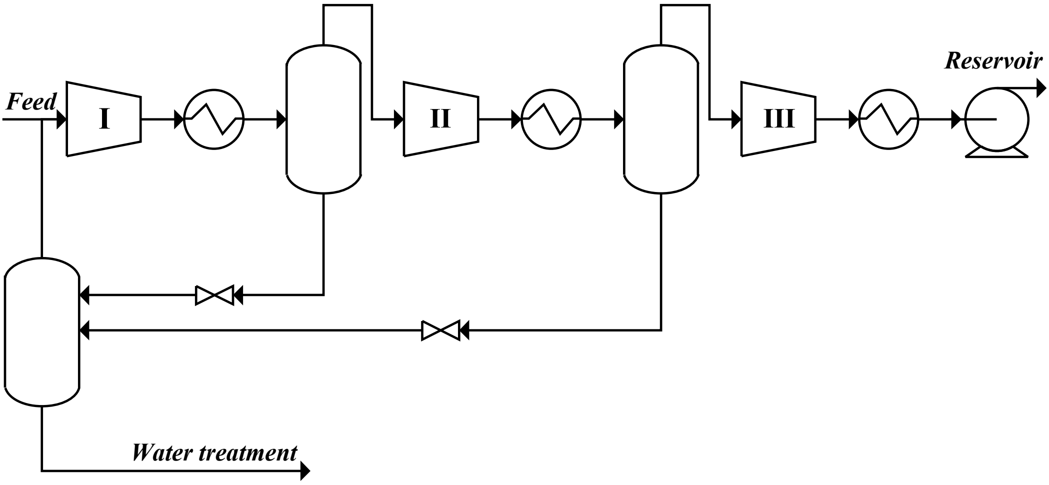

Figure 3-7 – CO_2 three-stage compression system without dehydration/gas treatment

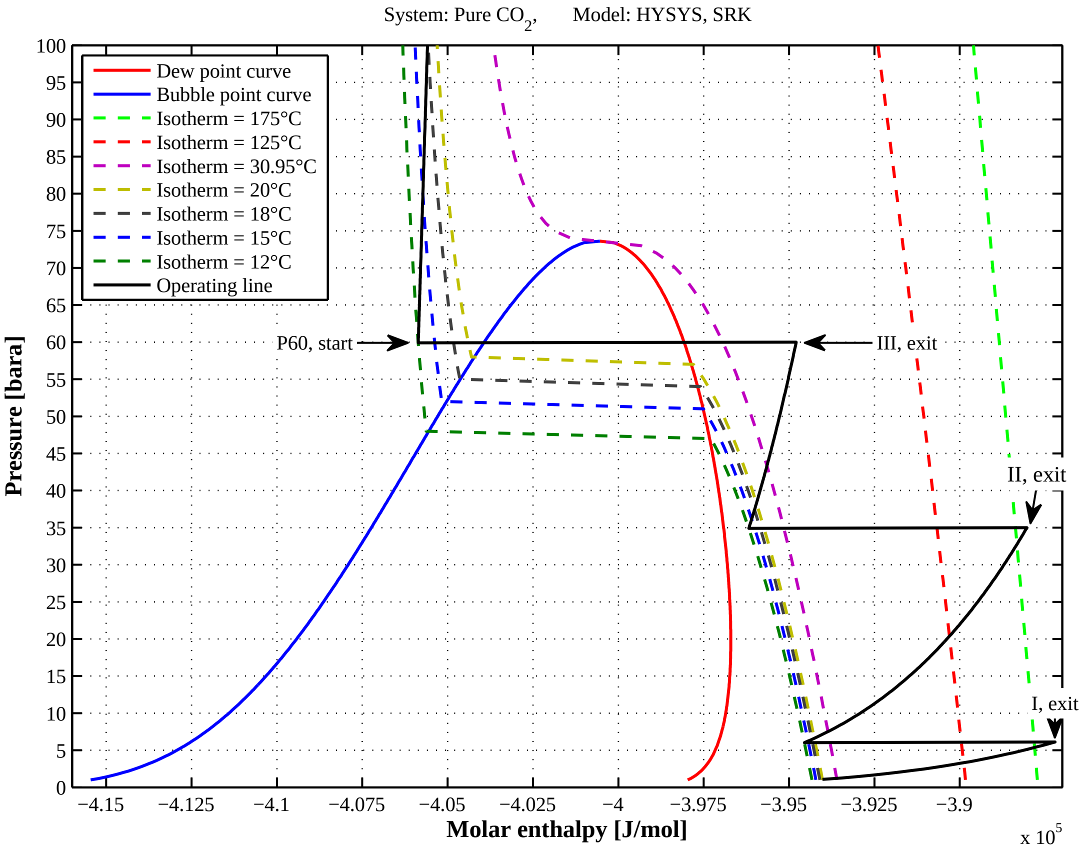

Figure 3-8 – *P-h* diagram for pure CO_2 with three stages, basis: Aspen HYSYS and SRK

Prioritised objectives/limitations for this case

1. Cooling to 12°C
2. Gas condensation of 60 bara
3. Gas/liquid separation (water removal) at 35 bara
4. Equal compressor pressure ratios

If you compare the three-stage *P-h* diagram (Figure 3-8) with the four-stage diagram (Figure 3-6), one can see that discharge temperature is higher (175°C vs. 125°C). Simply put, the higher temperature is a result of operating the system at a higher pressure-ratio without any extra cooling. As mentioned in Section 3.1.3, the discharge temperature of 175°C can be too high from a material point of view, and it can be necessary to alter the process configuration.

3.2.3 System with water saturated CO_2-rich gas (95 mol% CO_2, 2.5 mol% CH_4, 2.5 mol% N_2)

The effect of impurities on the compression system was investigated. A pressure-enthalpy diagram for CO_2-rich gas with 2.5 mol% methane and 2.5 mol% nitrogen is given as Figure 3-9. The process represents a four-stage compression system similar to Figure 3-5.

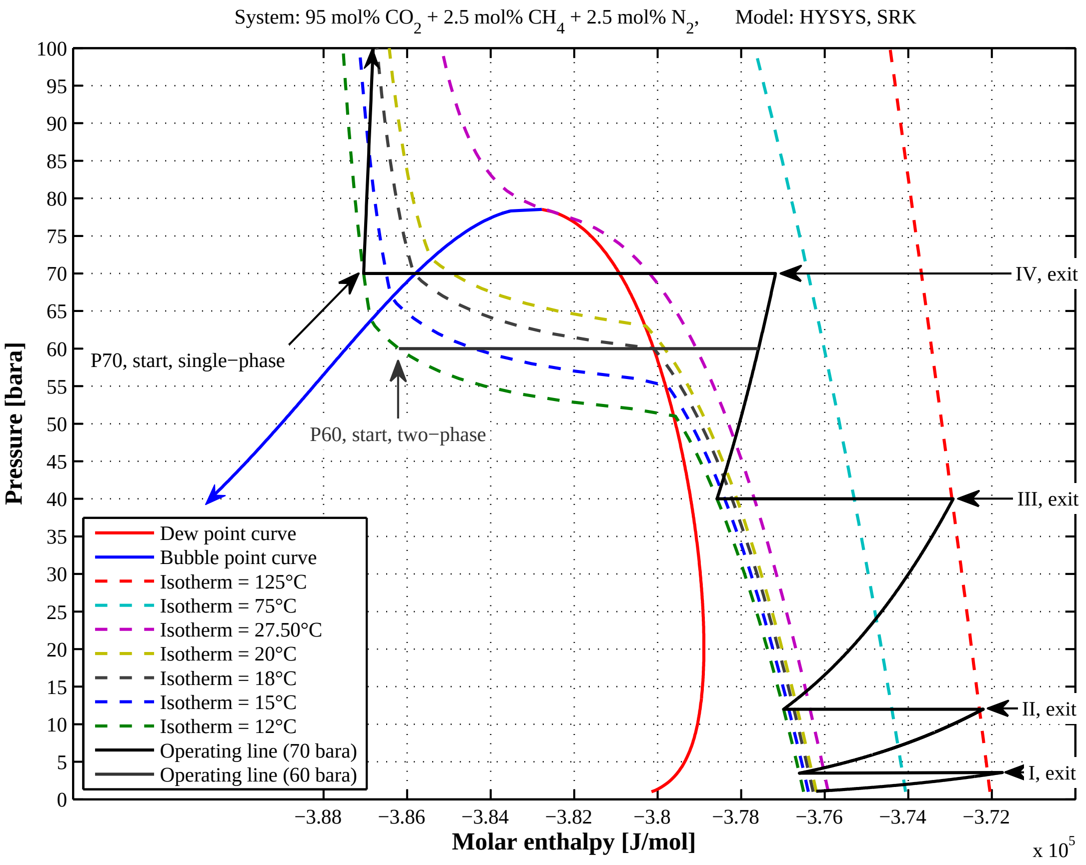

Figure 3-9 – *P-h* diagram for four-stage 95 mol% CO_2, 2.5 mol% CH_4 and 2.5 mol% N_2

Prioritised objectives/limitations for this case

1. Cooling to 12°C
2. Gas condensation at 60 bara
3. Gas/liquid separation (water removal) at 35 bara
4. Equal compressor pressure ratios

According to Figure 3-9 calculated by the standard SRK model and Aspen HYSYS, condensation of the CO_2-rich gas at 60 bara at 12°C (P60, Figure 3-9) would likely result in obtaining both liquid and gas (two-phase). This is caused by the change of *P-h* diagram due to introduction of methane and nitrogen, compared with pure CO_2 in Figure 3-6. Two-phase flow is undesirable since it could lead to subsequent problems in the pump or too much bleed (top outlet flow) in a subsequent tank (loss of compressed CO_2-rich gas). By alternation of the process design to gas condensation at 70 bara (P70, Figure 3-9), the two-phase problem can be avoided. Alternatively, the cooling temperature could be lowered leading to a full condensation. However, this is not recommended, since hydrates may be formed at around 10°C, (Figure 1-5, Section 1.1) or (Austegard et al. 2006).

3.2.4 System with water saturated CO_2-rich gas (95 mol% CO_2, 5 mol% impurities)

To show the effect of different components on the compression system, a *P-h* diagram was made for 5.0 mol% impurities. Figure 3-10 shows the effect of only methane as an impurity and equal moles of methane and nitrogen. The critical pressure of the ternary system (78.5 bara) is higher than the binary system (76.4 bara) and pure system (73.7 bara, Figure 3-6), which at most is almost a 5 bar difference.

Condensing the CO_2-CH_4 (binary) system at 60 bara and 12°C result in a single-phase. The point is very close to the bubble point curve (see P60, 2 comp., Figure 3-10), so the margin is very low, and two-phase can easily arise. As mentioned in Section 3.2.3, the CO_2-CH_4-N_2 system at 60 bara and 12°C is far from the single-phase region (P60, 3 comp.). According to the model, gas condensation at 70 bara and 12°C is plausible for both systems.

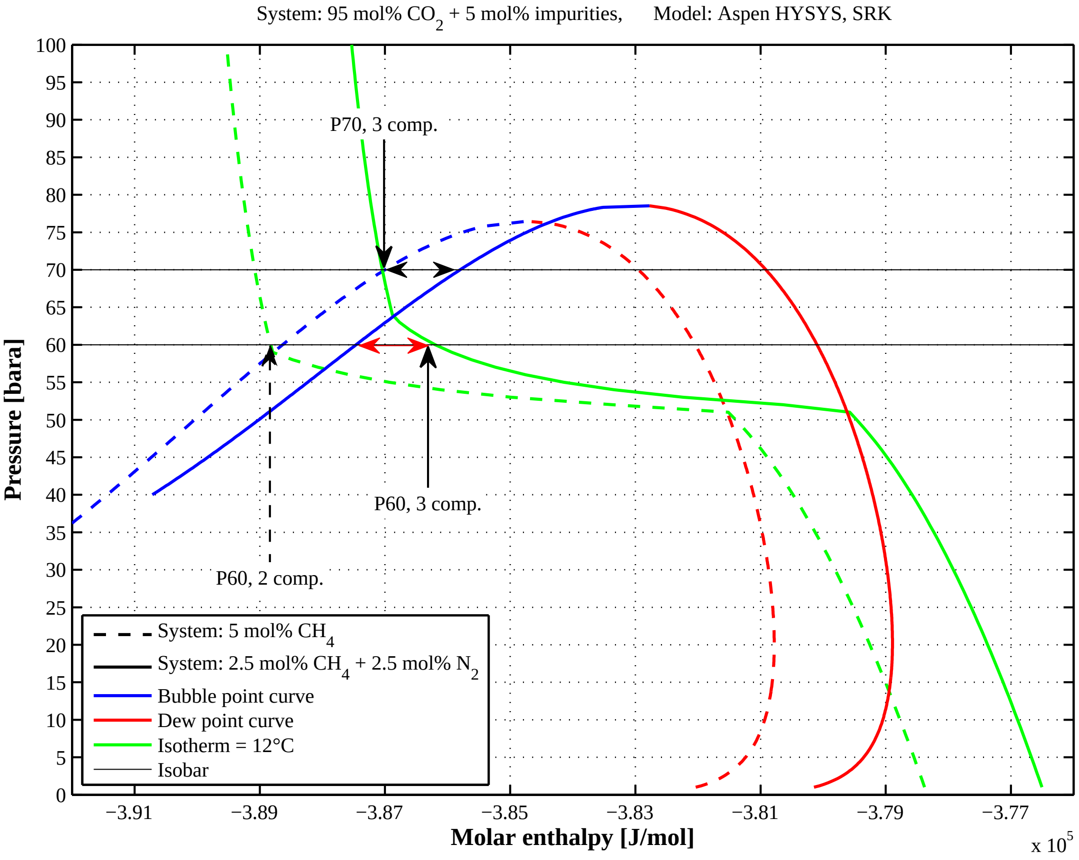

Figure 3-10 – *P-h* diagram for 95 mol% CO_2 and 5 mol% impurities, basis: Aspen HYSYS and SRK

3.2.5 System with water saturated CO_2-rich gas (CO_2-CH_4 system)

To show the effect of the concentration of an impurity, a *P-h* diagram was made for the carbon dioxide-methane system (Figure 3-11). The system is rich in CO_2, and the CH_4 concentration is of either one or five mol%.

The critical pressure of the binary system CO_2-CH_4 with 5.0 mol% CH_4 (76.4 bara) is higher than the 1.0 mol% CH_4 (74.3 bara) and pure system (73.7 bara, Figure 3-6). According to measurements of Xu et al., a binary system of CO_2-CH_4 with 13.2 mol% CH_4, the critical pressure is 79.8 bara (Xu et al. 1992). According to measurements of Bian et al., a binary system of CO_2-CH_4 with 3.38 mol% CH_4, the critical pressure is 77.0 bara (Bian et al. 1993). The location of the 12°C isotherm also change.

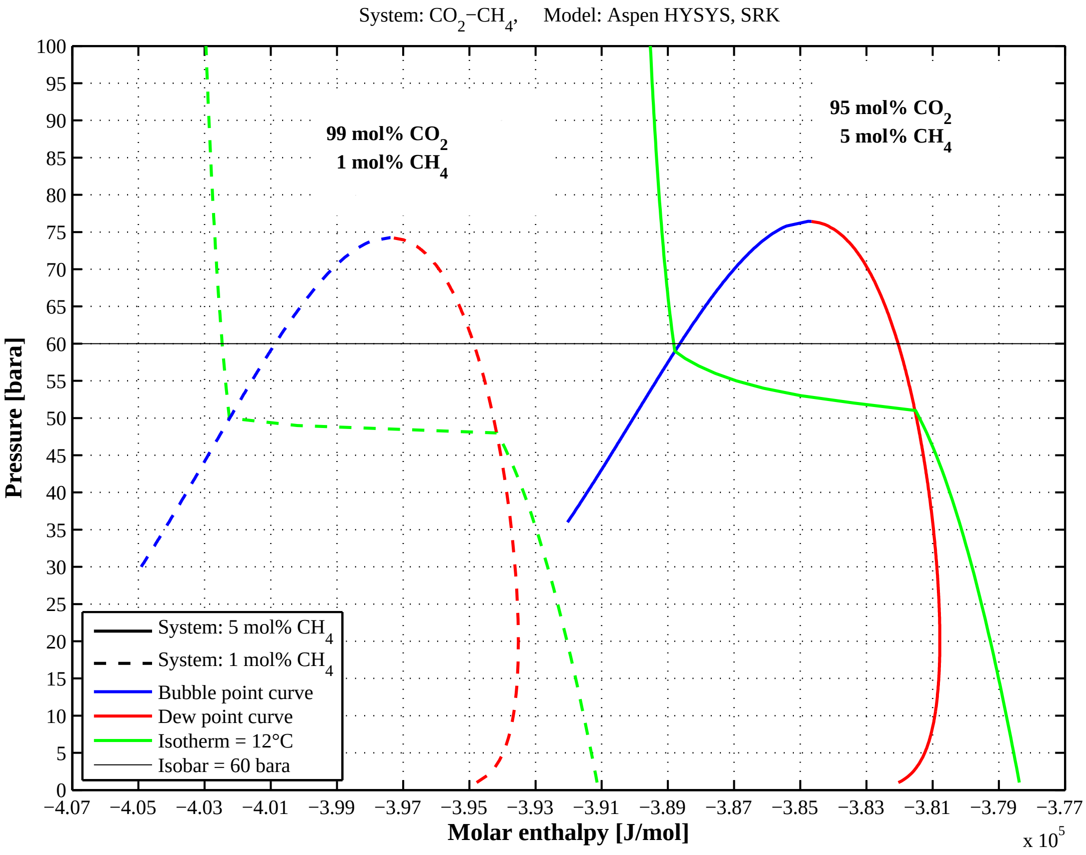

Figure 3-11 – *P-h* diagram for CO_2-CH_4, basis: Aspen HYSYS and SRK

3.2.6 System of compression-only (water saturated pure CO_2 system)

Figure 3-12 is a flowsheet representing the CO_2 processing system with compressors-only. The last compressor delivers a high enough pressure to ensure flow to reservoir. Figure 3-13 represents a pressure-enthalpy diagram for the process.

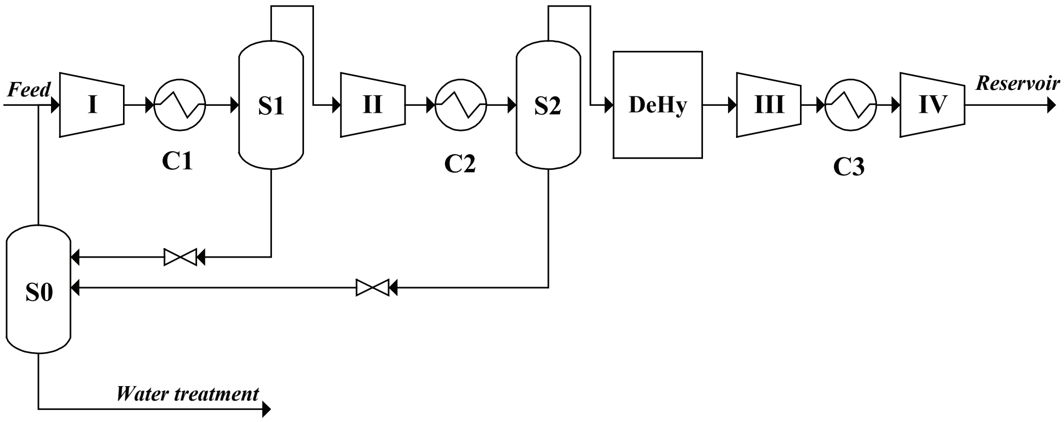

Figure 3-12 – CO_2 compression-only system; four-stage compression (I, II, III, IV), intermediate coolers (C1, C2 and C3), gas-liquid separators (S0, S1 and S2) and dehydration unit (DeHy).

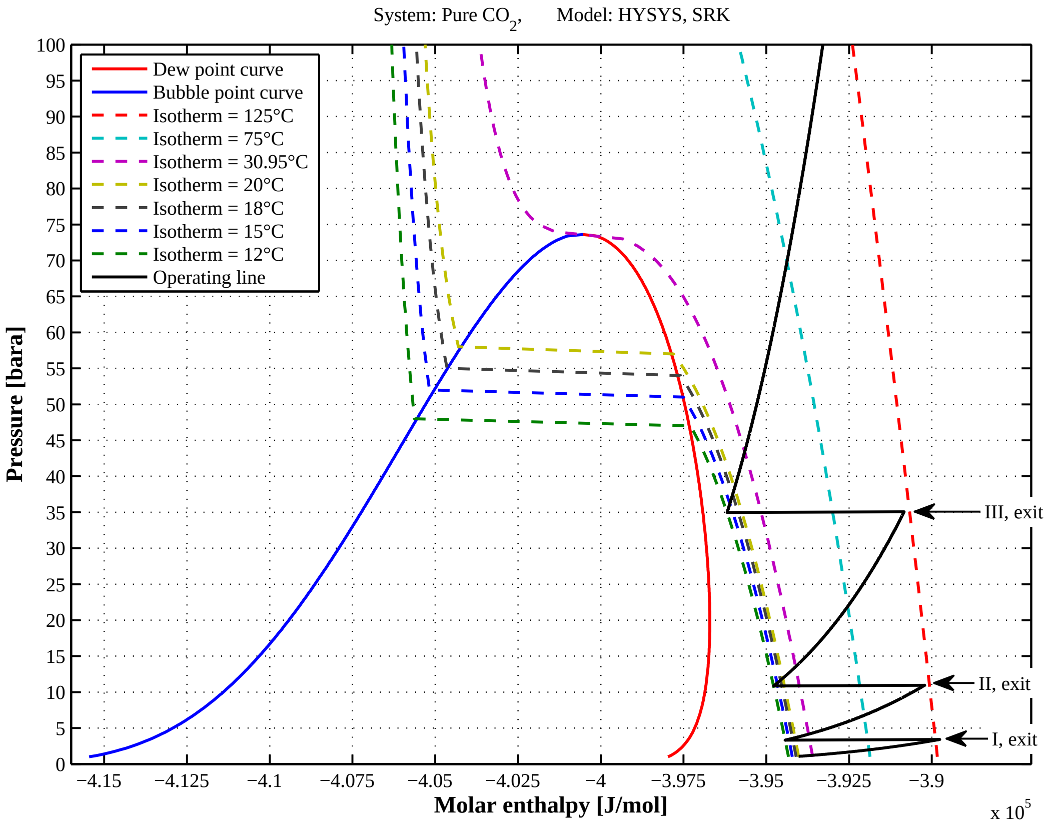

Figure 3-13 – P-h diagram for pure CO_2 compression system without reservoir pump

Figure 3-13 shows that two-phase problems can be completely avoided by use of compressors instead of compressors and a reservoir pump. It is not necessary more expensive to add one extra stage, compared to adding a pump with accompanying equipment. The dimensions of the pipes may differ due to a different density. The temperature of the fluid after compression will be higher than for compression and pump, but the pressure will be the same.

3.2.7 Maximum free-water removal without special treatment

Most acid gas injection systems include dehydration processes to remove the saturated water from the gas, to prevent corrosion and hydrate formation (Clark et al. 1998). A less costly alternative is to retain the water in the vapour phase and keep the content at a thermodynamically minimum by designing an optimised injection strategy (Clark et al. 1998).

As shown in Section 3.1.4, minimum water contents exist in equilibrium with gaseous carbon dioxide, dependent on pressure and temperature. The effect of pressure, temperature and impurity composition on this level has been investigated.

Figure 3-14 shows the effect of pressure and temperature on a pure carbon dioxide system saturated with water. The water content decrease with increasing pressure until a minimum is reached. For a given cooling temperature, this minimum can lead to maximum removal of free-water in a simple gas-liquid separator. For the whole temperature range (8°C – 18°C), an increase from 15 to 23 bara, leads to a clear reduction. After about 30-35 bar, the gain of pressure increase is relatively low.

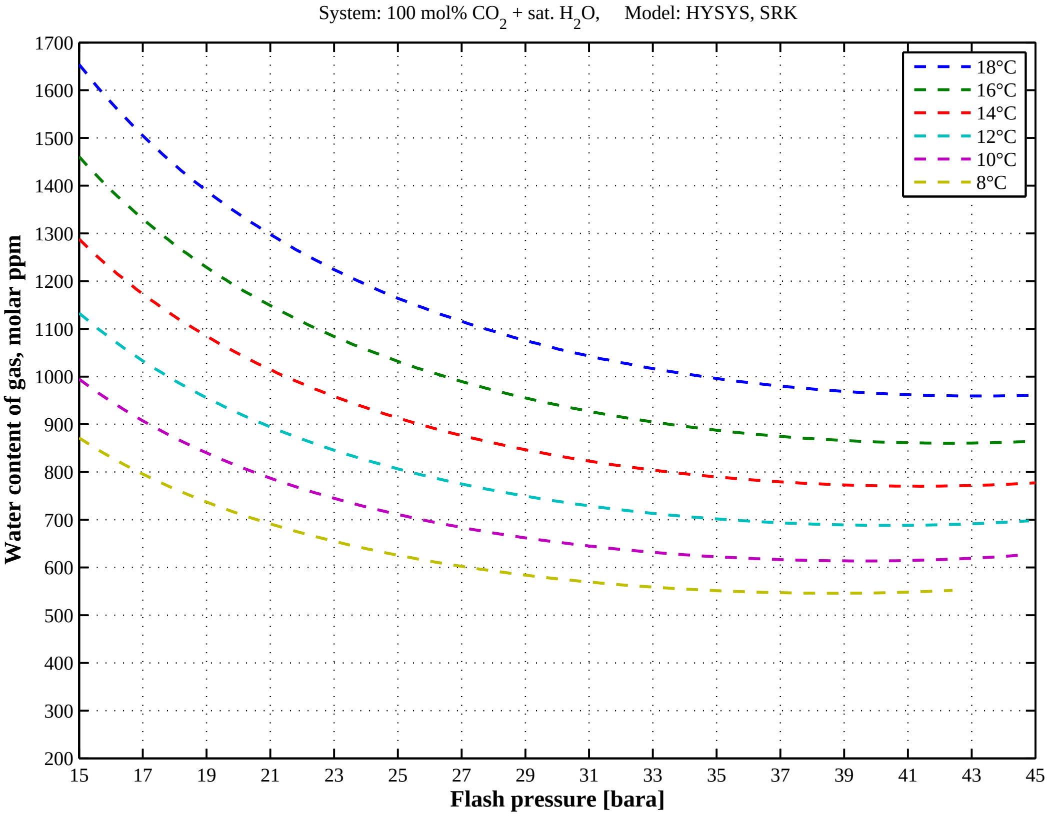

Figure 3-14 – Water content of pure gaseous carbon dioxide (SRK, Aspen HYSYS)

By examining Figure 3-15, which is the same diagram for pure methane, the same phenomenon does not occur. For pure methane, the water content decreases throughout the pressure range (15-50 bara). This difference suggested that mixtures of carbon dioxide and impurities should be evaluated. Also here, the effect of pressure increase is largest for about 15-25 bara (all temperatures). In general, the water is more soluble in gaseous carbon dioxide than gaseous methane.

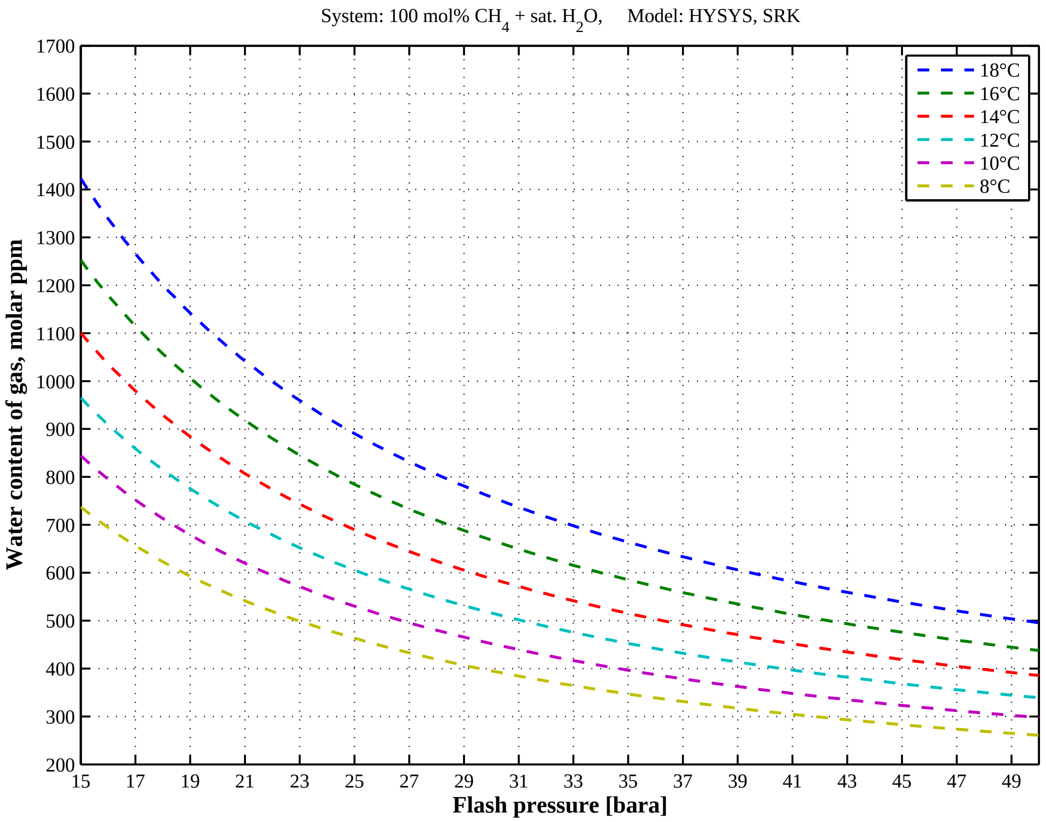

Figure 3-15 – Water content of pure gaseous methane (SRK, Aspen HYSYS)

Figure 3-16 and Figure 3-17 show the effect of impurities on the saturated water content of a CO_2-rich system. Figure 3-16 shows the small predicted deviations for impurity level up to a maximum of 5 mol%. The system of 5 mol% CH_4 has a lower water content than the 2.5 mol% CH_4 and 2.5 mol% N_2. Based on these figures, the effect is considered to be small.

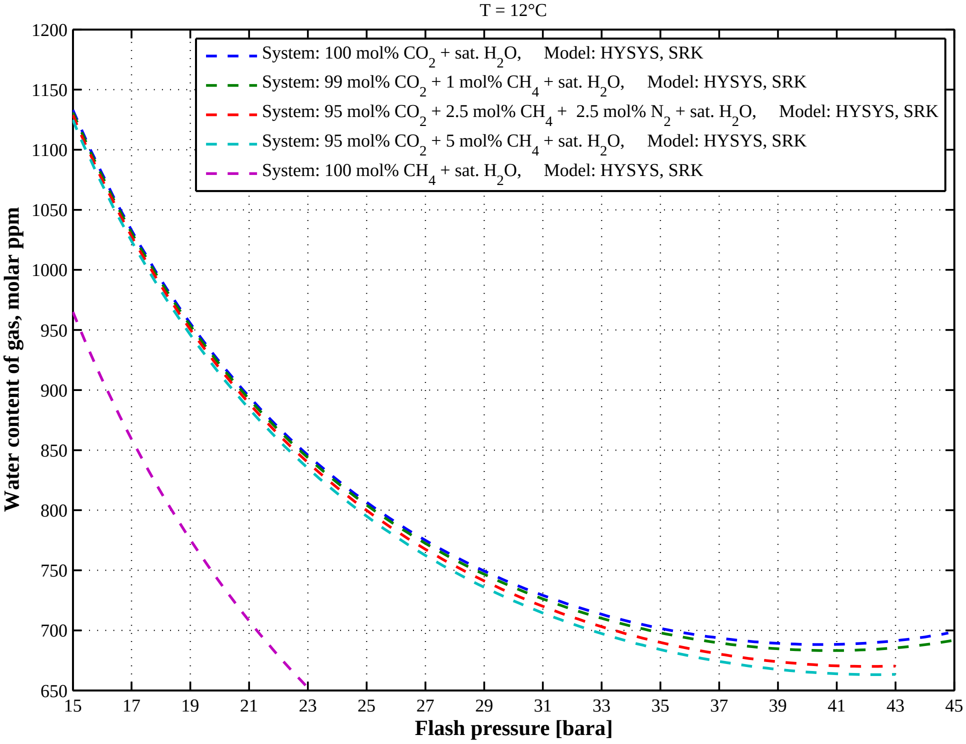

Figure 3-16 – Effect of impurities on water content of CO_2-rich gas (SRK, Aspen HYSYS)

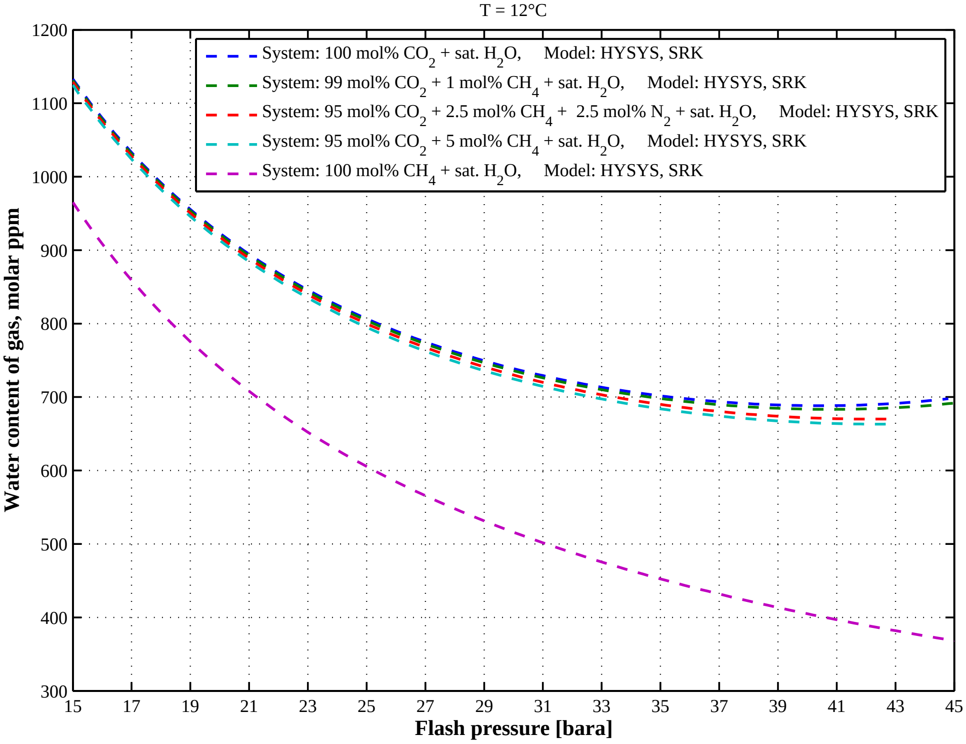

Figure 3-17 – Effect of impurities on water content of CO_2-rich gas (SRK, Aspen HYSYS)

Figure 3-18 shows predictions of water content of gaseous CO_2 at 25°C, for models SRK (Aspen HYSYS), regressed RK-Aspen (Aspen Properties) and regressed RK-Soave (Aspen Properties). The HYSYS model seem to predict within appreciable accuracy. The regressed Aspen Properties models predict overall a lower content. However, the all three models predict the same trend.

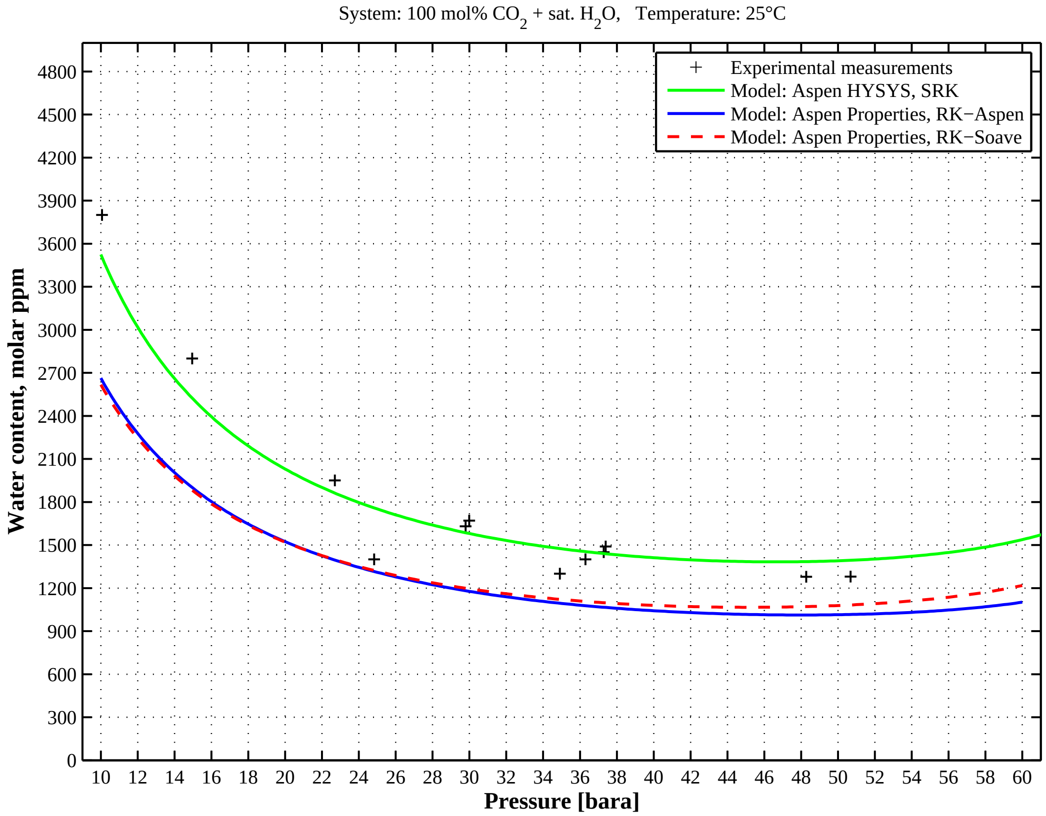

Figure 3-18 – Model predictions of saturated water content of gaseous carbon dioxide at 25°C, compared with experimental measurements (ref. Table 2-4)

In short, all the models and figures predict a minimum water content at a certain pressure for each temperature. The decrease after about 28-36 bar are low compared to 10-20+ bar. Therefore, it is strongly recommended to set discharge pressure (with intermediate cooling and gas-liquid separation) at this pressure leading to maximum removal of free-water. Possible effluent dehydration units will have less to remove, which can be cost reducing in forms of longer cycles for adsorbents or lower recirculation rates (less operating cost, pump/reboiler) for absorption.

3.2.8 Handling of impurities

A simple way of handling impurities was proposed by utilising the difference in volatility without adding major equipment. The flowsheet is given by Figure 3-19, which shows that it is located after the tank relative to the general flowsheet given by Figure 3-1.

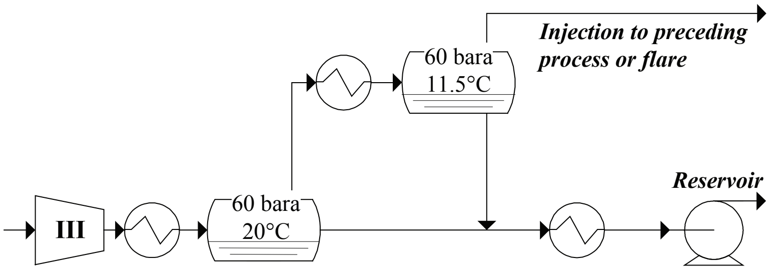

Figure 3-19 – Simple utilisation of difference in volatility, impurity removal

Figure 3-20 shows the result of a simulation, investigating the benefit of the impurity handling for a CO_2-rich system containing 2.5 mol% methane and 2.5 mol% nitrogen. The mole fraction of impurities of the entrance stream of the pump is represented by the left vertical axis. The level of purge (molar flow rate of purge stream relative to exit stream of compressor III) in % is given by the right vertical axis, and the blue line. The horizontal axis is temperature of the upper flash tank (marked with 11.5°C)

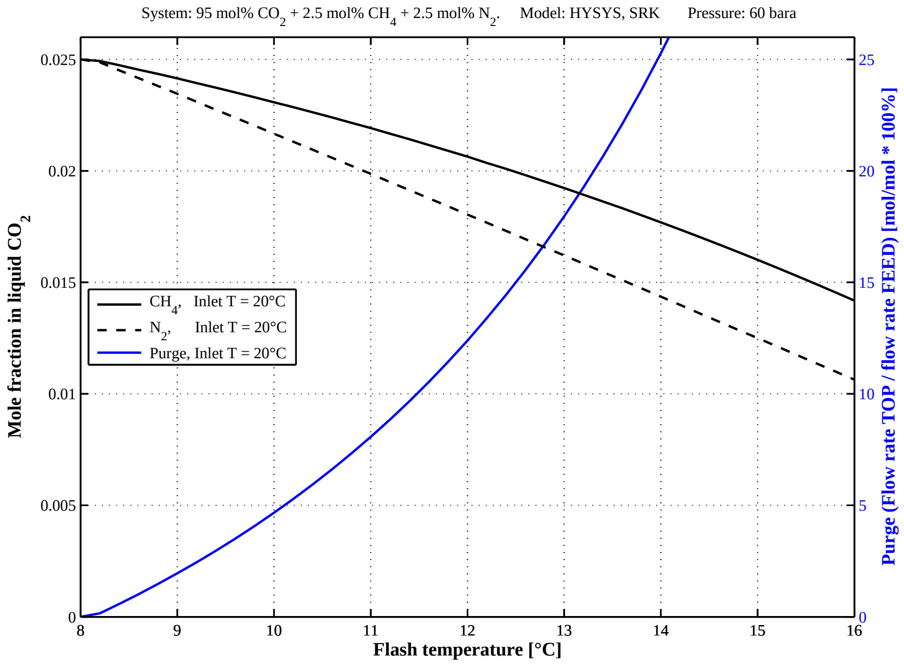

Figure 3-20 – Concentration of impurities in liquid CO_2 after flash

The results show that with even as high as a 10% purge and a flash temperature of 11.5°C, gives only a reduction of impurities from 5 mol% to about 4 mol%. The system has been further investigated with no particular good results, in terms of impurity removal. As suggested by Aspelund and Jordal, distillation can be used instead (Aspelund and Jordal 2007). This is considered straightforward after a dehydration unit, however, costs have not been considered.

3.3 Technical solutions for dehydration of CO_2 gas

The purpose of a dehydration processes is to remove water, in order to achieve:

- water content specification (maximum level restriction),
- prevent corrosion (Chapter 1.1), and
- prevent hydrate formation (Chapter 1.1) and condensation of free water.

Natural gas, natural gas liquids (NGLs) and associated gas condensates are commonly saturated with water when produced from reservoir (GPSA 2004). Common technical solutions for dehydration of these types of mixtures are (GPSA 2004):

- by adsorption/solid desiccants,
- by absorption/liquid desiccants,
- with calcium chloride,
- by refrigeration,
- by membrane permeation,
- by gas stripping (e.g. offshore produced condensate with counter-current dry gas), and
- by distillation.

Carbon dioxide resulting from capture processes is often saturated with water. According to John M. Campbell and Company there are several applicable dehydration options for CO_2 (Campbell 2005), similar to that of natural gas:

- by adsorption (solid desiccants like molecular sieves, silica gel etc.)
- by absorption (liquid desiccants like glycerol, glycols such as TEG and DEG, etc.), and
- with calcium chloride.

Smooth operation of the dehydration process is desirable, and can be important to consider when choosing between the different dehydration processes. In addition, equipment costs and operating costs should be considered, of course.

In hot climates where hydrate formation is unlikely, e.g. Abu Dhabi, and if the water specification is not too strict, a simple open-cycle refrigeration is proposed as an adequate option for dehydration (Kumar et al. 2010). The proposed process utilises a Joule-Thomson valve, heat integration and minor pressure losses.

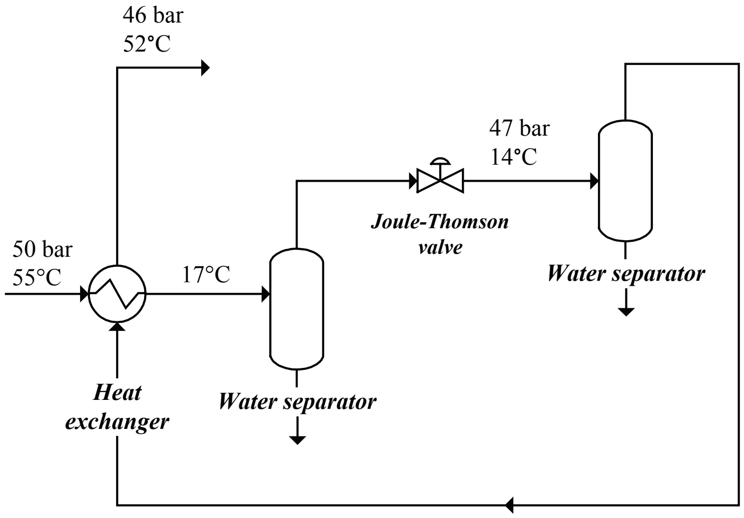

Figure 3-21 – Proposed open-cycle refrigeration system (for hot climates) (Kumar et al. 2010)

Absorption process

Using liquid desiccants for dehydration is common in the oil and gas process industry. Campbell reports existence of many early plants for CO_2 dehydration, with tri-ethylene glycol (TEG) or di-ethylene glycol (DEG) (Campbell 2005). Figure 3-22 shows a block diagram representing a TEG dehydration unit. Due to proximities, the figure also represents DEG and glycerol units (Campbell 2005). Nonetheless, the process conditions are likely to vary.

The concept of liquid desiccants is to utilize their property of increased solubility at higher pressure and lower temperature, and decreased solubility at lower pressure and higher temperature. Thereof, contacting the wet gas at high pressure and low temperature, absorbing water; hence, leading to a dry gas. Subsequently, depressurising and heating the rich solvent, leading to water removal. Thereafter, pressuring and cooling, making the solvent fully regenerated. However, some losses are likely to occur.

CO_2 containing water enters an inlet separator, which ensures knockout of free-water before the gas enters the contactor. Here, the gas flows upwards, as cooled lean solvent flows downwards. The contactor has trays or packing, which enhances the contact area between the two streams leading to a greater absorption. The counter-current flow and continuous absorption, makes sure that the purest CO_2 (at top) is in contact with the driest absorbent. The dehydrated CO_2 enters a scrubber before exiting the system.

The rich solvent is depressurised before entering a flash drum, where soluble gas (e.g. CO_2) is flashed off. A lean/rich heat exchanger, and further heat integration, can be used to preheat the liquid before entering the top of a stripper. In the stripping section, the rich solvent is heated up and water is stripped off as vapour. Additional stripping gas can also be used for enhancement. As the solvent travels downwards the stripping section, it becomes gradually leaner. At bottom the lean solvent exits and enter a booster, heat integration and a circulation pump before cooling. The cooling enhances the absorption capabilities, however, if too cold hydrates may be formed, which is very undesirable.

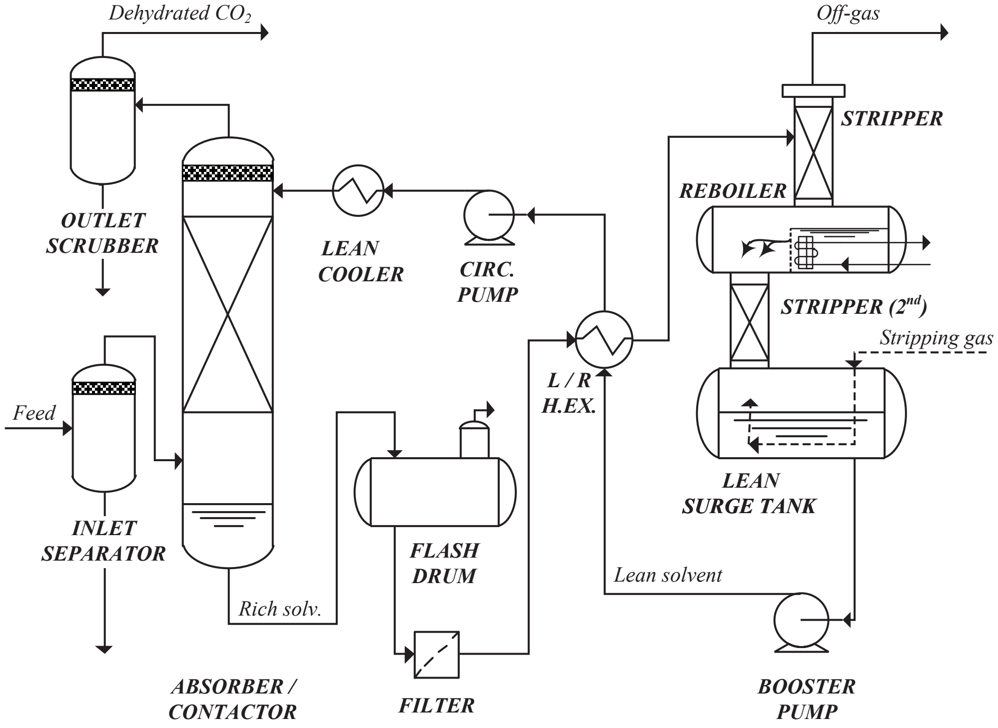

Figure 3-22 – DEG/TEG/glycerol dehydration system for carbon dioxide

The CO_2 entering a TEG unit usually contains more water than for a natural gas system. The CO_2 solubility in TEG is significantly higher than CH_4 (Campbell 2005). Moreover, TEG is soluble in supercritical CO_2 (Campbell 2005). All these properties, complicates this dehydration process compared to natural gas dehydration. Nonetheless, by oversizing the TEG unit and taking material constraints into account, it is considered to be fairly straightforward (Campbell 2005).

Adsorption process

A double bed adsorption process can be used for dehydration of carbon dioxide. Figure 3-23 shows a flowsheet for this double-bed process. Wet gas enters an inlet separator ensuring free-water removal, before entering the adsorbing bed. The process is run until the bed is filled with water to a specific level (break-through point etc.), before the wet inlet gas stream change direction to a regenerated bed. One bed is always in regeneration by heating a gas purge stream from the process. The hot stream will absorb water from the solid desiccants, and the stream can be re-introduced to an earlier stage of the compressor system. The hot stream might need to be cooled before re-introduced at a place where water can be knocked out. The solid desiccants in a regenerating bed also need to be adequately cooled before used as an adsorbing bed. Molecular sieve is used for dehydration to 50 ppm water in the Snøhvit CO_2 storage process (Maldal and Tappel 2004).

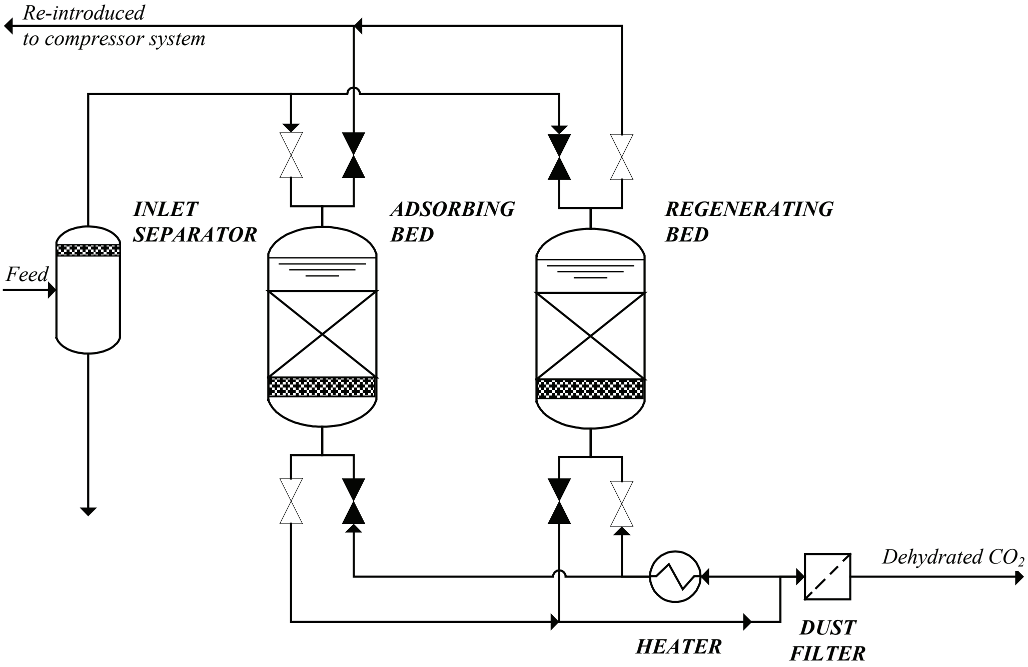

Figure 3-23 – Double-bed adsorption system for carbon dioxide dehydration

4 Conclusion and recommendations

Experimental data and model fitting

Considerable amount of experimental data were assembled for water solubility in CO_2, CH_4 and N_2, and of vapour-liquid equilibrium data for CO_2-CH_4 and CO_2-N_2 system. Regression of binary interaction parameters were carried out by using Aspen Properties and packages RK-Soave and RK-Aspen. The regression seems to be working; all the positive binary interaction parameters with water in either CO_2, CH_4 or N_2 seem likely. However, the lack of capability in the packages on simply including specific alpha functions (as Mathias-Copeman), makes the possibility of achieving great improvements less likely. SRK model of Aspen HYSYS seems to predict the water content at low pressures relatively well.

It has been shown that the regressed RK-Soave and RK-Aspen seem to fail to predict water content accurately. In addition, interactions between compounds in relevant mixtures seem to be less accurate. It is recommended that further work on model improvements should be carried out. By controlling the use of thermodynamic equations and special functions like the Mathias-Copeman alpha function, model improvements are likely. Experimental data like the ones assembled here can also be used to regress parameters improving the more advanced models. Such models can then be used in process simulators with greater modification capabilities.

Nevertheless, it is of belief that the observed trends and the result given are accurate enough to be of great importance for design and process operability. For further work, specific results should be validated with known well-predicting models (of greater accuracy).

Process operability and design

Different system and process options for CO_2 processing thereof compression, maximum free-water removal, dehydration and impurity removal have been investigated.

Available cooling quality (i.e. cooling temperature), hydrate formation temperature, and the influence of impurities have been simulated with focus on number of compression stages, compression ratios and single-phase flow. The following aspects have been found relevant:

- Material constrains on compressor discharge temperatures, can lead to requirement of an additional compression stage.
- Relevant impurities (CH_4 and N_2) at concentration of interest (maximum 5 mol%) can affect such that the condensation of CO_2 require a higher pressure for a given cooling temperature, in order to avoid two-phase flow in CO_2 injection pump.

- Different impurities (either CH_4 or N_2) have been found to have different effect on the system, and it seems like nitrogen has more significant affect than methane on two-phase development in pressure-enthalpy curves.

The effect of pressure and level of impurities on water content upon free-water removal and dehydration has been investigated. It seems to exist an ideal pressure range, where a minimum water content exist, which by proper design can maximise the removal of free-water and reduce the requirements and cost of a dehydration system. The minimum level may be low enough that dehydration may be omitted and further investigation on this topic is strongly recommended.

List of references

.

Al-Sahhaf, T.A., Kidnay, A.J., and Sloan, E.D. 1983. Liquid + Vapor Equilibria in the N2 + CO2 + CH4 System. Industrial & Engineering Chemistry Fundamentals **22**(4): 372-380.

Althaus, K. 1999. Messung und Berechnung von Wassergehalten kohlenwasserstoffhaltiger Gasgemische. VDI-Verlag., Düsseldorf.

Arai, Y., Kaminishi, G., and Saito, S. 1971. The experimental determination of the PVTX-relations for the carbon dioxide-nitrogen and the carbon dioxide-methane systems. Journal of Chemical Engineering of Japan **4**(2): 113–122.

Aspelund, A., and Jordal, K. 2007. Gas conditioning--The interface between CO2 capture and transport. International Journal of Greenhouse Gas Control **1**(3): 343-354.

AspenTech. 2010a. Aspen HYSYS V7.2. Aspen Technology, Inc., Burlington, MA., USA.

AspenTech. 2010b. Aspen Properties Help, V7.2. Aspen Technology, Inc., Burlington, MA., USA.

AspenTech. 2010c. Aspen Properties V7.2. Aspen Technology, Inc., Burlington, MA., USA.

Austegard, A., Solbraa, E., De Koeijer, G., and Mølnvik, M.J. 2006. Thermodynamic Models for Calculating Mutual Solubilities in H2O-CO2-CH4 Mixtures. Chemical Engineering Research and Design **84**(9): 781-794.

Bamberger, A., Sieder, G., and Maurer, G. 2000. High-pressure (vapor+liquid) equilibrium in binary mixtures of (carbon dioxide+water or acetic acid) at temperatures from 313 to 353 K. The Journal of Supercritical Fluids **17**(2): 97-110.

Bian, B., Wang, Y., Shi, J., Zhao, E., and Lu, B.C.Y. 1993. Simultaneous determination of vapor-liquid equilibrium and molar volumes for coexisting phases up to the critical temperature with a static method. Fluid Phase Equilibria **90**(1): 177-187.

Blanco, S.T., Velasco, I., Rauzy, E., and Otín, S. 1999. Water dew points of binary nitrogen+water and propane+water mixtures. Measurement and correlation. Fluid Phase Equilibria **161**(1): 107-117.

Bogoya, D., Müller, C., and Oellrich, L.R. 1993. Wiss. Abschlussber. 28. Internat., Seminar Univ. Karlsruhe: 54-63.

Briones, J.A., Mullins, J.C., Thies, M.C., and Kim, B.U. 1987. Ternary phase equilibria for acetic acid-water mixtures with supercritical carbon dioxide. Fluid Phase Equilibria **36**: 235-246. doi:10.1016/0378-3812(87)85026-4.

Brown, T.S., Niesen, V.G., Sloan, E.D., and Kidnay, A.J. 1989. Vapor-liquid equilibria for the binary systems of nitrogen, carbon dioxide, and n-butane at temperatures from 220 to 344 K. Fluid Phase Equilibria **53**: 7-14.

Campbell, J.M. 2005. CO2 Surface Facilities. John M. Campbell and Company, Norman, OK, USA.

Chapoy, A., Burgass, R., Tohidi, B., Austell, J.M., and Eickhoff, C. 2009. Effect of Common Impurities on the Phase Behaviour of Carbon Dioxide Rich Systems: Minimizing the Risk of Hydrate Formation and Two-Phase Flow. *In* Offshore Europe, Aberdeen, UK.

Chapoy, A., Coquelet, C., and Richon, D. 2003. Solubility measurement and modeling of water in the gas phase of the methane/water binary system at temperatures from 283.08 to 318.12 K and pressures up to 34.5 MPa. Fluid Phase Equilibria **214**(1): 101-117.

Chapoy, A., Mohammadi, A.H., Tohidi, B., and Richon, D. 2004. Gas Solubility Measurement and Modeling for the Nitrogen + Water System from 274.18 K to 363.02 K. Journal of Chemical & Engineering Data **49**(4): 1110-1115.

Clark, M.A., Svrcek, W.Y., Monnery, W.D., Jamaluddin, A.K.M., Bennion, D.B., Thomas, F.B., Wichert, E., Reed, A.E., and Johnson, D.J. 1998. Designing an optimized injection strategy for acid gas disposal without dehydration. pp. 49-56.

Cole, I.S., Corrigan, P., Sim, S., and Birbilis, N. 2011. Corrosion of pipelines used for CO2 transport in CCS: Is it a real problem? International Journal of Greenhouse Gas Control **In Press, Corrected Proof**.

Culberson, O.L., and McKetta, J.J. 1951. Phase Equilibria In Hydrocarbon-Water Systems IV - Vapor-Liquid Equilibrium Constants in the Methane-Water and Ethane-Water Systems.

Davalos, J., Anderson, W.R., Phelps, R.E., and Kidnay, A.J. 1976. Liquid-Vapor Equilibria at 250.00K for Systems Containing Methane, Ethane, and Carbon Dioxide. Journal of Chemical & Engineering Data **21**(1): 81-84.

Dohrn, R., Bünz, A.P., Devlieghere, F., and Thelen, D. 1993. Experimental measurements of phase equilibria for ternary and quaternary systems of glucose, water, CO2 and ethanol with a novel apparatus. Fluid Phase Equilibria **83**: 149-158.

Donnelly, H.G., and Katz, D.L. 1954. Phase Equilibria in the Carbon Dioxide–Methane System. Industrial & Engineering Chemistry **46**(3): 511-517.

Englezos, P., Kalogerakis, N., Trebble, M.A., and Bishnoi, P.R. 1990. Estimation of multiple binary interaction parameters in equations of state using VLE data. application to the Trebble-Bishnoi equation of state. Fluid Phase Equilibria **58**(1-2): 117-132.

Frøyna, E.W. 2004. Measurement of water content in gas. *In* Department of Chemical Engineering. Norwegian University of Science and Technology, Trondheim, Norway. p. 65+60.

Gillespie, P.C., and Wilson, G.M. 1980. Vapor-Liquid Equilibrium Data on Water-Substitute Gas Components: N2-H2O, H2-H2O, CO-H2O, H2-CO-H2O, and H2S-H2O, Research Report RR-41. Wiltec Research Co. Inc.

Gillespie, P.C., and Wilson, G.M. 1982. Vapor-liquid and liquid-liquid equilibria: water-methane, water-carbon dioxide, water-hydrogen sulfide, water-n-pentane and water-methane-npentane, Research Report RR-48. Wiltec Research Co. Inc.

GPSA. 2004. Engineering Data Book. 12th ed. Gas Processors Suppliers Association, Tulsa, OK, USA.

Helbæk, M., and Kjelstrup, S. 2006. Fysikalsk kjemi. 2nd ed. Fagbokforlag Vigmostad & Bjørke AS, Bergen, Norway.

Hovland, K.M. 2011. Australia planlegger CO2-skatt. *In* Teknisk Ukeblad. Teknisk Ukeblad Media AS, Oslo, Norway.

IPCC. 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Kaminishi, G.-I., Arai, Y., Saito, S., and Maeda, S. 1968. Vapor-Liquid Equilibria for Binary and Ternary Systems Containing Carbon Dioxide. Journal of Chemical Engineering of Japan **1**(2): 109-116.

King, A.D., and Coan, C.R. 1971. Solubility of water in compressed carbon dioxide, nitrous oxide, and ethane. Evidence for hydration of carbon dioxide and nitrous oxide in the gas phase. Journal of the American Chemical Society **93**(8): 1857-1862.

King, M.B., Mubarak, A., Kim, J.D., and Bott, T.R. 1992. The mutual solubilities of water with supercritical and liquid carbon dioxides. The Journal of Supercritical Fluids **5**(4): 296-302.

Kongsnes, E. 2008. Lovpriser CO2-avgift. *In* Aftenbladet. Mediehuset Stavanger Aftenblad, Stavanger, Norway.

Kosyakov, N.E., Ivchenko, B.I., and Krishtopa, P.P. 1982. Solubility of moisture in compressed gases at low temperatures. Voprosy Khimii i Khimicheskoi Tekhnologii(47): 33–36.

Kumar, S., Zarzour, O., and King, G. 2010. Design of CO2 Dehydration and Compression Facilities. *In* Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE.

Maldal, T., and Tappel, I.M. 2004. CO2 underground storage for Snøhvit gas field development. Energy **29**(9-10): 1403-1411.

Mathias, P.M., and Copeman, T.W. 1983. Extension of the Peng-Robinson equation of state to complex mixtures: Evaluation of the various forms of the local composition concept. Fluid Phase Equilibria **13**: 91-108.

Mohammadi, A.H., Chapoy, A., Richon, D., and Tohidi, B. 2004. Experimental Measurement and Thermodynamic Modeling of Water Content in Methane and Ethane Systems. Industrial & Engineering Chemistry Research **43**(22): 7148-7162.

Mohammadi, A.H., Chapoy, A., Tohidi, B., and Richon, D. 2005. Water Content Measurement and Modeling in the Nitrogen + Water System. Journal of Chemical & Engineering Data **50**(2): 541-545.

Mraw, S.C., Hwang, S.-C., and Kobayashi, R. 1978. Vapor-liquid equilibrium of the methane-carbon dioxide system at low temperatures. Journal of Chemical & Engineering Data **23**(2): 135-139.

Müller, G., Bender, E., and Maurer, G. 1988. Das Dampf-Flüssigkeitsgleichgewicht des ternären Systems Ammoniak-Kohlendioxid-Wasser bei hohen Wassergehalten im Bereich zwischen 373 und 473 Kelvin. Verlag Chemie, Weinheim, Germany.

Nakayama, T., Sagara, H., Arai, K., and Saito, S. 1987. High pressure liquid---liquid equilibria for the system of water, ethanol and 1,1-difluoroethane at 323.2 K. Fluid Phase Equilibria **38**(1-2): 109-127.

Neumann, A., and Walch, W. 1968. Dampf/Flüssigkeits-Gleichgewicht CO2/CH4 im Bereich tiefer Temperaturen und kleiner CO2-Molenbrüche. Chemie Ingenieur Technik **40**(5): 241-244.

Olds, R.H., Sage, B.H., and Lacey, W.N. 1942. Phase Equilibria in Hydrocarbon Systems.Composition of the Dew-Point Gas of the Methane-Water System. Industrial & Engineering Chemistry **34**(10): 1223-1227.

Pagnamenta, R. 2009. National Grid to pipe carbon dioxide emissions under North Sea. *In* The Times. Times Newspapers Ltd, London, England, UK.

Prausnitz, J.M., Lichtenthaler, R.N., and Azevedo, E.G.d. 1999. Molecular thermodynamics of fluid-phase equilibria. Prentice-Hall PTR, Upper Saddle River, N.J.

Rigby, M., and Prausnitz, J.M. 1968. Solubility of water in compressed nitrogen, argon, and methane. The Journal of Physical Chemistry **72**(1): 330-334.

Saddington, A.W., and Krase, N.W. 1934. Vapor-Liquid Equilibria in the System Nitrogen-Water. Journal of the American Chemical Society **56**(2): 353-361.

Seider, W.D., Seader, J.D., Lewin, D.R., and Widagdo, S. 2008. Product and process design principles: synthesis, analysis, and evaluation. 3rd ed. John Wiley & Sons, Hoboken, N.J., USA.

Sharma, S.C. 1969. Equilibrium Water Content of Gaseous Mixtures. The University of Oklahoma, Norman, Oklahoma, USA.

Soave, G. 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. Chemical Engineering Science **27**(6): 1197-1203.

Solbraa, E. 2003. NeqSim (Non-Equilibrium Simulator). The Department of Refrigeration and Air Conditioning, Norwegian University of Science and Technology (NTNU), Norway, http://folk.ntnu.no/solbraa/neqsim/NeqSim.htm.

Somait, F.A., and Kidnay, A.J. 1978. Liquid-vapor equilibriums at 270.00 K for systems containing nitrogen, methane, and carbon dioxide. Journal of Chemical & Engineering Data **23**(4): 301-305.

Song, K.Y., and Kobayashi, R. 1990. The water content of a carbon dioxide-rich gas mixture containing 5.31 Mol % methane along the three-phase and supercritical conditions. Journal of Chemical & Engineering Data **35**(3): 320-322.

Total. 2007. Project Information Dossier: Lacq CO2 Capture and Geological Storage Pilot Project. Available from http://www.total.com/MEDIAS/MEDIAS_INFOS/1872/EN/CO2-Lacq-Total-Project-Information-dossier.pdf [accessed 15 June 2011].

Tödheide, K., and Franck, E.U. 1963. Das Zweiphasengebiet und die kritische Kurve im System Kohlendioxid-Wasser bis zu Drucken von 3500 bar. Z. Phys. Chem. **37**: 387–401.

UNFCCC. 1992. Kyoto Protocol to the United Nations Framework Convention on Climate Change.

Valtz, A., Chapoy, A., Coquelet, C., Paricaud, P., and Richon, D. 2004. Vapour-liquid equilibria in the carbon dioxide-water system, measurement and modelling from 278.2 to 318.2 K. Fluid Phase Equilibria **226**: 333-344.

Webb, T. 2011. Budget 2011: Carbon tax brings higher electricity bills – and nuclear windfalls. *In* The Guardian. The Guardian, London, England, UK.

Webster, L.A., and Kidnay, A.J. 2001. Vapor−Liquid Equilibria for the Methane−Propane−Carbon Dioxide Systems at 230 K and 270 K. Journal of Chemical & Engineering Data **46**(3): 759-764.

Wei, M.S.W., Brown, T.S., Kidnay, A.J., and Sloan, E.D. 1995. Vapor + Liquid Equilibria for the Ternary System Methane + Ethane + Carbon Dioxide at 230 K and Its Constituent Binaries at Temperatures from 207 to 270 K. Journal of Chemical & Engineering Data **40**(4): 726-731.

Xu, N., Dong, J., Wang, Y., and Shi, J. 1992. High pressure vapor liquid equilibria at 293 K for systems containing nitrogen, methane and carbon dioxide. Fluid Phase Equilibria **81**: 175-186.

Yan, W., Kontogeorgis, G.M., and Stenby, E.H. 2009. Application of the CPA equation of state to reservoir fluids in presence of water and polar chemicals. Fluid Phase Equilibria **276**(1): 75-85.

Yarym-Agaev, N.L., Sinyavskaya, R.P., Koliushko, I.I., and Levinton, L.Y. 1985. Phase equilibria in the water---methane and methanol---methane binary systems under high pressures. Zhur. Priklad. Khim. **58**(1): 165.

Yokoyama, C., Wakana, S., Kaminishi, G., and Takahashi, S. 1988. Vapor-liquid equilibria in the methane-diethylene glycol-water system at 298.15 and 323.15 K. Journal of Chemical & Engineering Data **33**(3): 274-276.

Yorizane, M., Yoshimura, S., and Masuoka, H. 1970. Vapor Liquid Equilibrium at High Pressure N2-CO2, H2-CO2 system. Kagaku Kogaku **34**(9): 953-957.

Yorizane, M., Yoshimura, S., Masuoka, H., Miyano, Y., and Kakimoto, Y. 1985. New procedure for vapor-liquid equilibria. Nitrogen + carbon dioxide, methane + Freon 22, and methane + Freon 12. Journal of Chemical & Engineering Data **30**(2): 174-176.

Yucelen, B., and Kidnay, A.J. 1999. Vapor-liquid equilibria in the nitrogen+carbon dioxide+propane system from 240 to 330 K at pressures to 15 MPa. Journal of Chemical and Engineering Data **44**(5): 926-931.

Appendix A – Experimental data from literature

Reference	**Author(s)**	**Yr**	**T [℃]**	**No. of exp. pts. <= 100℃**
(Tödheie and Frank 1963)	Tödheide, K., and E. U. Franck	1963	[50 , 200]	8
(King and Coan 1971)	King, A. D., and C. R. Coan	1971	[25 , 100]	22
(Gillespie and Wilson 1982)	Gillespie, P. C., and G. M. Wilson.	1982	[15 , 260]	16
(Song and Kobayashi 1987)	Song, K. Y., and R. Kobayashi	1987	[-22 , 30]	11
(Briones et al. 1987)	Briones, J. A., J. C. Mullins, M. C. Thies, and B. U. Kim	1987	50	8
(Nakayama et al. 1987)	Nakayama, T., H. Sagara, K. Arai, and S. Saito	1987	[25]	3
(Müller, Bender, Maurer 1988)	Müller, G., E. Bender, and G. Maurer	1988	[100 , 200]	7
(King et al. 1992)	King, M. B., A. Mubarak, J. D. Kim, and T. R. Bott	1992	[15 , 40]	41
(Dohrn et al. 1993)	Dohrn, R., A. P. Bünz, F. Devlieghere, and D. Thelen	1993	[50]	3
(Bamberger et al. 2000)	Bamberger, A., G. Sieder, and G. Maurer	2000	[50 , 80]	29
(Frøyna 2004)	Frøyna, E. W.	2004	[-20 , 20]	24
(Valtz et al. 2004)	Valtz, A., A. Chapoy, C. Coquelet, P. Paricaud, and D. Richon	2004	[5 , 45]	30

Water solubility in carbon dioxide

	T	***P***	**y**	***y***
	℃	bar	H_2O	CO_2
(King and Coan 1971)	25	22.70	0.00195	0.99805
(King and Coan 1971)	25	29.79	0.00163	0.99837
(King and Coan 1971)	25	29.99	0.00167	0.99833
(King and Coan 1971)	25	37.29	0.00145	0.99855
(King and Coan 1971)	25	37.39	0.00149	0.99851
(King and Coan 1971)	50	17.33	0.00841	0.99159
(King and Coan 1971)	50	25.53	0.00595	0.99405
(King and Coan 1971)	50	25.84	0.00598	0.99402
(King and Coan 1971)	50	36.38	0.00466	0.99534
(King and Coan 1971)	50	36.38	0.00463	0.99537
(King and Coan 1971)	50	46.31	0.00396	0.99604
(King and Coan 1971)	75	23.31	0.02000	0.98000
(King and Coan 1971)	75	37.39	0.01250	0.98750
(King and Coan 1971)	75	37.49	0.01260	0.98740
(King and Coan 1971)	75	51.27	0.01040	0.98960
(King and Coan 1971)	75	51.47	0.01020	0.98980
(King and Coan 1971)	100	36.78	0.03280	0.96720
(King and Coan 1971)	100	37.19	0.03230	0.96770
(King and Coan 1971)	100	44.79	0.02770	0.97230
(King and Coan 1971)	100	44.79	0.02740	0.97260
(King and Coan 1971)	100	51.47	0.02480	0.97520
(King and Coan 1971)	100	51.47	0.02510	0.97490

	T	**P**	**y**	***y***
	℃	bar	H_2O	CO_2
(Tödheie and Frank 1963)	100	200	0.029	0.971
(Tödheie and Frank 1963)	100	500	0.030	0.970
(Tödheie and Frank 1963)	100	1000	0.030	0.970
(Tödheie and Frank 1963)	100	1500	0.029	0.971
(Tödheie and Frank 1963)	100	2000	0.029	0.971
(Tödheie and Frank 1963)	100	2500	0.029	0.971
(Tödheie and Frank 1963)	100	3000	0.028	0.972
(Tödheie and Frank 1963)	100	3500	0.028	0.972

	T	***P***	**y**	***y***
	℃	bar	H_2O	CO_2
(Gillespie and Wilson 1982)	15.56	50.68	0.000819	0.999181
(Gillespie and Wilson 1982)	25.00	50.68	0.001280	0.998720
(Gillespie and Wilson 1982)	29.44	55.16	0.001570	0.998430
(Gillespie and Wilson 1982)	31.06	6.90	0.006940	0.993060
(Gillespie and Wilson 1982)	31.06	25.34	0.002390	0.997610
(Gillespie and Wilson 1982)	31.06	50.68	0.001630	0.998370
(Gillespie and Wilson 1982)	75.00	6.90	0.060140	0.939860
(Gillespie and Wilson 1982)	75.00	25.34	0.018160	0.981840
(Gillespie and Wilson 1982)	75.00	50.68	0.010870	0.989130
(Gillespie and Wilson 1982)	75.00	101.36	0.007270	0.992730
(Gillespie and Wilson 1982)	75.00	202.71	0.009380	0.990620
(Gillespie and Wilson 1982)	93.33	6.90	0.120300	0.879700
(Gillespie and Wilson 1982)	93.33	25.34	0.034710	0.965290
(Gillespie and Wilson 1982)	93.33	50.68	0.019700	0.980300
(Gillespie and Wilson 1982)	93.33	101.36	0.013740	0.986260
(Gillespie and Wilson 1982)	93.33	202.71	0.014320	0.985680

	T	***P***	**y**	***y***
	℃	bar	H_2O	CO_2
(Song and Kobayashi 1987)	21.10	6.90	0.0043276	0.9956724
(Song and Kobayashi 1987)	2.00	13.79	0.0006836	0.9993164
(Song and Kobayashi 1987)	15.56	20.69	0.0010656	0.9989344
(Song and Kobayashi 1987)	12.00	34.48	0.0006030	0.9993970
(Song and Kobayashi 1987)	20.00	34.48	0.0010010	0.9989990
(Song and Kobayashi 1987)	17.00	48.27	0.0008229	0.9991771
(Song and Kobayashi 1987)	25.00	48.27	0.0012787	0.9987213
(Song and Kobayashi 1987)	15.56	52.40	0.0006400	0.9993600
(Song and Kobayashi 1987)	20.20	57.92	0.0008999	0.9991001
(Song and Kobayashi 1987)	26.67	66.88	0.0012700	0.9987300
(Song and Kobayashi 1987)	29.50	71.71	0.0014981	0.9985019

	T	**P**	**y**	***y***
	℃	bar	H_2O	CO_2
(Briones et al. 1987)	*50.00*	68.20	0.00339	*0.99661*
(Briones et al. 1987)	*50.00*	75.30	0.00345	*0.99655*
(Briones et al. 1987)	*50.00*	87.20	0.00364	*0.99636*
(Briones et al. 1987)	*50.00*	100.60	0.00429	*0.99571*
(Briones et al. 1987)	*50.00*	101.30	0.00436	*0.99564*
(Briones et al. 1987)	*50.00*	122.10	0.00543	*0.99457*
(Briones et al. 1987)	*50.00*	147.50	0.00608	*0.99392*
(Briones et al. 1987)	*50.00*	176.80	0.00643	*0.99357*

	T	**P**	**y**	***y***
	℃	bar	H_2O	CO_2
(Nakayama et al. 1987)	*25.05*	36.30	0.0014	*0.9986*
(Nakayama et al. 1987)	*25.05*	64.20	0.0011	*0.9989*
(Nakayama et al. 1987)	*25.05*	64.10	0.0014	*0.9986*

	T	**P**	**y**	***y***
	℃	bar	H_2O	CO_2
(King et al. 1992)	15	51.70	0.00222	0.99778
(King et al. 1992)	15	76.00	0.00235	0.99765
(King et al. 1992)	15	101.30	0.00241	0.99759
(King et al. 1992)	15	126.70	0.00255	0.99745
(King et al. 1992)	15	152.00	0.00262	0.99738
(King et al. 1992)	15	177.30	0.00272	0.99728
(King et al. 1992)	15	202.70	0.00280	0.99720
(King et al. 1992)	20	58.80	0.00261	0.99739
(King et al. 1992)	20	70.90	0.00272	0.99728
(King et al. 1992)	20	76.00	0.00276	0.99724
(King et al. 1992)	20	81.10	0.00278	0.99722
(King et al. 1992)	20	101.30	0.00293	0.99707
(King et al. 1992)	20	126.70	0.00287	0.99713
(King et al. 1992)	20	141.90	0.00307	0.99693
(King et al. 1992)	20	152.00	0.00320	0.99680
(King et al. 1992)	20	177.30	0.00322	0.99678
(King et al. 1992)	20	202.70	0.00334	0.99666
(King et al. 1992)	25	65.90	0.00300	0.99700
(King et al. 1992)	25	70.90	0.00307	0.99693
(King et al. 1992)	25	76.00	0.00309	0.99691
(King et al. 1992)	25	91.20	0.00314	0.99686
(King et al. 1992)	25	101.30	0.00327	0.99673
(King et al. 1992)	25	111.50	0.00337	0.99663
(King et al. 1992)	25	126.70	0.00341	0.99659
(King et al. 1992)	25	141.90	0.00344	0.99656
(King et al. 1992)	25	152.00	0.00354	0.99646
(King et al. 1992)	25	177.30	0.00369	0.99631
(King et al. 1992)	25	202.70	0.00378	0.99622
(King et al. 1992)	35	91.20	0.00384	0.99616
(King et al. 1992)	35	101.30	0.00407	0.99593
(King et al. 1992)	35	111.50	0.00414	0.99586
(King et al. 1992)	35	126.70	0.00435	0.99565
(King et al. 1992)	35	136.80	0.00440	0.99560
(King et al. 1992)	35	152.00	0.00457	0.99543
(King et al. 1992)	35	202.70	0.00498	0.99502
(King et al. 1992)	40	101.30	0.00428	0.99572
(King et al. 1992)	40	111.50	0.00440	0.99560
(King et al. 1992)	40	126.70	0.00467	0.99533
(King et al. 1992)	40	152.00	0.00507	0.99493
(King et al. 1992)	40	177.30	0.00543	0.99457
(King et al. 1992)	40	202.70	0.00580	0.99420

	T	***P***	**y**	***y***
	℃	*bar*	H_2O	CO_2
(Müller, Bender, Maurer 1988)	*100*	*3.25*	0.288	*0.712*
(Müller, Bender, Maurer 1988)	*100*	*6.00*	0.155	*0.845*
(Müller, Bender, Maurer 1988)	*100*	*9.20*	0.107	*0.893*
(Müller, Bender, Maurer 1988)	*100*	*11.91*	0.077	*0.923*
(Müller, Bender, Maurer 1988)	*100*	*14.52*	0.069	*0.931*
(Müller, Bender, Maurer 1988)	*100*	*18.16*	0.054	*0.946*
(Müller, Bender, Maurer 1988)	*100*	*23.07*	0.045	*0.955*

	T	**P**	**y**	**y**
	℃	*bar*	H_2O	CO_2
(Bamberger et al. 2000)	*50.05*	*40.50*	0.0046	*0.9954*
(Bamberger et al. 2000)	*50.05*	*50.60*	0.0036	*0.9964*
(Bamberger et al. 2000)	*50.05*	*60.60*	0.0037	*0.9963*
(Bamberger et al. 2000)	*50.05*	*70.80*	0.0034	*0.9966*
(Bamberger et al. 2000)	*50.05*	*80.80*	0.0034	*0.9966*
(Bamberger et al. 2000)	*50.05*	*90.90*	0.0041	*0.9959*
(Bamberger et al. 2000)	*50.05*	*100.90*	0.0045	*0.9955*
(Bamberger et al. 2000)	*50.05*	*111.00*	0.0050	*0.9950*
(Bamberger et al. 2000)	*50.05*	*121.00*	0.0055	*0.9945*
(Bamberger et al. 2000)	*50.05*	*141.10*	0.0061	*0.9939*
(Bamberger et al. 2000)	*60.05*	*40.50*	0.0066	*0.9934*
(Bamberger et al. 2000)	*60.05*	*50.60*	0.0055	*0.9945*
(Bamberger et al. 2000)	*60.05*	*60.60*	0.0055	*0.9945*
(Bamberger et al. 2000)	*60.05*	*70.80*	0.0051	*0.9949*
(Bamberger et al. 2000)	*60.05*	*80.80*	0.0050	*0.9950*
(Bamberger et al. 2000)	*60.05*	*90.90*	0.0047	*0.9953*
(Bamberger et al. 2000)	*60.05*	*100.90*	0.0049	*0.9951*
(Bamberger et al. 2000)	*60.05*	*111.00*	0.0053	*0.9947*
(Bamberger et al. 2000)	*60.05*	*121.00*	0.0058	*0.9942*
(Bamberger et al. 2000)	*60.05*	*141.10*	0.0078	*0.9922*
(Bamberger et al. 2000)	*79.95*	*40.50*	0.0143	*0.9857*
(Bamberger et al. 2000)	*79.95*	*60.60*	0.0109	*0.9891*
(Bamberger et al. 2000)	*79.95*	*70.80*	0.0104	*0.9896*
(Bamberger et al. 2000)	*79.95*	*80.80*	0.0097	*0.9903*
(Bamberger et al. 2000)	*79.95*	*90.90*	0.0092	*0.9908*
(Bamberger et al. 2000)	*79.95*	*100.90*	0.0093	*0.9907*
(Bamberger et al. 2000)	*79.95*	*111.00*	0.0090	*0.9910*
(Bamberger et al. 2000)	*79.95*	*121.00*	0.0096	*0.9904*
(Bamberger et al. 2000)	*79.95*	*131.00*	0.0100	*0.9900*

	T	**P**	**y**	**y**
	℃	*bar*	H_2O	CO_2
(Dohrn et al. 1993)	*50*	*101*	0.00547	*0.99453*
(Dohrn et al. 1993)	*50*	*201*	0.00682	*0.99318*
(Dohrn et al. 1993)	*50*	*301*	0.00782	*0.99218*

	T	**P**	**y**	**y**
	℃	*bar*	H_2O	CO_2
(Frøyna 2004)	-20	15.00	0.0000718	*0.9999282*
(Frøyna 2004)	-20	5.00	0.0002856	*0.9997144*
(Frøyna 2004)	-20	15.00	0.0001189	*0.9998811*
(Frøyna 2004)	-15	5.00	0.0006342	*0.9993658*
(Frøyna 2004)	-10	5.00	0.0005583	*0.9994417*
(Frøyna 2004)	-10	5.00	0.0007888	*0.9992112*
(Frøyna 2004)	-10	15.00	0.0002030	*0.9997970*
(Frøyna 2004)	-10	15.00	0.0002144	*0.9997856*
(Frøyna 2004)	0	5.00	0.0011736	*0.9988264*
(Frøyna 2004)	0	5.00	0.0012100	*0.9987900*
(Frøyna 2004)	0	15.00	0.0004099	*0.9995901*
(Frøyna 2004)	0	15.00	0.0004351	*0.9995649*
(Frøyna 2004)	10	5.00	0.0021799	*0.9978201*
(Frøyna 2004)	10	5.00	0.0024046	*0.9975954*
(Frøyna 2004)	10	15.00	0.0007800	*0.9992200*
(Frøyna 2004)	10	15.00	0.0008436	*0.9991564*
(Frøyna 2004)	10	40.00	0.0004901	*0.9995099*
(Frøyna 2004)	10	40.00	0.0005537	*0.9994463*
(Frøyna 2004)	15	15.00	0.0010328	*0.9989672*
(Frøyna 2004)	20	5.00	0.0045340	*0.9954660*
(Frøyna 2004)	20	15.00	0.0015785	*0.9984215*
(Frøyna 2004)	20	15.00	0.0013382	*0.9986618*
(Frøyna 2004)	20	40.00	0.0008677	*0.9991323* IV
(Frøyna 2004)	20	40.00	0.0007500	*0.9992500*

	T	**P**	**y**	**y**
	℃	*bar*	H_2O	CO_2
(Valtz et al. 2004)	*5.07*	*5.01*	0.0015	*0.9985*
(Valtz et al. 2004)	*5.07*	*7.55*	0.0011	*0.9989*
(Valtz et al. 2004)	*5.07*	*10.16*	0.0007	*0.9993*
(Valtz et al. 2004)	*15.11*	*4.96*	0.0031	*0.9969*
(Valtz et al. 2004)	*15.11*	*11.03*	0.0014	*0.9986*
(Valtz et al. 2004)	*15.11*	*19.41*	0.0009	*0.9991*
(Valtz et al. 2004)	*25.13*	*5.04*	0.0065	*0.9935*
(Valtz et al. 2004)	*25.13*	*10.07*	0.0038	*0.9962*
(Valtz et al. 2004)	*25.13*	*14.96*	0.0028	*0.9972*
(Valtz et al. 2004)	*25.13*	*24.83*	0.0014	*0.9986*
(Valtz et al. 2004)	*25.13*	*34.91*	0.0013	*0.9987*
(Valtz et al. 2004)	*35.06*	*5.82*	0.0096	*0.9904*
(Valtz et al. 2004)	*35.06*	*8.19*	0.0079	*0.9921*
(Valtz et al. 2004)	*35.06*	*18.89*	0.0034	*0.9966*
(Valtz et al. 2004)	*35.06*	*29.70*	0.0023	*0.9977*
(Valtz et al. 2004)	*35.06*	*30.29*	0.0023	*0.9977*
(Valtz et al. 2004)	*35.06*	*40.05*	0.0020	*0.9980*
(Valtz et al. 2004)	*35.06*	*49.85*	0.0017	*0.9983*
(Valtz et al. 2004)	*35.06*	*59.49*	0.0016	*0.9984*
(Valtz et al. 2004)	*35.06*	*70.56*	0.0017	*0.9983*
(Valtz et al. 2004)	*35.06*	*79.30*	0.0023	*0.9977*
(Valtz et al. 2004)	*35.06*	*79.63*	0.0025	*0.9975*
(Valtz et al. 2004)	*45.07*	*4.64*	0.0250	*0.9750*
(Valtz et al. 2004)	*45.07*	*10.44*	0.0125	*0.9875*
(Valtz et al. 2004)	*45.07*	*18.63*	0.0065	*0.9935*
(Valtz et al. 2004)	*45.07*	*30.01*	0.0044	*0.9956*
(Valtz et al. 2004)	*45.07*	*39.80*	0.0038	*0.9962*
(Valtz et al. 2004)	*45.07*	*49.56*	0.0035	*0.9965*
(Valtz et al. 2004)	*45.07*	*59.92*	0.0033	*0.9967*
(Valtz et al. 2004)	*45.07*	*69.30*	0.0029	*0.9971*

Appendix B – Experimental data from literature

Reference	**Author(s)**	**Yr**	**T [℃]**	**No. of exp. pts. <= 100℃**
(Olds, Sage, and Lacey 1942)	Olds, R. H., B. H. Sage, and W. N. Lacey	1942	[38 , 104]	35 (incl. 104℃)
(Culberson and McKetta 1951)	Culberson, O. L., and J. J. McKetta.	1951	38	15
(Rigby and Prausnitz 1968)	Rigby, M., and J. M. Prausnitz	1968	[25 , 100]	12
(Sharma 1969)	Sharma, S. C.	1969	[38 , 71]	15
(Kosyakov, Ivchenko, and Krishtopa 1982)	Kosyakov, N. E., B. I. Ivchenko, and P. P. Krishtopa	1982	0 & 10	5
(Gillespie and Wilson 1982)	Gillespie, P. C., and G. M. Wilson	1982	50 & 75	6
(Yarym-Agaev et al. 1985)	Yarym-Agaev, N. L., R. P. Sinyavskaya, I. I. Koliushko, and L. Y. Levinton	1985	40 & 65	10
(Yokoyama et al. 1988)	Yokoyama, C., S. Wakana, G. Kaminishi, and S. Takahashi.	1988	25 & 50	5
(Bogoya, Müller, and Oellrich 1993)	Bogoya, D., C. Müller, and L. R. Oellrich	1993	[5 , 15]	5
(Althaus 1999)	Althaus, K.	1999	[5 , 20]	15
(Chapoy, Coquelet, and Richon 2003)	Chapoy, A., C. Coquelet, and D. Richon	2003	[30 , 45]	21
(Mohammadi et al. 2004)	Mohammadi, A. H., A. Chapoy, D. Richon, and B. Tohidi	2004	[10 , 40]	17
(Frøyna 2004)	Frøyna, E. W.	2004	[10 , 20]	8

Water solubility in methane

	T ℃	***P*** *bar*	**y** H_2O	*y* CH_4
(Olds, Sage, and Lacey 1942)	37.78	*83.11*	0.001278	*0.998722*
(Olds, Sage, and Lacey 1942)	37.78	*86.16*	0.001467	*0.998533*
(Olds, Sage, and Lacey 1942)	37.78	*134.86*	0.000671	*0.999329*
(Olds, Sage, and Lacey 1942)	37.78	*137.16*	0.000671	*0.999329*
(Olds, Sage, and Lacey 1942)	37.78	*208.19*	0.000645	*0.999355*
(Olds, Sage, and Lacey 1942)	37.78	*208.63*	0.000630	*0.999370*
(Olds, Sage, and Lacey 1942)	37.78	*279.19*	0.000423	*0.999577*
(Olds, Sage, and Lacey 1942)	37.78	*346.66*	0.000506	*0.999494*
(Olds, Sage, and Lacey 1942)	37.78	*417.13*	0.000484	*0.999516*
(Olds, Sage, and Lacey 1942)	37.78	*485.24*	0.000423	*0.999577*
(Olds, Sage, and Lacey 1942)	37.78	*553.65*	0.000427	*0.999573*
(Olds, Sage, and Lacey 1942)	37.78	*623.47*	0.000408	*0.999592*
(Olds, Sage, and Lacey 1942)	71.11	*26.73*	0.013350	*0.986650*
(Olds, Sage, and Lacey 1942)	71.11	*62.90*	0.006417	*0.993583*
(Olds, Sage, and Lacey 1942)	71.11	*96.45*	0.004503	*0.995497*
(Olds, Sage, and Lacey 1942)	71.11	*144.00*	0.003394	*0.996606*
(Olds, Sage, and Lacey 1942)	71.11	*210.64*	0.002721	*0.997279*
(Olds, Sage, and Lacey 1942)	71.11	*282.06*	0.002301	*0.997699*
(Olds, Sage, and Lacey 1942)	71.11	*351.53*	0.002128	*0.997872*
(Olds, Sage, and Lacey 1942)	71.11	*417.95*	0.001890	*0.998110*
(Olds, Sage, and Lacey 1942)	71.11	*681.57*	0.001692	*0.998308*
(Olds, Sage, and Lacey 1942)	104.44	*29.87*	0.04281	*0.957190*
(Olds, Sage, and Lacey 1942)	104.44	*65.91*	0.020690	*0.979310*
(Olds, Sage, and Lacey 1942)	104.44	*93.16*	0.01545	*0.984550*
(Olds, Sage, and Lacey 1942)	104.44	*138.11*	0.011200	*0.988800*
(Olds, Sage, and Lacey 1942)	104.44	*209.24*	0.008459	*0.991541*
(Olds, Sage, and Lacey 1942)	104.44	*279.02*	0.007123	*0.992877*
(Olds, Sage, and Lacey 1942)	104.44	*354.13*	0.006253	*0.993747*
(Olds, Sage, and Lacey 1942)	104.44	*417.83*	0.005788	*0.994212*
(Olds, Sage, and Lacey 1942)	104.44	*482.62*	0.005336	*0.994664*
(Olds, Sage, and Lacey 1942)	104.44	*547.27*	0.005238	*0.994762*
(Olds, Sage, and Lacey 1942)	104.44	*558.82*	0.004943	*0.995057*
(Olds, Sage, and Lacey 1942)	104.44	*622.56*	0.004882	*0.995118*
(Olds, Sage, and Lacey 1942)	104.44	*623.34*	0.004620	*0.995380*
(Olds, Sage, and Lacey 1942)	104.44	*683.90*	0.004722	*0.995278*

	T ℃	**P** bar	**y** H_2O	*y* CH_4
(Althaus 1999)	*5.05*	5	0.001750	*0.998250*
(Althaus 1999)	*5.05*	15	0.000616	*0.999384*
(Althaus 1999)	*5.05*	40	0.000250	*0.999750*
(Althaus 1999)	*10.05*	15	0.000851	*0.999149*
(Althaus 1999)	*10.05*	40	0.000357	*0.999643*
(Althaus 1999)	*10.05*	60	0.000251	*0.999749*
(Althaus 1999)	*15.05*	15	0.001180	*0.998820*
(Althaus 1999)	*15.05*	40	0.000485	*0.999515*
(Althaus 1999)	*15.05*	60	0.000350	*0.999650*
(Althaus 1999)	*15.05*	80	0.000284	*0.999716*
(Althaus 1999)	*15.05*	100	0.000244	*0.999756*
(Althaus 1999)	*20.05*	40	0.000665	*0.999335*
(Althaus 1999)	*20.05*	60	0.000470	*0.999530*
(Althaus 1999)	*20.05*	80	0.000386	*0.999614*
(Althaus 1999)	*20.05*	100	0.000332	*0.999668*

	T ℃	**P** bar	**y** H_2O	*y* CH_4
(Sharma 1969)	37.75	14.8	0.00516	*0.99484*
(Sharma 1969)	37.75	42.3	0.00188	*0.99812*
(Sharma 1969)	37.75	69.9	0.00134	*0.99866*
(Sharma 1969)	37.75	104	0.00092	*0.99908*
(Sharma 1969)	37.75	139	0.00075	*0.99925*
(Sharma 1969)	54.45	14.8	0.01130	*0.98870*
(Sharma 1969)	54.45	42.3	0.00430	*0.99570*
(Sharma 1969)	54.45	69.9	0.00279	*0.99721*
(Sharma 1969)	54.45	104	0.00193	*0.99807*
(Sharma 1969)	54.45	144	0.00171	*0.99829*
(Sharma 1969)	71.15	14.8	0.02565	*0.97435*
(Sharma 1969)	71.15	42.3	0.00933	*0.99067*
(Sharma 1969)	71.15	69.9	0.00550	*0.99450*
(Sharma 1969)	71.15	104	0.00425	*0.99575*
(Sharma 1969)	71.15	139	0.00368	*0.99632*

	T ℃	**P** bar	**y** H_2O	*y* CH_4
(Yarym-Agaev et al. 1985)	40.05	25	0.003030	*0.996970*
(Yarym-Agaev et al. 1985)	40.05	50	0.001870	*0.998130*
(Yarym-Agaev et al. 1985)	40.05	75	0.001340	*0.998660*
(Yarym-Agaev et al. 1985)	40.05	100	0.001120	*0.998880*
(Yarym-Agaev et al. 1985)	40.05	125	0.000926	*0.999074*
(Yarym-Agaev et al. 1985)	65.05	25	0.009830	*0.990170*
(Yarym-Agaev et al. 1985)	65.05	50	0.006090	*0.993910*
(Yarym-Agaev et al. 1985)	65.05	75	0.004480	*0.995520*
(Yarym-Agaev et al. 1985)	65.05	100	0.003480	*0.996520*
(Yarym-Agaev et al. 1985)	65.05	125	0.002980	*0.997020*

	T	**P**	**y**	*y*
	℃	bar	H_2O	CH_4
(Yokoyama et al. 1988)	25.05	30	0.001181	*0.998819*
(Yokoyama et al. 1988)	25.05	50	0.000741	*0.999259*
(Yokoyama et al. 1988)	50.05	30	0.004476	*0.995524*
(Yokoyama et al. 1988)	50.05	50	0.002789	*0.997211*
(Yokoyama et al. 1988)	50.05	80	0.002105	*0.997895*

	T	**P**	**y**	*y*
	℃	bar	H_2O	CH_4
(Culberson and McKetta 1951)	37.75	52.3	0.001770	*0.998230*
(Culberson and McKetta 1951)	37.75	110.3	0.000762	*0.999238*
(Culberson and McKetta 1951)	37.75	163.8	0.000745	*0.999255*
(Culberson and McKetta 1951)	37.75	249.2	0.000483	*0.999517*

	T	***P***	**y**	*y*
	℃	*bar*	H_2O	CH_4
(Rigby and Prausnitz 1968)	25.0	*23.54*	0.001483	*0.998517*
(Rigby and Prausnitz 1968)	25.0	*30.51*	0.001175	*0.998825*
(Rigby and Prausnitz 1968)	25.0	*40.55*	0.000915	*0.999085*
(Rigby and Prausnitz 1968)	50.0	*30.14*	0.004474	*0.995526*
(Rigby and Prausnitz 1968)	50.0	*48.38*	0.002921	*0.997079*
(Rigby and Prausnitz 1968)	50.0	*68.17*	0.002185	*0.997815*
(Rigby and Prausnitz 1968)	75.0	*31.21*	0.01335	*0.98665*
(Rigby and Prausnitz 1968)	75.0	*54.73*	0.00803	*0.99197*
(Rigby and Prausnitz 1968)	75.0	*67.27*	0.00671	*0.99329*
(Rigby and Prausnitz 1968)	100.0	*57.41*	0.01992	*0.98008*
(Rigby and Prausnitz 1968)	100.0	*71.89*	0.01643	*0.98357*
(Rigby and Prausnitz 1968)	100.0	*93.47*	0.01309	*0.98691*

	T	***P***	**y**	**y**
	℃	*bar*	H_2O	CH_4
(Gillespie and Wilson 1982)	*50.00*	*13.79*	0.00964	*0.99036*
(Gillespie and Wilson 1982)	*50.00*	*62.06*	0.00245	*0.99755*
(Gillespie and Wilson 1982)	*50.00*	*137.90*	0.00136	*0.99864*
(Gillespie and Wilson 1982)	*75.00*	*13.79*	0.02935	*0.97065*
(Gillespie and Wilson 1982)	*75.00*	*62.06*	0.00710	*0.99290*
(Gillespie and Wilson 1982)	*75.00*	*137.90*	0.00366	*0.99634*

	T	P	y	y
	℃	bar	H_2O	CH_4
(Mohammadi et al. 2004)	9.83	11.47	0.001143	0.998857
(Mohammadi et al. 2004)	9.93	10.05	0.001240	0.998760
(Mohammadi et al. 2004)	10.00	10.03	0.001260	0.998740
(Mohammadi et al. 2004)	14.96	10.00	0.001780	0.998220
(Mohammadi et al. 2004)	15.00	10.05	0.001770	0.998230
(Mohammadi et al. 2004)	19.86	20.51	0.001170	0.998830
(Mohammadi et al. 2004)	19.86	9.92	0.002410	0.997590
(Mohammadi et al. 2004)	19.86	5.10	0.004640	0.995360
(Mohammadi et al. 2004)	19.96	9.90	0.002400	0.997600
(Mohammadi et al. 2004)	24.82	5.63	0.005690	0.994310
(Mohammadi et al. 2004)	24.85	16.97	0.001959	0.998041
(Mohammadi et al. 2004)	24.86	6.08	0.005193	0.994807
(Mohammadi et al. 2004)	24.86	28.46	0.001218	0.998782
(Mohammadi et al. 2004)	24.96	10.10	0.003270	0.996730
(Mohammadi et al. 2004)	29.96	10.30	0.004400	0.995600
(Mohammadi et al. 2004)	34.96	9.90	0.005820	0.994180
(Mohammadi et al. 2004)	39.97	10.90	0.007340	0.992660

	T	P	y	y
	℃	bar	H_2O	CH_4
(Chapoy, Coquelet, and Richon 2003)	29.96	11.00	0.004440	0.995560
(Chapoy, Coquelet, and Richon 2003)	29.96	60.60	0.000771	0.999229
(Chapoy, Coquelet, and Richon 2003)	29.96	98.40	0.000478	0.999522
(Chapoy, Coquelet, and Richon 2003)	29.96	175.00	0.000290	0.999710
(Chapoy, Coquelet, and Richon 2003)	29.96	250.60	0.000196	0.999804
(Chapoy, Coquelet, and Richon 2003)	29.96	345.60	0.000151	0.999849
(Chapoy, Coquelet, and Richon 2003)	34.96	11.00	0.005820	0.994180
(Chapoy, Coquelet, and Richon 2003)	34.96	59.90	0.001020	0.998980
(Chapoy, Coquelet, and Richon 2003)	34.96	98.40	0.000680	0.999320
(Chapoy, Coquelet, and Richon 2003)	34.96	174.90	0.000424	0.999576
(Chapoy, Coquelet, and Richon 2003)	34.96	250.90	0.000334	0.999666
(Chapoy, Coquelet, and Richon 2003)	34.96	345.80	0.000280	0.999720
(Chapoy, Coquelet, and Richon 2003)	39.97	11.00	0.007460	0.992540
(Chapoy, Coquelet, and Richon 2003)	39.97	60.56	0.001520	0.998480
(Chapoy, Coquelet, and Richon 2003)	39.97	99.80	0.000972	0.999028
(Chapoy, Coquelet, and Richon 2003)	39.97	174.70	0.000588	0.999412
(Chapoy, Coquelet, and Richon 2003)	39.97	251.70	0.000484	0.999516
(Chapoy, Coquelet, and Richon 2003)	39.97	346.10	0.000424	0.999576
(Chapoy, Coquelet, and Richon 2003)	44.97	10.03	0.009890	0.990110
(Chapoy, Coquelet, and Richon 2003)	44.97	60.17	0.002180	0.997820
(Chapoy, Coquelet, and Richon 2003)	44.97	100.10	0.001280	0.998720
(Chapoy, Coquelet, and Richon 2003)	44.97	175.00	0.000791	0.999209
(Chapoy, Coquelet, and Richon 2003)	44.97	251.20	0.000644	0.999356
(Chapoy, Coquelet, and Richon 2003)	44.97	346.10	0.000560	0.999440

	T	P	y	y
	℃	bar	H_2O	CH_4
(Kosyakov, Ivchenko, and Krishtopa 1982)	0.05	10.10	0.000650	0.999350
(Kosyakov, Ivchenko, and Krishtopa 1982)	0.05	20.30	0.000340	0.999660
(Kosyakov, Ivchenko, and Krishtopa 1982)	10.05	20.30	0.000640	0.999360
(Kosyakov, Ivchenko, and Krishtopa 1982)	10.05	40.50	0.000346	0.999654
(Kosyakov, Ivchenko, and Krishtopa 1982)	10.05	60.80	0.000220	0.999780

	T	P	y	y
	℃	bar	H_2O	CH_4
(Bogoya, Müller, and Oellrich 1993)	5.05	30.00	0.000299	0.999701
(Bogoya, Müller, and Oellrich 1993)	10.05	30.00	0.000435	0.999565
(Bogoya, Müller, and Oellrich 1993)	10.05	60.00	0.000234	0.999766
(Bogoya, Müller, and Oellrich 1993)	15.05	30.00	0.000606	0.999394
(Bogoya, Müller, and Oellrich 1993)	15.05	60.00	0.000325	0.999675

	T	**P**	**y**	**y**
	℃	bar	H_2O	CH_4
(Frøyna 2004)	*10*	15	0.0008530	*0.9991470*
(Frøyna 2004)	*10*	40	0.0003139	*0.9996861*
(Frøyna 2004)	*10*	60	0.0002402	*0.9997598*
(Frøyna 2004)	*20*	15	0.0015029	*0.9984971*
(Frøyna 2004)	*20*	40	0.0005935	*0.9994065*
(Frøyna 2004)	*20*	60	0.0004281	*0.9995719*
(Frøyna 2004)	*20*	100	0.0003031	*0.9996969*
(Frøyna 2004)	*20*	180	0.0002544	*0.9997456*

Appendix C – Experimental data from literature

Reference	Author(s)	Yr	T [℃]	No. of exp. pts. <= 100℃
(Saddington and Krase 1934)	Saddington, A. W., and N. W. Krase	1934	[50 , 230]	8
(Rigby and Prausnitz 1968)	Rigby, M., and J. M. Prausnitz	1968	[25 , 100]	13
(Gillespie and Wilson 1980)	Gillespie, P. C., and G. M. Wilson	1980	[38 , 316]	10
(Kosyakov, Ivchenko, and Krishtopa 1982)	Kosyakov, H. E., B. I. Ivchenko, and P. P. Krishtopa	1983	[0 , 20]	18
(Bogoya et al. 1993)	Bogoya, D., C. Müller, and L. R. Oellrich	1993	[0 , 15]	8
(Althaus 1999)	Althaus, K.	1999	[0 , 20]	22
(Blanco et al. 1999)	Blanco, S. T., I. Velasco, E. Rauzy, and S. Otín	1999	[1 , 11]	24
(Chapoy et al. 2004)	Chapoy, A., A. H. Mohammadi, B. Tohidi, and D. Richon	2004	38 & 93	10
(Frøyna 2004)	Frøyna, E. W.	2004	[0 , 20]	21
(Mohammadi et al. 2005)	Mohammadi, A. H., A. Chapoy, B. Tohidi, and D. Richon	2005	[10 , 90]	35

Water solubility in nitrogen

	T	***P***	**y (MASS)**	***y (MASS)***
	℃	*bar*	H_2O	*N_2*
(Saddington and Krase 1934)	50.0	*101.33*	0.00118	*0.99882*
(Saddington and Krase 1934)	50.0	*202.65*	0.00085	*0.99915*
(Saddington and Krase 1934)	50.0	*303.98*	0.00073	*0.99927*
(Saddington and Krase 1934)	75.0	*303.98*	0.00262	*0.99738*
(Saddington and Krase 1934)	80.0	*101.33*	0.00403	*0.99597*
(Saddington and Krase 1934)	85.0	*202.65*	0.00290	*0.99710*
(Saddington and Krase 1934)	100.0	*101.33*	0.00726	*0.99274*
(Saddington and Krase 1934)	100.0	*303.98*	0.00372	*0.99628*

	T	***P***	**y**	***y***
	℃	*bar*	H_2O	*N_2*
(Rigby and Prausnitz 1968)	25.0	*22.49*	0.001529	*0.998471*
(Rigby and Prausnitz 1968)	25.0	*30.90*	0.001149	*0.998851*
(Rigby and Prausnitz 1968)	25.0	*38.70*	0.000941	*0.999059*
(Rigby and Prausnitz 1968)	50.0	*21.09*	0.00626	*0.99374*
(Rigby and Prausnitz 1968)	50.0	*37.42*	0.00368	*0.99632*
(Rigby and Prausnitz 1968)	50.0	*59.82*	0.00242	*0.99758*
(Rigby and Prausnitz 1968)	50.0	*77.00*	0.001956	*0.998044*
(Rigby and Prausnitz 1968)	75.0	*42.21*	0.01009	*0.98991*
(Rigby and Prausnitz 1968)	75.0	*61.15*	0.00721	*0.99279*
(Rigby and Prausnitz 1968)	75.0	*89.73*	0.00523	*0.99477*
(Rigby and Prausnitz 1968)	100.0	*57.17*	0.01994	*0.98006*
(Rigby and Prausnitz 1968)	100.0	*79.48*	0.01503	*0.98497*
(Rigby and Prausnitz 1968)	100.0	*101.52*	0.01218	*0.98782*

	T	**P**	**y**	***y***
	℃	bar	H_2O	*N_2*
(Blanco et al. 1999)	1.0	89.11	0.00008	*0.99992*
(Blanco et al. 1999)	1.0	39.89	0.00014	*0.99986*
(Blanco et al. 1999)	1.2	59.75	0.00010	*0.99990*
(Blanco et al. 1999)	2.0	24.71	0.00026	*0.99974*
(Blanco et al. 1999)	2.1	99.71	0.00008	*0.99992*
(Blanco et al. 1999)	2.4	45.56	0.00014	*0.99986*
(Blanco et al. 1999)	2.7	69.61	0.00010	*0.99990*
(Blanco et al. 1999)	3.0	109.60	0.00008	*0.99992*
(Blanco et al. 1999)	3.6	49.99	0.00014	*0.99986*
(Blanco et al. 1999)	4.0	79.65	0.00010	*0.99990*
(Blanco et al. 1999)	4.3	29.53	0.00026	*0.99974*
(Blanco et al. 1999)	4.8	54.47	0.00014	*0.99986*
(Blanco et al. 1999)	5.3	89.77	0.00010	*0.99990*
(Blanco et al. 1999)	5.6	60.00	0.00014	*0.99986*
(Blanco et al. 1999)	6.2	34.55	0.00026	*0.99974*
(Blanco et al. 1999)	6.5	100.60	0.00010	*0.99990*
(Blanco et al. 1999)	6.6	64.46	0.00014	*0.99986*
(Blanco et al. 1999)	7.5	69.76	0.00014	*0.99986*
(Blanco et al. 1999)	7.8	39.44	0.00026	*0.99974*
(Blanco et al. 1999)	8.4	74.86	0.00014	*0.99986*
(Blanco et al. 1999)	9.2	44.44	0.00026	*0.99974*
(Blanco et al. 1999)	9.4	84.91	0.00014	*0.99986*
(Blanco et al. 1999)	10.1	49.21	0.00026	*0.99974*
(Blanco et al. 1999)	10.8	99.22	0.00014	*0.99986*

	T	**P**	**y**	***y***
	℃	bar	H_2O	*N_2*
(Althaus 1999)	0.05	5	0.0012450	*0.9987550*
(Althaus 1999)	0.05	15	0.0004266	*0.9995734*
(Althaus 1999)	0.05	40	0.0001708	*0.9998292*
(Althaus 1999)	0.05	60	0.0001268	*0.9998732*
(Althaus 1999)	0.05	80	0.0001063	*0.9998938*
(Althaus 1999)	0.05	100	0.0000907	*0.9999093*
(Althaus 1999)	5.05	5	0.0017800	*0.9982200*
(Althaus 1999)	5.05	15	0.0006007	*0.9993993*
(Althaus 1999)	5.05	60	0.0001775	*0.9998225*
(Althaus 1999)	5.05	80	0.0001511	*0.9998489*
(Althaus 1999)	5.05	100	0.0001220	*0.9998780*
(Althaus 1999)	10.05	5	0.0025030	*0.9974970*
(Althaus 1999)	10.05	15	0.0008380	*0.9991620*
(Althaus 1999)	10.05	40	0.0003542	*0.9996458*
(Althaus 1999)	10.05	60	0.0002482	*0.9997518*
(Althaus 1999)	10.05	80	0.0002045	*0.9997955*
(Althaus 1999)	10.05	100	0.0001756	*0.9998244*
(Althaus 1999)	20.05	15	0.0016320	*0.9983680*
(Althaus 1999)	20.05	40	0.0006535	*0.9993465*
(Althaus 1999)	20.05	60	0.0004672	*0.9995328*
(Althaus 1999)	20.05	80	0.0003752	*0.9996248*
(Althaus 1999)	20.05	100	0.0003265	*0.9996735*

	T	**P**	**y**	**y**
	℃	*bar*	H_2O	N_2
(Gillespie and Wilson 1980)	*37.78*	*3.45*	0.02020	*0.97980*
(Gillespie and Wilson 1980)	*37.78*	*13.79*	0.00502	*0.99498*
(Gillespie and Wilson 1980)	*37.78*	*31.03*	0.00236	*0.99764*
(Gillespie and Wilson 1980)	*37.78*	*65.50*	0.00122	*0.99878*
(Gillespie and Wilson 1980)	*37.78*	*137.90*	0.00069	*0.99931*
(Gillespie and Wilson 1980)	*93.33*	*3.45*	0.23300	*0.76700*
(Gillespie and Wilson 1980)	*93.33*	*13.79*	0.06050	*0.93950*
(Gillespie and Wilson 1980)	*93.33*	*31.03*	0.02770	*0.97230*
(Gillespie and Wilson 1980)	*93.33*	*65.50*	0.01370	*0.98630*
(Gillespie and Wilson 1980)	*93.33*	*137.90*	0.00747	*0.99253*

	T	**P**	**y**	**y**
	℃	*bar*	H_2O	N_2
(Chapoy et al. 2004)	37.8	*13.80*	0.00502	*0.99498*
(Chapoy et al. 2004)	37.8	*31.00*	0.00236	*0.99764*
(Chapoy et al. 2004)	37.8	*65.50*	0.00122	*0.99878*
(Chapoy et al. 2004)	37.8	*103.40*	0.00085	*0.99915*
(Chapoy et al. 2004)	37.8	*137.90*	0.00069	*0.99931*
(Chapoy et al. 2004)	93.3	*3.40*	0.23300	*0.76700*
(Chapoy et al. 2004)	93.3	*13.80*	0.06050	*0.93950*
(Chapoy et al. 2004)	93.3	*31.00*	0.02770	*0.97230*
(Chapoy et al. 2004)	93.3	*65.50*	0.01370	*0.98630*
(Chapoy et al. 2004)	93.3	*137.90*	0.00747	*0.99253*

	T	**P**	**y**	**y**
	℃	bar	H_2O	N_2
(Frøyna 2004)	*0*	5	0.0014668	*0.9985332*
(Frøyna 2004)	*0*	25	0.0002960	*0.9997040*
(Frøyna 2004)	*0*	50	0.0001424	*0.9998576*
(Frøyna 2004)	*0*	100	0.0001011	*0.9998989*
(Frøyna 2004)	*5*	5	0.0018393	*0.9981607*
(Frøyna 2004)	*5*	25	0.0004284	*0.9995716*
(Frøyna 2004)	*5*	50	0.0002228	*0.9997772*
(Frøyna 2004)	*10*	5	0.0025568	*0.9974432*
(Frøyna 2004)	*10*	25	0.0005228	*0.9994772*
(Frøyna 2004)	*10*	50	0.0003161	*0.9996839*
(Frøyna 2004)	*10*	75	0.0002279	*0.9997721*
(Frøyna 2004)	*10*	100	0.0001823	*0.9998177*
(Frøyna 2004)	*10*	200	0.0001050	*0.9998950*
(Frøyna 2004)	*15*	5	0.0034773	*0.9965227*
(Frøyna 2004)	*15*	25	0.0007218	*0.9992782*
(Frøyna 2004)	*15*	50	0.0003912	*0.9996088*
(Frøyna 2004)	*20*	5	0.0047236	*0.9952764*
(Frøyna 2004)	*20*	25	0.0009852	*0.9990148*
(Frøyna 2004)	*20*	50	0.0005303	*0.9994697*
(Frøyna 2004)	*20*	75	0.0003901	*0.9996099*
(Frøyna 2004)	*20*	100	0.0003095	*0.9996905*

	T	**P**	**y**	**y**
	℃	bar	H_2O	N_2
(Bogoya et al. 1993)	*0*	30	0.000218	*0.999782*
(Bogoya et al. 1993)	*5*	30	0.000309	*0.999691*
(Bogoya et al. 1993)	*10*	30	0.000433	*0.999567*
(Bogoya et al. 1993)	*15*	30	0.000599	*0.999401*
(Bogoya et al. 1993)	*0*	60	0.000116	*0.999884*
(Bogoya et al. 1993)	*5*	60	0.000162	*0.999838*
(Bogoya et al. 1993)	*10*	60	0.000225	*0.999775*
(Bogoya et al. 1993)	*15*	60	0.000314	*0.999686*

	T ℃	**P** bar	**y** H_2O	**y** N_2
(Kosyakov, Ivchenko, and Krishtopa 1982)	0	10	0.000660	0.999340
(Kosyakov, Ivchenko, and Krishtopa 1982)	0	20	0.000346	0.999654
(Kosyakov, Ivchenko, and Krishtopa 1982)	0	41	0.000180	0.999820
(Kosyakov, Ivchenko, and Krishtopa 1982)	0	61	0.000138	0.999862
(Kosyakov, Ivchenko, and Krishtopa 1982)	0	81	0.000110	0.999890
(Kosyakov, Ivchenko, and Krishtopa 1982)	0	101	0.000090	0.999910
(Kosyakov, Ivchenko, and Krishtopa 1982)	0	121	0.000083	0.999917
(Kosyakov, Ivchenko, and Krishtopa 1982)	10	20	0.000725	0.999275
(Kosyakov, Ivchenko, and Krishtopa 1982)	10	41	0.000398	0.999602
(Kosyakov, Ivchenko, and Krishtopa 1982)	10	61	0.000282	0.999718
(Kosyakov, Ivchenko, and Krishtopa 1982)	10	81	0.000226	0.999774
(Kosyakov, Ivchenko, and Krishtopa 1982)	10	101	0.000190	0.999810
(Kosyakov, Ivchenko, and Krishtopa 1982)	10	121	0.000155	0.999845
(Kosyakov, Ivchenko, and Krishtopa 1982)	20	41	0.000776	0.999224
(Kosyakov, Ivchenko, and Krishtopa 1982)	20	61	0.000552	0.999448
(Kosyakov, Ivchenko, and Krishtopa 1982)	20	81	0.000427	0.999573
(Kosyakov, Ivchenko, and Krishtopa 1982)	20	101	0.000371	0.999629
(Kosyakov, Ivchenko, and Krishtopa 1982)	20	121	0.000288	0.999712

	T ℃	**P** bar	**y** H_2O	**y** N_2
(Mohammadi et al. 2005)	9.7	6.07	0.002040	0.99796
(Mohammadi et al. 2005)	9.8	17.99	0.000714	0.99929
(Mohammadi et al. 2005)	9.8	30.36	0.000446	0.99955
(Mohammadi et al. 2005)	9.9	44.08	0.000317	0.99968
(Mohammadi et al. 2005)	20.0	5.58	0.004250	0.99575
(Mohammadi et al. 2005)	20.0	18.28	0.001360	0.99864
(Mohammadi et al. 2005)	20.0	29.91	0.000844	0.99916
(Mohammadi et al. 2005)	20.0	48.10	0.000558	0.99944
(Mohammadi et al. 2005)	30.9	5.78	0.007930	0.99207
(Mohammadi et al. 2005)	31.2	12.57	0.003700	0.99630
(Mohammadi et al. 2005)	31.4	25.39	0.001880	0.99812
(Mohammadi et al. 2005)	31.5	46.38	0.001120	0.99888
(Mohammadi et al. 2005)	40.2	4.98	0.015300	0.98470
(Mohammadi et al. 2005)	40.0	12.46	0.006090	0.99391
(Mohammadi et al. 2005)	40.1	28.36	0.002780	0.99722
(Mohammadi et al. 2005)	40.0	47.81	0.001750	0.99825
(Mohammadi et al. 2005)	49.7	4.99	0.024000	0.97600
(Mohammadi et al. 2005)	50.0	14.20	0.008720	0.99128
(Mohammadi et al. 2005)	49.8	33.97	0.003960	0.99604
(Mohammadi et al. 2005)	49.8	48.41	0.002920	0.99708
(Mohammadi et al. 2005)	59.4	4.61	0.042700	0.95730
(Mohammadi et al. 2005)	59.3	14.48	0.013400	0.98660
(Mohammadi et al. 2005)	59.4	24.54	0.008550	0.99145
(Mohammadi et al. 2005)	59.4	43.58	0.004880	0.99512
(Mohammadi et al. 2005)	69.2	4.25	0.071900	0.92810
(Mohammadi et al. 2005)	69.2	4.62	0.065800	0.93420
(Mohammadi et al. 2005)	69.2	14.66	0.021900	0.97810
(Mohammadi et al. 2005)	69.3	28.99	0.010300	0.98970
(Mohammadi et al. 2005)	69.2	49.62	0.006660	0.99334
(Mohammadi et al. 2005)	78.7	5.40	0.084900	0.91510
(Mohammadi et al. 2005)	79.0	14.80	0.033500	0.96650
(Mohammadi et al. 2005)	78.8	29.57	0.016200	0.98380
(Mohammadi et al. 2005)	78.8	47.97	0.011100	0.98890
(Mohammadi et al. 2005)	89.9	5.55	0.126000	0.87400
(Mohammadi et al. 2005)	89.9	48.74	0.016100	0.98390

Appendix D – Experimental data from literature

Reference	**Author(s)**	**Yr**	**T [℃]**	**No. of exp. pts. <= 100℃**
(Donnelly and Katz 1954)	Donnelly, H. G., and D. L. Katz	1954	[-73, -2]	53
(Kaminishi et al. 1968)	Kaminishi, G.-I., Y. Arai, S. Saito, and S. Maeda	1968	[-40, 10]	14
(Neumann and Walch 1968)	Neumann, A., and W. Walch	1968	[-100, -87]	36
(Arai, Kaminishi, and Saito 1971)	Arai, Y., G. Kaminishi, and S. Saito	1971	[-20, 15]	2
(Davalos et al. 1976)	Davalos, J., W. R. Anderson, R. E. Phelps, and A. J. Kidnay	1976	[-43,-3]	36
(Mraw, Hwang, and Kobayashi 1978)	Mraw, S. C., S.-C. Hwang, and R. Kobayashi	1978	[-120, -54]	8
(Somait and Kidnay 1978)	Somait, F. A., and A. J. Kidnay	1978	-3	10
(Al-Sahhaf, Kidnay, and Sloan 1983)	Al-Sahhaf, T. A., A. J. Kidnay, and E. D. Sloan	1983	[-53, -3]	30
(Xu et al. 1992)	Xu, N., J. Dong, Y. Wang, and J. Shi	1992	15 & 20	23
(Bian et al. 1993)	Bian, B., Y. Wang, J. Shi, E. Zhao, and B. C. Y. Lu	1993	28	7
(Wei et al. 1995)	Wei, M. S. W., T. S. Brown, A. J. Kidnay, and E. D. Sloan	1995	[-43, -3]	52
(Webster and Kidnay 2001)	Webster, L. A., and A. J. Kidnay	2001	-43 & -3	39

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	T	*P*	x	*x*	y	*y*
	℃	*bar*	CH_4	*CO_2*	CH_4	*CO_2*
(Donnelly and Katz 1954)	*-73.33*	*44.89*	0.7770	*0.2230*	0.9260	*0.0740*
(Donnelly and Katz 1954)	*-73.33*	*44.89*	0.7650	*0.2350*	0.9250	*0.0750*
(Donnelly and Katz 1954)	*-73.33*	*50.47*	0.9100	*0.0900*	0.9410	*0.0590*
(Donnelly and Katz 1954)	*-73.33*	*50.47*	0.9220	*0.0780*	0.9500	*0.0500*
(Donnelly and Katz 1954)	*-63.89*	*51.23*	0.5180	*0.4820*	0.8790	*0.1210*
(Donnelly and Katz 1954)	*-63.89*	*52.06*	0.6110	*0.3890*	0.8780	*0.1220*
(Donnelly and Katz 1954)	*-63.89*	*52.06*	0.5960	*0.4040*	0.8800	*0.1200*
(Donnelly and Katz 1954)	*-63.89*	*53.51*	0.6420	*0.3580*	0.8820	*0.1180*
(Donnelly and Katz 1954)	*-63.89*	*55.50*	0.7820	*0.2180*	0.8960	*0.1040*
(Donnelly and Katz 1954)	*-63.89*	*55.50*	0.8010	*0.1990*	0.9030	*0.0970*
(Donnelly and Katz 1954)	*-53.89*	*45.44*	0.2610	*0.7390*	0.8130	*0.1870*
(Donnelly and Katz 1954)	*-53.89*	*53.30*	0.3440	*0.6560*	0.8150	*0.1850*
(Donnelly and Katz 1954)	*-53.89*	*53.30*	0.3500	*0.6500*	0.8200	*0.1800*
(Donnelly and Katz 1954)	*-53.89*	*64.26*	0.6610	*0.3390*	0.8360	*0.1640*
(Donnelly and Katz 1954)	*-53.89*	*64.26*	0.6640	*0.3360*	0.8300	*0.1700*
(Donnelly and Katz 1954)	*-49.44*	*14.82*	0.0435	*0.9565*	0.5090	*0.4910*
(Donnelly and Katz 1954)	*-49.44*	*34.34*	0.1465	*0.8535*	0.7510	*0.2490*
(Donnelly and Katz 1954)	*-49.44*	*40.06*	0.1720	*0.8280*	0.7770	*0.2230*
(Donnelly and Katz 1954)	*-49.44*	*40.40*	0.1945	*0.8055*	0.7720	*0.2280*
(Donnelly and Katz 1954)	*-49.44*	*53.92*	0.3090	*0.6910*	0.7920	*0.2080*
(Donnelly and Katz 1954)	*-49.44*	*53.92*	0.3150	*0.6850*	0.8000	*0.2000*
(Donnelly and Katz 1954)	*-49.44*	*60.12*	0.3920	*0.6080*	0.7970	*0.2030*
(Donnelly and Katz 1954)	*-49.44*	*60.12*	0.4360	*0.5640*	0.7960	*0.2040*
(Donnelly and Katz 1954)	*-49.44*	*61.99*	0.4650	*0.5350*	0.8050	*0.1950*
(Donnelly and Katz 1954)	*-49.44*	*63.71*	0.4830	*0.5170*	0.7830	*0.2170*
(Donnelly and Katz 1954)	*-49.44*	*65.43*	0.5250	*0.4750*	0.7900	*0.2100*
(Donnelly and Katz 1954)	*-31.67*	*23.93*	0.0413	*0.9587*	0.4040	*0.5960*
(Donnelly and Katz 1954)	*-31.67*	*31.03*	0.0860	*0.9140*	0.5210	*0.4790*
(Donnelly and Katz 1954)	*-31.67*	*40.75*	0.1370	*0.8630*	0.6050	*0.3950*
(Donnelly and Katz 1954)	*-31.67*	*47.02*	0.1660	*0.8340*	0.6290	*0.3710*
(Donnelly and Katz 1954)	*-31.67*	*52.61*	0.1910	*0.8090*	0.6520	*0.3480*
(Donnelly and Katz 1954)	*-31.67*	*62.68*	0.2860	*0.7140*	0.6760	*0.3240*
(Donnelly and Katz 1954)	*-31.67*	*66.74*	0.2730	*0.7270*	0.6790	*0.3210*
(Donnelly and Katz 1954)	*-31.67*	*68.40*	0.3220	*0.6780*	0.6860	*0.3140*
(Donnelly and Katz 1954)	*-31.67*	*75.71*	0.4260	*0.5740*	0.6800	*0.3200*
(Donnelly and Katz 1954)	*-31.67*	*79.02*	0.5010	*0.4990*	0.6720	*0.3280*
(Donnelly and Katz 1954)	*-13.33*	*31.92*	0.0315	*0.9685*	0.1885	*0.8115*
(Donnelly and Katz 1954)	*-13.33*	*34.68*	0.0360	*0.9640*	0.2350	*0.7650*
(Donnelly and Katz 1954)	*-13.33*	*36.89*	0.0510	*0.9490*	0.2660	*0.7340*
(Donnelly and Katz 1954)	*-13.33*	*40.34*	0.0530	*0.9470*	0.3060	*0.6940*
(Donnelly and Katz 1954)	*-13.33*	*50.54*	0.1095	*0.8905*	0.4250	*0.5750*
(Donnelly and Katz 1954)	*-13.33*	*60.33*	0.1640	*0.8360*	0.4850	*0.5150*
(Donnelly and Katz 1954)	*-13.33*	*60.33*	0.1690	*0.8310*	0.4830	*0.5170*
(Donnelly and Katz 1954)	*-13.33*	*68.12*	0.2240	*0.7760*	0.5050	*0.4950*
(Donnelly and Katz 1954)	*-13.33*	*68.47*	0.2230	*0.7770*	0.5090	*0.4910*
(Donnelly and Katz 1954)	*-13.33*	*70.81*	0.2350	*0.7650*	0.4950	*0.5050*
(Donnelly and Katz 1954)	*-1.67*	*50.54*	0.0675	*0.9325*	0.2530	*0.7470*
(Donnelly and Katz 1954)	*-1.67*	*55.92*	0.0840	*0.9160*	0.3000	*0.7000*
(Donnelly and Katz 1954)	*-1.67*	*59.99*	0.1030	*0.8970*	0.3290	*0.6710*
(Donnelly and Katz 1954)	*-1.67*	*68.12*	0.1600	*0.8400*	0.3670	*0.6330*
(Donnelly and Katz 1954)	*-1.67*	*68.40*	0.1570	*0.8430*	0.3690	*0.6310*
(Donnelly and Katz 1954)	*-1.67*	*72.54*	0.1650	*0.8350*	0.3870	*0.6130*
(Donnelly and Katz 1954)	*-1.67*	*76.40*	0.1910	*0.8090*	0.3900	*0.6100*

	T	***P***	***x***	**x**	***y***	**y**
	℃	*bar*	*CH_4*	CO_2	*CH_4*	CO_2
(Neumann and Walch 1968)	-99.8	*27.26*	*1.00000*	0.00000	*1.00000*	0.00000
(Neumann and Walch 1968)	-99.8	*27.16*	*0.99850*	0.00150	*0.99947*	0.00053
(Neumann and Walch 1968)	-99.8	*27.05*	*0.99685*	0.00315	*0.99892*	0.00108
(Neumann and Walch 1968)	-99.8	*26.95*	*0.99500*	0.00500	*0.99831*	0.00169
(Neumann and Walch 1968)	-99.8	*26.85*	*0.99270*	0.00730	*0.99759*	0.00241
(Neumann and Walch 1968)	-99.8	*26.75*	*0.99015*	0.00985	*0.99686*	0.00314
(Neumann and Walch 1968)	-99.8	*26.65*	*0.98710*	0.01290	*0.99608*	0.00392
(Neumann and Walch 1968)	-94.4	*32.83*	*1.00000*	0.00000	*1.00000*	0.00000
(Neumann and Walch 1968)	-94.4	*32.73*	*0.99955*	0.00045	*0.99982*	0.00018
(Neumann and Walch 1968)	-94.4	*32.53*	*0.99850*	0.00150	*0.99942*	0.00058
(Neumann and Walch 1968)	-94.4	*32.42*	*0.99795*	0.00205	*0.99921*	0.00079
(Neumann and Walch 1968)	-94.4	*32.22*	*0.99670*	0.00330	*0.99874*	0.00126
(Neumann and Walch 1968)	-94.4	*32.02*	*0.99500*	0.00500	*0.99811*	0.00189
(Neumann and Walch 1968)	-94.4	*31.82*	*0.99300*	0.00700	*0.99737*	0.00263
(Neumann and Walch 1968)	-94.4	*31.61*	*0.99035*	0.00965	*0.99642*	0.00358
(Neumann and Walch 1968)	-94.4	*31.41*	*0.98525*	0.01475	*0.99477*	0.00523
(Neumann and Walch 1968)	-89.9	*38.20*	*1.00000*	0.00000	*1.00000*	0.00000
(Neumann and Walch 1968)	-89.9	*38.00*	*0.99920*	0.00080	*0.99961*	0.00039
(Neumann and Walch 1968)	-89.9	*37.90*	*0.99875*	0.00125	*0.99940*	0.00060
(Neumann and Walch 1968)	-89.9	*37.69*	*0.99770*	0.00230	*0.99892*	0.00108
(Neumann and Walch 1968)	-89.9	*37.49*	*0.99655*	0.00345	*0.99840*	0.00160
(Neumann and Walch 1968)	-89.9	*37.29*	*0.99530*	0.00470	*0.99783*	0.00217
(Neumann and Walch 1968)	-89.9	*37.09*	*0.99390*	0.00610	*0.99719*	0.00281
(Neumann and Walch 1968)	-89.9	*36.88*	*0.99235*	0.00765	*0.99650*	0.00350
(Neumann and Walch 1968)	-89.9	*36.68*	*0.99030*	0.00970	*0.99558*	0.00442
(Neumann and Walch 1968)	-89.9	*36.48*	*0.98550*	0.01450	*0.99368*	0.00632
(Neumann and Walch 1968)	-87.0	*41.65*	*1.00000*	0.00000	*1.00000*	0.00000
(Neumann and Walch 1968)	-87.0	*41.54*	*0.99925*	0.00075	*0.99956*	0.00044
(Neumann and Walch 1968)	-87.0	*41.44*	*0.99840*	0.00160	*0.99909*	0.00091
(Neumann and Walch 1968)	-87.0	*41.34*	*0.99745*	0.00255	*0.99857*	0.00143
(Neumann and Walch 1968)	-87.0	*41.14*	*0.99535*	0.00465	*0.99746*	0.00254
(Neumann and Walch 1968)	-87.0	*40.94*	*0.99330*	0.00670	*0.99638*	0.00362
(Neumann and Walch 1968)	-87.0	*40.73*	*0.99105*	0.00895	*0.99527*	0.00473
(Neumann and Walch 1968)	-87.0	*40.53*	*0.98870*	0.01130	*0.99417*	0.00583
(Neumann and Walch 1968)	-87.0	*40.33*	*0.98625*	0.01375	*0.99321*	0.00679
(Neumann and Walch 1968)	-87.0	*40.13*	*0.98325*	0.01675	*0.99208*	0.00792

	T	***P***	**x**	***x***	**y**	***y***
	℃	*bar*	CH_4	*CO_2*	CH_4	*CO_2*
(Kaminishi et al. 1968)	-40	*52.7*	0.251	*0.749*	0.717	*0.283*
(Kaminishi et al. 1968)	-40	*62.0*	0.360	*0.640*	0.727	*0.273*
(Kaminishi et al. 1968)	-40	*71.9*	0.519	*0.481*	0.703	*0.297*
(Kaminishi et al. 1968)	-20	*52.7*	0.150	*0.850*	0.515	*0.485*
(Kaminishi et al. 1968)	-20	*62.0*	0.213	*0.787*	0.556	*0.444*
(Kaminishi et al. 1968)	-20	*71.9*	0.294	*0.706*	0.566	*0.434*
(Kaminishi et al. 1968)	-20	*78.0*	0.357	*0.643*	0.563	*0.437*
(Kaminishi et al. 1968)	-20	*81.1*	0.400	*0.600*	0.540	*0.460*
(Kaminishi et al. 1968)	0	*52.7*	0.070	*0.930*	0.254	*0.746*
(Kaminishi et al. 1968)	0	*77.0*	0.204	*0.796*	0.370	*0.630*
(Kaminishi et al. 1968)	0	*81.9*	0.246	*0.754*	0.367	*0.633*
(Kaminishi et al. 1968)	10	*62.0*	0.069	*0.931*	0.188	*0.812*
(Kaminishi et al. 1968)	10	*71.9*	0.115	*0.885*	0.240	*0.760*
(Kaminishi et al. 1968)	10	*81.9*	0.177	*0.823*	0.250	*0.750*

	T	***P***	**x**	***x***	**y**	***y***
	℃	*bar*	CH_4	*CO_2*	CH_4	*CO_2*
(Arai, Kaminishi, and Saito 1971)	-20	*82.9*	0.444	*0.556*	0.499	*0.501*
(Arai, Kaminishi, and Saito 1971)	0	*85.2*	0.276	*0.724*	0.321	*0.679*

	T	***P***	**x**	***x***	**y**	***y***
	℃	*bar*	CH_4	CO_2	CH_4	CO_2
(Davalos et al. 1976)	-43.15	8.92	0.000	1.000	0.000	1.000
(Davalos et al. 1976)	-43.15	15.20	0.027	0.973	0.399	0.601
(Davalos et al. 1976)	-43.15	20.27	0.050	0.950	0.525	0.475
(Davalos et al. 1976)	-43.15	32.42	0.115	0.885	0.683	0.317
(Davalos et al. 1976)	-43.15	40.53	0.170	0.830	0.728	0.272
(Davalos et al. 1976)	-43.15	48.64	0.235	0.765	0.751	0.249
(Davalos et al. 1976)	-43.15	55.73	0.318	0.682	0.764	0.236
(Davalos et al. 1976)	-43.15	61.91	0.397	0.603	0.752	0.248
(Davalos et al. 1976)	-43.15	62.82	0.394	0.606	0.762	0.238
(Davalos et al. 1976)	-43.15	65.86	0.472	0.528	0.757	0.243
(Davalos et al. 1976)	-43.15	68.90	0.534	0.466	0.751	0.249
(Davalos et al. 1976)	-43.15	69.35	0.526	0.474	0.732	0.268
(Davalos et al. 1976)	-43.15	70.00	0.543	0.457	0.730	0.270
(Davalos et al. 1976)	-43.15	70.74	0.561	0.439	0.725	0.275
(Davalos et al. 1976)	-43.15	71.41	0.584	0.416	0.716	0.284
(Davalos et al. 1976)	-23.15	17.85	0.000	1.000	0.000	1.000
(Davalos et al. 1976)	-23.15	20.27	0.010	0.990	0.104	0.896
(Davalos et al. 1976)	-23.15	23.63	0.023	0.977	0.223	0.777
(Davalos et al. 1976)	-23.15	30.40	0.053	0.947	0.361	0.639
(Davalos et al. 1976)	-23.15	40.53	0.105	0.895	0.491	0.509
(Davalos et al. 1976)	-23.15	50.66	0.166	0.834	0.575	0.425
(Davalos et al. 1976)	-23.15	60.80	0.237	0.763	0.605	0.395
(Davalos et al. 1976)	-23.15	70.93	0.326	0.674	0.615	0.385
(Davalos et al. 1976)	-23.15	78.02	0.400	0.600	0.605	0.395
(Davalos et al. 1976)	-23.15	79.54	0.405	0.595	0.564	0.436
(Davalos et al. 1976)	-23.15	80.94	0.446	0.554	0.558	0.442
(Davalos et al. 1976)	-3.15	31.95	0.000	1.000	0.000	1.000
(Davalos et al. 1976)	-3.15	35.56	0.014	0.986	0.083	0.917
(Davalos et al. 1976)	-3.15	37.01	0.018	0.982	0.108	0.892
(Davalos et al. 1976)	-3.15	40.28	0.032	0.968	0.162	0.838
(Davalos et al. 1976)	-3.15	42.14	0.040	0.960	0.190	0.810
(Davalos et al. 1976)	-3.15	50.63	0.077	0.923	0.282	0.718
(Davalos et al. 1976)	-3.15	58.58	0.113	0.887	0.353	0.647
(Davalos et al. 1976)	-3.15	70.21	0.166	0.834	0.405	0.595
(Davalos et al. 1976)	-3.15	80.64	0.260	0.740	0.411	0.589
(Davalos et al. 1976)	-3.15	85.20	0.319	0.681	0.375	0.625

	T	***P***	**x**	***x***	**y**	***y***
	℃	*bar*	CH_4	CO_2	CH_4	CO_2
(Somait and Kidnay 1978)	-3.15	31.99	0.0000	1.0000	0.0000	1.0000
(Somait and Kidnay 1978)	-3.15	38.35	0.0237	0.9763	0.1269	0.8731
(Somait and Kidnay 1978)	-3.15	43.93	0.0455	0.9545	0.2082	0.7918
(Somait and Kidnay 1978)	-3.15	48.79	0.0666	0.9334	0.2629	0.7371
(Somait and Kidnay 1978)	-3.15	52.69	0.0838	0.9162	0.2962	0.7038
(Somait and Kidnay 1978)	-3.15	60.80	0.1226	0.8774	0.3519	0.6481
(Somait and Kidnay 1978)	-3.15	66.27	0.1533	0.8467	0.3774	0.6226
(Somait and Kidnay 1978)	-3.15	77.01	0.2224	0.7776	0.4006	0.5994
(Somait and Kidnay 1978)	-3.15	82.48	0.2740	0.7260	0.3895	0.6105
(Somait and Kidnay 1978)	-3.15	84.32	0.3060	0.6940	0.3726	0.6274

	T	***P***	**x**	***x***	**y**	***y***
	℃	*bar*	CH_4	CO_2	CH_4	CO_2
(Mraw, Hwang, and Kobayashi 1978)	-120.00	11.89	0.99410	0.00590	0.99901	0.00099
(Mraw, Hwang, and Kobayashi 1978)	-120.00	11.95	0.99895	0.00105	0.99984	0.00016
(Mraw, Hwang, and Kobayashi 1978)	-80.00	43.09	0.89170	0.10830	0.94900	0.05100
(Mraw, Hwang, and Kobayashi 1978)	-80.00	46.20	0.91360	0.08640	0.96690	0.03310
(Mraw, Hwang, and Kobayashi 1978)	-70.00	51.71	0.82290	0.17710	0.89750	0.10250
(Mraw, Hwang, and Kobayashi 1978)	-70.00	53.11	0.85930	0.14070	0.89360	0.10640
(Mraw, Hwang, and Kobayashi 1978)	-70.00	53.45	0.87840	0.12160	0.87840	0.12160
(Mraw, Hwang, and Kobayashi 1978)	-53.89	64.87	0.74830	0.25170	0.74830	0.25170

	T	***P***	**x**	***x***	**y**	***y***
	℃	*bar*	CH_4	CO_2	CH_4	CO_2
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.89	5.81	0.0000	1.0000	0.0000	1.0000
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.89	13.98	0.0339	0.9661	0.5457	0.4543
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.89	13.98	0.0579	0.9421	0.6493	0.3507
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.89	19.00	0.0859	0.9141	0.7103	0.2897
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.89	24.32	0.1308	0.8692	0.7592	0.2408
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.89	31.20	0.1923	0.8077	0.7890	0.2110
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	12.87	0.0000	1.0000	0.0000	1.0000
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	21.04	0.0328	0.9672	0.3480	0.6520
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	30.59	0.0761	0.9239	0.5160	0.4840
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	40.89	0.1315	0.8685	0.6050	0.3950
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	51.98	0.2074	0.7926	0.6550	0.3450
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	61.20	0.2873	0.7127	0.6742	0.3258
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	66.57	0.3475	0.6525	0.6771	0.3229
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	70.73	0.4016	0.5984	0.6728	0.3272
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	72.65	0.4315	0.5685	0.6672	0.3328
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	73.97	0.4525	0.5475	0.6624	0.3376
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	75.94	0.4914	0.5086	0.6473	0.3527
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	76.60	0.5048	0.4952	0.6388	0.3612
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	77.72	0.5475	0.4525	0.6199	0.3801
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	32.03	0.0000	1.0000	0.0000	1.0000
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	36.73	0.0183	0.9817	0.1048	0.8952
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	38.10	0.0235	0.9765	0.1273	0.8727
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	43.87	0.0457	0.9543	0.2086	0.7914
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	51.83	0.0793	0.9207	0.2885	0.7115
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	59.43	0.1167	0.8833	0.3451	0.6549
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	61.56	0.1261	0.8739	0.3543	0.6457
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	70.83	0.1785	0.8215	0.3901	0.6099
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	79.69	0.2463	0.7537	0.3980	0.6020
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	82.23	0.2737	0.7263	0.3916	0.6084
(Al-Sahhaf, Kidnay, and Sloan 1983)	-3.15	84.15	0.3060	0.6940	0.3742	0.6258

	T	**P**	**x**	**x**	**y**	**y**
	℃	bar	CH_4	CO_2	CH_4	CO_2
(Xu et al. 1992)	15.35	51.20	0.000	1.000	0.000	1.000
(Xu et al. 1992)	15.35	55.90	0.015	0.985	0.052	0.948
(Xu et al. 1992)	15.35	62.10	0.042	0.958	0.108	0.892
(Xu et al. 1992)	15.35	66.00	0.061	0.939	0.137	0.863
(Xu et al. 1992)	15.35	66.10	0.061	0.939	0.138	0.862
(Xu et al. 1992)	15.35	71.10	0.086	0.914	0.167	0.833
(Xu et al. 1992)	15.35	75.10	0.112	0.888	0.185	0.815
(Xu et al. 1992)	15.35	78.20	0.128	0.872	0.195	0.805
(Xu et al. 1992)	15.35	78.70	0.129	0.871	0.194	0.806
(Xu et al. 1992)	15.35	81.50	0.175	0.825	0.175	0.825
(Xu et al. 1992)	20.25	57.30	0.000	1.000	0.000	1.000
(Xu et al. 1992)	20.25	61.40	0.017	0.983	0.040	0.960
(Xu et al. 1992)	20.25	62.30	0.020	0.980	0.048	0.952
(Xu et al. 1992)	20.25	63.20	0.025	0.975	0.058	0.942
(Xu et al. 1992)	20.25	66.40	0.039	0.961	0.086	0.914
(Xu et al. 1992)	20.25	68.20	0.050	0.950	0.094	0.906
(Xu et al. 1992)	20.25	71.80	0.063	0.937	0.115	0.885
(Xu et al. 1992)	20.25	73.20	0.071	0.929	0.122	0.878
(Xu et al. 1992)	20.25	74.00	0.076	0.924	0.126	0.874
(Xu et al. 1992)	20.25	74.30	0.079	0.921	0.128	0.872
(Xu et al. 1992)	20.25	77.20	0.097	0.903	0.135	0.865
(Xu et al. 1992)	20.25	78.90	0.113	0.887	0.135	0.865
(Xu et al. 1992)	20.25	79.80	0.132	0.868	0.132	0.868

	T	**P**	**x**	**x**	**y**	**y**
	℃	bar	CH_4	CO_2	CH_4	CO_2
(Bian et al. 1993)	27.85	68.60	0.0000	1.0000	0.0000	1.0000
(Bian et al. 1993)	27.85	70.30	0.0053	0.9947	0.0099	0.9901
(Bian et al. 1993)	27.85	71.90	0.0120	0.9880	0.0210	0.9790
(Bian et al. 1993)	27.85	73.60	0.0175	0.9825	0.0277	0.9723
(Bian et al. 1993)	27.85	74.70	0.0216	0.9784	0.0325	0.9675
(Bian et al. 1993)	27.85	75.60	0.0254	0.9746	0.0355	0.9645
(Bian et al. 1993)	27.85	77.00	0.0338	0.9662	0.0338	0.9662

	T	**P**	**x**	**x**	**y**	**y**
	℃	bar	CH_4	CO_2	CH_4	CO_2
(Wei et al. 1995)	-43.15	8.92	0.0000	1.0000	0.0000	1.0000
(Wei et al. 1995)	-43.15	10.78	0.0070	0.9930	0.1553	0.8447
(Wei et al. 1995)	-43.15	14.53	0.0221	0.9779	0.3480	0.6520
(Wei et al. 1995)	-43.15	17.86	0.0365	0.9635	0.4550	0.5450
(Wei et al. 1995)	-43.15	20.92	0.0503	0.9497	0.5218	0.4782
(Wei et al. 1995)	-43.15	25.51	0.0730	0.9270	0.5929	0.4071
(Wei et al. 1995)	-43.15	29.16	0.0920	0.9080	0.6320	0.3680
(Wei et al. 1995)	-43.15	35.03	0.1269	0.8731	0.6770	0.3230
(Wei et al. 1995)	-43.15	39.68	0.1577	0.8423	0.7005	0.2995
(Wei et al. 1995)	-43.15	45.65	0.2042	0.7958	0.7237	0.2763
(Wei et al. 1995)	-43.15	51.16	0.2560	0.7440	0.7368	0.2632
(Wei et al. 1995)	-43.15	56.40	0.3171	0.6829	0.7449	0.2551
(Wei et al. 1995)	-43.15	58.85	0.3416	0.6584	0.7466	0.2534
(Wei et al. 1995)	-43.15	60.86	0.3805	0.6195	0.7461	0.2539
(Wei et al. 1995)	-43.15	63.53	0.4187	0.5813	0.7448	0.2552
(Wei et al. 1995)	-43.15	65.86	0.4523	0.5477	0.7411	0.2589
(Wei et al. 1995)	-43.15	66.63	0.4762	0.5238	0.7369	0.2631
(Wei et al. 1995)	-43.15	67.36	0.4952	0.5048	0.7338	0.2662
(Wei et al. 1995)	-43.15	69.01	0.5407	0.4593	0.7247	0.2753
(Wei et al. 1995)	-43.15	69.91	0.5814	0.4186	0.7004	0.2996
(Wei et al. 1995)	-23.15	17.83	0.0000	1.0000	0.0000	1.0000
(Wei et al. 1995)	-23.15	19.67	0.0065	0.9935	0.0782	0.9218
(Wei et al. 1995)	-23.15	20.71	0.0106	0.9894	0.1174	0.8826
(Wei et al. 1995)	-23.15	23.15	0.0201	0.9799	0.1952	0.8048
(Wei et al. 1995)	-23.15	24.88	0.0269	0.9731	0.2408	0.7592
(Wei et al. 1995)	-23.15	27.59	0.0379	0.9621	0.3001	0.6999
(Wei et al. 1995)	-23.15	29.64	0.0465	0.9535	0.3381	0.6619
(Wei et al. 1995)	-23.15	31.31	0.0536	0.9464	0.3655	0.6345
(Wei et al. 1995)	-23.15	34.46	0.0676	0.9324	0.4090	0.5910
(Wei et al. 1995)	-23.15	38.36	0.0863	0.9137	0.4533	0.5467
(Wei et al. 1995)	-23.15	42.00	0.1041	0.8959	0.4855	0.5145
(Wei et al. 1995)	-23.15	47.92	0.1368	0.8632	0.5262	0.4738
(Wei et al. 1995)	-23.15	53.78	0.1715	0.8285	0.5559	0.4441
(Wei et al. 1995)	-23.15	61.50	0.2246	0.7754	0.5812	0.4188
(Wei et al. 1995)	-23.15	67.15	0.2711	0.7289	0.5914	0.4086
(Wei et al. 1995)	-23.15	73.99	0.3366	0.6634	0.5856	0.4144
(Wei et al. 1995)	-23.15	76.84	0.3718	0.6282	0.5761	0.4239
(Wei et al. 1995)	-23.15	79.83	0.4163	0.5837	0.5523	0.4477
(Wei et al. 1995)	-23.15	80.53	0.4252	0.5748	0.5408	0.4592
(Wei et al. 1995)	-3.15	32.09	0.0000	1.0000	0.0000	1.0000
(Wei et al. 1995)	-3.15	35.58	0.0151	0.9849	0.0766	0.9234
(Wei et al. 1995)	-3.15	36.73	0.0198	0.9802	0.1047	0.8953
(Wei et al. 1995)	-3.15	38.83	0.0305	0.9695	0.1461	0.8539
(Wei et al. 1995)	-3.15	41.46	0.0377	0.9623	0.1778	0.8222
(Wei et al. 1995)	-3.15	45.06	0.0504	0.9496	0.2203	0.7797
(Wei et al. 1995)	-3.15	49.15	0.0724	0.9276	0.2661	0.7339
(Wei et al. 1995)	-3.15	58.51	0.1154	0.8846	0.3372	0.6628
(Wei et al. 1995)	-3.15	70.93	0.1834	0.8166	0.3942	0.6058
(Wei et al. 1995)	-3.15	78.68	0.2407	0.7593	0.4061	0.5939
(Wei et al. 1995)	-3.15	81.97	0.2696	0.7304	0.3952	0.6048
(Wei et al. 1995)	-3.15	82.82	0.2803	0.7197	0.3887	0.6113
(Wei et al. 1995)	-3.15	83.81	0.2995	0.7005	0.3782	0.6218

	T	**P**	**x**	**x**	**y**	**y**
	℃	bar	CH_4	CO_2	CH_4	CO_2
(Webster and Kidnay 2001)	-43.15	8.94	0.0000	1.0000	0.0000	1.0000
(Webster and Kidnay 2001)	-43.15	14.20	0.0213	0.9787	0.3385	0.6615
(Webster and Kidnay 2001)	-43.15	16.51	0.0307	0.9693	0.4196	0.5804
(Webster and Kidnay 2001)	-43.15	19.31	0.0441	0.9559	0.4900	0.5100
(Webster and Kidnay 2001)	-43.15	22.57	0.0597	0.9403	0.5512	0.4488
(Webster and Kidnay 2001)	-43.15	24.88	0.0714	0.9286	0.5851	0.4149
(Webster and Kidnay 2001)	-43.15	33.75	0.1199	0.8801	0.6670	0.3330
(Webster and Kidnay 2001)	-43.15	44.97	0.1994	0.8006	0.7199	0.2801
(Webster and Kidnay 2001)	-43.15	55.73	0.3093	0.6907	0.7432	0.2568
(Webster and Kidnay 2001)	-43.15	58.36	0.3404	0.6596	0.7454	0.2546
(Webster and Kidnay 2001)	-43.15	62.41	0.4010	0.5990	0.7443	0.2557
(Webster and Kidnay 2001)	-43.15	64.17	0.4323	0.5677	0.7442	0.2558
(Webster and Kidnay 2001)	-43.15	65.12	0.4530	0.5470	0.7422	0.2578
(Webster and Kidnay 2001)	-43.15	66.49	0.4862	0.5138	0.7371	0.2629
(Webster and Kidnay 2001)	-43.15	66.54	0.4815	0.5185	0.7382	0.2618
(Webster and Kidnay 2001)	-43.15	68.59	0.5201	0.4799	0.7312	0.2688
(Webster and Kidnay 2001)	-43.15	68.59	0.5208	0.4792	0.7314	0.2686
(Webster and Kidnay 2001)	-43.15	69.12	0.5302	0.4698	0.7286	0.2714
(Webster and Kidnay 2001)	-43.15	69.70	0.5393	0.4607	0.7245	0.2755
(Webster and Kidnay 2001)	-43.15	70.04	0.5521	0.4479	0.7222	0.2778
(Webster and Kidnay 2001)	-43.15	70.72	0.5682	0.4318	0.7156	0.2844
(Webster and Kidnay 2001)	-43.15	71.12	0.5774	0.4226	0.7102	0.2898
(Webster and Kidnay 2001)	-43.15	71.45	0.5888	0.4112	0.7066	0.2934
(Webster and Kidnay 2001)	-3.15	32.03	0.0000	1.0000	0.0000	1.0000
(Webster and Kidnay 2001)	-3.15	38.83	0.0264	0.9736	0.1352	0.8648
(Webster and Kidnay 2001)	-3.15	39.13	0.0276	0.9724	0.1402	0.8598
(Webster and Kidnay 2001)	-3.15	41.04	0.0342	0.9658	0.1680	0.8320
(Webster and Kidnay 2001)	-3.15	44.13	0.0477	0.9523	0.2093	0.7907
(Webster and Kidnay 2001)	-3.15	47.87	0.0640	0.9360	0.2517	0.7483
(Webster and Kidnay 2001)	-3.15	49.87	0.0723	0.9277	0.2706	0.7294
(Webster and Kidnay 2001)	-3.15	54.33	0.0919	0.9081	0.3085	0.6915
(Webster and Kidnay 2001)	-3.15	65.37	0.1479	0.8521	0.3702	0.6298
(Webster and Kidnay 2001)	-3.15	69.59	0.1739	0.8261	0.3847	0.6153
(Webster and Kidnay 2001)	-3.15	73.05	0.1949	0.8051	0.3945	0.6055
(Webster and Kidnay 2001)	-3.15	79.46	0.2435	0.7565	0.3977	0.6023
(Webster and Kidnay 2001)	-3.15	81.31	0.2602	0.7398	0.3934	0.6066
(Webster and Kidnay 2001)	-3.15	82.07	0.2688	0.7312	0.3894	0.6106
(Webster and Kidnay 2001)	-3.15	83.89	0.2901	0.7099	0.3762	0.6238
(Webster and Kidnay 2001)	-3.15	84.19	0.2991	0.7009	0.3704	0.6296

Appendix E – Experimental data from literature

Reference	**Author(s)**	**Yr**	**T [℃]**	**No. of exp. pts. <= 100℃**
(Yorizane, Yoshimura, and Masuoka 1970)	Yorizane, M., S. Yoshimura, and H. Masuoka	1970	0	12
(Arai, Kaminishi, and Saito 1971)	Arai, Y., G. Kaminishi, and S. Saito	1971	[0, 15]	4
(Somait and Kidnay 1978)	Somait, F. A., and A. J. Kidnay	1978	-3	34
(Al-Sahhaf, Kidnay, and Sloan 1983)	Al-Sahhaf, T. A., A. J. Kidnay, and E. D. Sloan	1983	-53 & -33	29
(Yorizane et al. 1985)	Yorizane, M., S. Yoshimura, H. Masuoka, Y. Miyano, and Y. Kakimoto	1985	[0, 25]	34
(Brown et al. 1989)	Brown, T. S., V. G. Niesen, E. D. Sloan, and A. J. Kidnay	1989	-23 & -3	17
(Xu et al. 1992)	Xu, N., J. Dong, Y. Wang, and J. Shi	1992	15 & 20	20
(Bian et al. 1993)	Bian, B., Y. Wang, J. Shi, E. Zhao, and B. C. Y. Lu	1993	28 & 30	14
(Yucelen and Kidnay 1999)	Yucelen, B., and A. J. Kidnay	1999	[-33, -3]	8

Vapour-liquid equilibria of carbon dioxide and nitrogen

	T ℃	***P*** *bar*	**x** N_2	***x*** CO_2	**y** N_2	***y*** CO_2
(Yorizane, Yoshimura, and Masuoka 1970)	0	34.9	0.000	1.000	0.000	1.000
(Yorizane, Yoshimura, and Masuoka 1970)	0	40.5	0.011	0.989	0.091	0.909
(Yorizane, Yoshimura, and Masuoka 1970)	0	50.7	0.031	0.969	0.215	0.785
(Yorizane, Yoshimura, and Masuoka 1970)	0	60.8	0.051	0.949	0.300	0.700
(Yorizane, Yoshimura, and Masuoka 1970)	0	70.9	0.071	0.929	0.347	0.653
(Yorizane, Yoshimura, and Masuoka 1970)	0	81.1	0.101	0.899	0.375	0.625
(Yorizane, Yoshimura, and Masuoka 1970)	0	91.2	0.126	0.874	0.392	0.608
(Yorizane, Yoshimura, and Masuoka 1970)	0	101.3	0.158	0.842	0.397	0.603
(Yorizane, Yoshimura, and Masuoka 1970)	0	111.5	0.200	0.800	0.390	0.610
(Yorizane, Yoshimura, and Masuoka 1970)	0	116.5	0.251	0.749	0.356	0.644
(Yorizane, Yoshimura, and Masuoka 1970)	0	117.5	0.272	0.728	0.338	0.662
(Yorizane, Yoshimura, and Masuoka 1970)	0	118.2	0.297	0.703	0.297	0.703

	T ℃	***P*** *bar*	**x** N_2	***x*** CO_2	**y** N_2	***y*** CO_2
(Arai, Kaminishi, and Saito 1971)	15	51.2	0.000	1.000		
(Arai, Kaminishi, and Saito 1971)	15	51.0			0.000	1.000
(Arai, Kaminishi, and Saito 1971)	0	118.0	0.254	0.746		
(Arai, Kaminishi, and Saito 1971)	15	90.9	0.103	0.897		
(Arai, Kaminishi, and Saito 1971)	15	97.6	0.155	0.845		
(Arai, Kaminishi, and Saito 1971)	0	118.0			0.306	0.694
(Arai, Kaminishi, and Saito 1971)	15	97.6			0.173	0.827
(Arai, Kaminishi, and Saito 1971)	15	90.7			0.202	0.798

	T ℃	***P*** *bar*	**x** N_2	***x*** CO_2	**y** N_2	***y*** CO_2
(Somait and Kidnay 1978)	-3.15	31.99	0.0000	1.0000	0.0000	1.0000
(Somait and Kidnay 1978)	-3.15	34.25	0.0040	0.9960	0.0472	0.9528
(Somait and Kidnay 1978)	-3.15	36.28	0.0078	0.9922	0.0851	0.9149
(Somait and Kidnay 1978)	-3.15	38.00	0.0108	0.9892	0.1140	0.8860
(Somait and Kidnay 1978)	-3.15	39.52	0.0135	0.9865	0.1331	0.8669
(Somait and Kidnay 1978)	-3.15	41.22	0.0168	0.9832	0.1598	0.8402
(Somait and Kidnay 1978)	-3.15	42.05	0.0182	0.9818	0.1683	0.8317
(Somait and Kidnay 1978)	-3.15	42.81	0.0197	0.9803	0.1783	0.8217
(Somait and Kidnay 1978)	-3.15	45.90	0.0263	0.9737	0.2156	0.7844
(Somait and Kidnay 1978)	-3.15	47.60	0.0289	0.9711	0.2323	0.7677
(Somait and Kidnay 1978)	-3.15	47.75	0.0292	0.9708	0.2325	0.7675
(Somait and Kidnay 1978)	-3.15	51.52	0.0368	0.9632	0.2674	0.7326
(Somait and Kidnay 1978)	-3.15	56.99	0.0476	0.9524	0.3069	0.6931
(Somait and Kidnay 1978)	-3.15	60.49	0.0545	0.9455	0.3280	0.6720
(Somait and Kidnay 1978)	-3.15	64.44	0.0630	0.9370	0.3473	0.6527
(Somait and Kidnay 1978)	-3.15	70.93	0.0778	0.9222	0.3770	0.6230
(Somait and Kidnay 1978)	-3.15	77.21	0.0921	0.9079	0.3961	0.6039
(Somait and Kidnay 1978)	-3.15	83.80	0.1080	0.8920	0.4126	0.5874
(Somait and Kidnay 1978)	-3.15	86.13	0.1142	0.8858	0.4139	0.5861
(Somait and Kidnay 1978)	-3.15	89.83	0.1231	0.8769	0.4190	0.5810
(Somait and Kidnay 1978)	-3.15	92.92	0.1319	0.8681	0.4173	0.5827
(Somait and Kidnay 1978)	-3.15	96.26	0.1430	0.8570	0.4210	0.5790
(Somait and Kidnay 1978)	-3.15	102.05	0.1585	0.8415	0.4188	0.5812
(Somait and Kidnay 1978)	-3.15	107.14	0.1769	0.8231	0.4134	0.5866
(Somait and Kidnay 1978)	-3.15	110.53	0.1904	0.8096	0.4094	0.5906
(Somait and Kidnay 1978)	-3.15	112.52	0.1986	0.8014	0.4061	0.5939
(Somait and Kidnay 1978)	-3.15	115.49	0.2142	0.7858	0.3986	0.6014
(Somait and Kidnay 1978)	-3.15	118.87	0.2332	0.7668	0.3800	0.6200
(Somait and Kidnay 1978)	-3.15	118.87	0.2360	0.7640	0.3808	0.6192
(Somait and Kidnay 1978)	-3.15	119.49	0.2486	0.7514	0.3762	0.6238
(Somait and Kidnay 1978)	-3.15	120.25	0.2454	0.7546	0.3720	0.6280
(Somait and Kidnay 1978)	-3.15	120.73	0.2505	0.7495	0.3664	0.6336
(Somait and Kidnay 1978)	-3.15	121.35	0.2556	0.7444	0.3640	0.6360
(Somait and Kidnay 1978)	-3.15	123.42	0.3530	0.6470	0.3530	0.6470

	T ℃	***P*** *bar*	**x** N_2	***x*** CO_2	**y** N_2	***y*** CO_2
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	6.00	0.0000	1.0000	0.0000	1.0000
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	15.09	0.0132	0.9868	0.5518	0.4482
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	30.75	0.0362	0.9638	0.7423	0.2577
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	45.95	0.0601	0.9399	0.7974	0.2026
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	63.13	0.0883	0.9117	0.8214	0.1786
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	82.58	0.1209	0.8791	0.8281	0.1719
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	111.14	0.1742	0.8258	0.8165	0.1835
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	124.32	0.2016	0.7984	0.8028	0.1972
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	137.96	0.2324	0.7676	0.7869	0.2131
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	155.06	0.2771	0.7229	0.7516	0.2484
(Al-Sahhaf, Kidnay, and Sloan 1983)	-53.15	167.06	0.3155	0.6845	0.7215	0.2785
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	12.87	0.0000	1.0000	0.0000	1.0000
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	21.00	0.0129	0.9871	0.3312	0.6688
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	32.08	0.0307	0.9693	0.5151	0.4849
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	40.89	0.0454	0.9546	0.5890	0.4110
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	56.74	0.0734	0.9266	0.6572	0.3428
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	62.62	0.0838	0.9162	0.6710	0.3290
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	72.35	0.1022	0.8978	0.6873	0.3127
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	85.90	0.1297	0.8703	0.6981	0.3019
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	99.45	0.1592	0.8408	0.6992	0.3008
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	107.28	0.1775	0.8225	0.6960	0.3040
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	114.66	0.1958	0.8042	0.6897	0.3103
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	122.25	0.2165	0.7835	0.6806	0.3194
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	126.59	0.2296	0.7704	0.6745	0.3255
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	138.65	0.2696	0.7304	0.6517	0.3483
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	144.72	0.2944	0.7056	0.6288	0.3712
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	154.24	0.3491	0.6509	0.5929	0.4071
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	157.68	0.3816	0.6184	0.5633	0.4367
(Al-Sahhaf, Kidnay, and Sloan 1983)	-33.15	161.47	0.4777	0.5223	0.5202	0.4798

	T	**P**	**x**	***x***	**y**	***y***
	℃	*bar*	N_2	*CO_2*	N_2	*CO_2*
(Yorizane et al. 1985)	0.05	45.00	0.1540	0.8460	0.0200	0.9800
(Yorizane et al. 1985)	0.05	45.10	0.1580	0.8420	0.0190	0.9810
(Yorizane et al. 1985)	0.05	50.90	0.2140	0.7860	0.0370	0.9630
(Yorizane et al. 1985)	0.05	57.10	0.2640	0.7360	0.0540	0.9460
(Yorizane et al. 1985)	0.05	66.10	0.2980	0.7020	0.0660	0.9340
(Yorizane et al. 1985)	0.05	67.00	0.3180	0.6820	0.0720	0.9280
(Yorizane et al. 1985)	0.05	78.30	0.3560	0.6440	0.1050	0.8950
(Yorizane et al. 1985)	0.05	83.90	0.3750	0.6250	0.1100	0.8900
(Yorizane et al. 1985)	0.05	99.50	0.3970	0.6030	0.1560	0.8440
(Yorizane et al. 1985)	0.05	99.90	0.3860	0.6140	0.1470	0.8530
(Yorizane et al. 1985)	0.05	109.20	0.3780	0.6220	0.1840	0.8160
(Yorizane et al. 1985)	0.05	114.50	0.3680	0.6320	0.2140	0.7860
(Yorizane et al. 1985)	20.05	65.90	0.0670	0.9330	0.0210	0.9790
(Yorizane et al. 1985)	20.05	66.00	0.0660	0.9340	0.0210	0.9790
(Yorizane et al. 1985)	20.05	75.60	0.1170	0.8830	0.0500	0.9500
(Yorizane et al. 1985)	20.05	75.90	0.1180	0.8820	0.0490	0.9510
(Yorizane et al. 1985)	20.05	83.10	0.1380	0.8620	0.0680	0.9320
(Yorizane et al. 1985)	20.05	83.30	0.1390	0.8610	0.0700	0.9300
(Yorizane et al. 1985)	20.05	83.50	0.1400	0.8600	0.0700	0.9300
(Yorizane et al. 1985)	20.05	83.70	0.1400	0.8600	0.0700	0.9300
(Yorizane et al. 1985)	20.05	84.30	0.1390	0.8610	0.0730	0.9270
(Yorizane et al. 1985)	20.05	85.30	0.1430	0.8570	0.0770	0.9230
(Yorizane et al. 1985)	20.05	88.60	0.1420	0.8580	0.0930	0.9070
(Yorizane et al. 1985)	20.05	89.10	0.1450	0.8550	0.0930	0.9070
(Yorizane et al. 1985)	20.05	92.60	0.1450	0.8550	0.1020	0.8980
(Yorizane et al. 1985)	20.05	93.20	0.1470	0.8530	0.1110	0.8890
(Yorizane et al. 1985)	20.05	93.70	0.1490	0.8510	0.1140	0.8860
(Yorizane et al. 1985)	20.05	95.50	0.1500	0.8500	0.1180	0.8820
(Yorizane et al. 1985)	20.05	96.00	0.1480	0.8520	0.1230	0.8770
(Yorizane et al. 1985)	25.05	74.00	0.0580	0.9420	0.0260	0.9740
(Yorizane et al. 1985)	25.05	74.10	0.0570	0.9430	0.0270	0.9730
(Yorizane et al. 1985)	25.05	81.40	0.0840	0.9160	0.0530	0.9470
(Yorizane et al. 1985)	25.05	81.70	0.0880	0.9120	0.0500	0.9500
(Yorizane et al. 1985)	25.05	85.10	0.0980	0.9020	0.0670	0.9330

	T	**P**	**x**	***x***	**y**	***y***
	℃	*bar*	N_2	*CO_2*	N_2	*CO_2*
(Brown et al. 1989)	-23.15	17.84	0.0000	1.0000	0.0000	1.0000
(Brown et al. 1989)	-23.15	25.99	0.0136	0.9864	0.2561	0.7439
(Brown et al. 1989)	-23.15	36.88	0.0331	0.9669	0.4239	0.5761
(Brown et al. 1989)	-23.15	45.89	0.0488	0.9512	0.5001	0.4999
(Brown et al. 1989)	-23.15	55.41	0.0664	0.9336	0.5494	0.4506
(Brown et al. 1989)	-23.15	65.97	0.0870	0.9130	0.5849	0.4151
(Brown et al. 1989)	-23.15	75.32	0.1069	0.8931	0.6049	0.3951
(Brown et al. 1989)	-23.15	96.32	0.1532	0.8468	0.6223	0.3777
(Brown et al. 1989)	-23.15	111.51	0.1931	0.8069	0.6163	0.3837
(Brown et al. 1989)	-23.15	119.36	0.2173	0.7827	0.6063	0.3937
(Brown et al. 1989)	-23.15	134.16	0.2708	0.7292	0.5727	0.4273
(Brown et al. 1989)	-23.15	140.66	0.3008	0.6992	0.5437	0.4563
(Brown et al. 1989)	-3.15	32.00	0.0000	1.0000	0.0000	1.0000
(Brown et al. 1989)	-3.15	48.57	0.0316	0.9684	0.2423	0.7577
(Brown et al. 1989)	-3.15	60.84	0.0561	0.9439	0.3309	0.6691
(Brown et al. 1989)	-3.15	76.50	0.0901	0.9099	0.3942	0.6058
(Brown et al. 1989)	-3.15	91.02	0.1279	0.8721	0.4205	0.5795

	T	**P**	**x**	***x***	**y**	***y***
	℃	*bar*	N_2	*CO_2*	N_2	*CO_2*
(Xu et al. 1992)	15.15	51.10	0.000	1.000	0.000	1.000
(Xu et al. 1992)	15.15	66.10	0.035	0.965	0.125	0.875
(Xu et al. 1992)	15.15	67.00	0.036	0.964	0.127	0.873
(Xu et al. 1992)	15.15	76.10	0.062	0.938	0.172	0.828
(Xu et al. 1992)	15.15	76.30	0.064	0.936	0.180	0.820
(Xu et al. 1992)	15.15	83.80	0.088	0.912	0.202	0.798
(Xu et al. 1992)	15.15	90.10	0.107	0.893	0.204	0.796
(Xu et al. 1992)	15.15	95.90	0.140	0.860	0.193	0.807
(Xu et al. 1992)	15.15	97.00	0.148	0.852	0.192	0.808
(Xu et al. 1992)	20.15	57.20	0.000	1.000	0.000	1.000
(Xu et al. 1992)	20.15	60.00	0.005	0.995	0.023	0.977
(Xu et al. 1992)	20.15	64.70	0.017	0.983	0.057	0.943
(Xu et al. 1992)	20.15	64.90	0.017	0.983	0.059	0.941
(Xu et al. 1992)	20.15	69.80	0.029	0.971	0.088	0.912
(Xu et al. 1992)	20.15	74.20	0.041	0.959	0.111	0.889
(Xu et al. 1992)	20.15	81.00	0.061	0.939	0.136	0.864
(Xu et al. 1992)	20.15	87.00	0.076	0.924	0.137	0.863
(Xu et al. 1992)	20.15	89.00	0.086	0.914	0.133	0.867
(Xu et al. 1992)	20.15	90.30	0.096	0.904	0.129	0.871
(Xu et al. 1992)	20.15	91.10	0.116	0.884	0.116	0.884

	T	**P**	**x**	***x***	**y**	***y***
	℃	*bar*	N_2	*CO_2*	N_2	*CO_2*
(Bian et al. 1993)	28.15	68.80	0.0000	1.0000	0.0000	1.0000
(Bian et al. 1993)	28.15	72.20	0.0069	0.9931	0.0152	0.9848
(Bian et al. 1993)	28.15	73.30	0.0101	0.9899	0.0206	0.9794
(Bian et al. 1993)	28.15	76.10	0.0182	0.9818	0.0326	0.9674
(Bian et al. 1993)	28.15	79.00	0.0258	0.9742	0.0390	0.9610
(Bian et al. 1993)	28.15	80.10	0.0348	0.9652	0.0389	0.9611
(Bian et al. 1993)	28.15	80.50	0.0379	0.9621	0.0379	0.9621
(Bian et al. 1993)	30.15	72.70	0.0013	0.9987	0.0023	0.9977
(Bian et al. 1993)	30.15	74.40	0.0060	0.9940	0.0096	0.9904
(Bian et al. 1993)	30.15	75.30	0.0086	0.9914	0.0133	0.9867
(Bian et al. 1993)	30.15	75.40	0.0090	0.9910	0.0136	0.9864
(Bian et al. 1993)	30.15	76.10	0.0107	0.9893	0.0153	0.9847
(Bian et al. 1993)	30.15	77.30	0.0147	0.9853	0.0189	0.9811
(Bian et al. 1993)	30.15	77.90	0.0184	0.9816	0.0184	0.9816

	T	***P***	**x**	***x***	**y**	***y***
	℃	*bar*	N_2	CO_2	N_2	CO_2
(Yucelen and Kidnay 1999)	*-33.15*	*12.85*	0.0000	*1.0000*	0.0000	*1.0000*
(Yucelen and Kidnay 1999)	*-33.15*	*109.30*	0.1830	*0.8170*	0.6977	*0.3023*
(Yucelen and Kidnay 1999)	*-33.15*	*130.00*	0.2467	*0.7533*	0.6692	*0.3308*
(Yucelen and Kidnay 1999)	*-3.15*	*32.09*	0.0000	*1.0000*	0.0000	*1.0000*
(Yucelen and Kidnay 1999)	*-3.15*	*35.67*	0.0064	*0.9936*	0.0759	*0.9241*
(Yucelen and Kidnay 1999)	*-3.15*	*37.19*	0.0088	*0.9912*	0.1036	*0.8964*
(Yucelen and Kidnay 1999)	*-3.15*	*50.76*	0.0358	*0.9642*	0.2629	*0.7371*
(Yucelen and Kidnay 1999)	*-3.15*	*119.70*	0.2456	*0.7544*	0.3822	*0.6178*