# High pressure fluid phase behavior of the systems $CF_4 - H_2O$ and $CF_4 - H_2O - NaCI$

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## PREFACE

This report is the result of a six month graduation period, from July 1995 to February 1996, at the laboratory of Applied Thermodynamics and Phase Equilibria. This period concludes the study of Chemical Engineering at the Delft University of Technology.

During this time I had a lot of support from ir P.J. Smits, whose PhD research was the basis for this work. I want to thank him for his dedication and guidance.

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### SUMMARY

SuperCritical Water Oxidation (SCWO) is a highly efficient method to destruct all kinds of toxic wastes, such as explosives and freons. Destruction efficiencies of 99.9 % can be reached.

In order to study model systems for SCWO processes, high pressure phase equilibria of  $CF_4 - H_2O$  and  $CF_4 - H_2O$  - NaCl mixtures have been measured in the pressure range from 20 to 200 MPa and in the temperature range from 580 to 673 K. The measurements were performed in a high-pressure autoclave with sapphire windows and magnetic stirring, with visual observation of the bubble point.

For the binary  $CF_4 - H_2O$  system, 10 isopleths were determined in the composition range of  $CF_4$  mole fractions from 0.0121 to 0.0583. The isopleths showed a temperature minimum between 60 and 100 MPa. For two  $CF_4 - H_2O$  mixtures, a critical point could be measured. From these critical points it could be concluded that the  $CF_4 - H_2O$  system exhibits type-III fluid phase behavior, with (gas+gas) immiscibility of the second kind.

For the ternary  $CF_4 - H_2O$  - NaCl system, 11 isopleths were determined with 0.5, 1.1, 2.1, and 3.3 weight percent NaCl (relative to water). For these mixtures the  $CF_4$  mole fractions ranged from 0.0076 to 0.0335. The mixtures with 0.5 weight percent NaCl had no effect on the phase behavior. The mixtures with 1.1, 2.1, and 3.3 weight percent NaCl shifted the immiscibility region by approximately 5, 15, and 20 K to higher temperatures, respectively.

For both the binary and the ternary system, barotropy occurred between 80 and 100 MPa.

The measurements that were performed cover only a small  $CF_4$  composition range. This is caused by the fact that at higher  $CF_4$  mole fraction, the temperatures exceed the maximum allowable operation temperature of the autoclave.

Furthermore, preliminary experiments for future work were performed for the systems  $CCIF_3 - H_2O$  and  $CHF_3 - H_2O$ . Some data points of the  $CCIF_3 - H_2O$  system were measured, with 0.0306 and 0.0320 mole fraction  $CCIF_3$ . One isopleth of the  $CHF_3 - H_2O$  system was measured, with 0.0499 mole fraction  $CHF_3$ .

The immiscibility region of the  $CCIF_3 - H_2O$  system, as compared to the same composition of the  $CF_4 - H_2O$  system, is located at temperatures that are approximately 20 K lower. Barotropy occurs between 70 and 80 MPa.

The immiscibility region of the  $CHF_3 - H_2O$  system, as compared to the same composition of the  $CF_4 - H_2O$  system, is located at temperatures more than 100 K lower. Barotropy occurs between 80 and 90 MPa.

The experimental results for the binary system  $CF_4 - H_2O$  were modelled using the Associated-Perturbed-Anisotropic-Chain Theory (APACT). Compared to earlier calculations with similar systems, the performance of APACT did not meet our expectations. As an alternative, the same data were modelled using the Peng-Robinson equation of state, with one constant value for the binary interaction parameter. The results were satisfactory.

Therefore, also the ternary system  $CF_4 - H_2O$  - NaCl was treated with the Peng-Robinson equation of state. This resulted in less satisfactory results than with the  $CF_4 - H_2O$  system. For the ternary system one set of constant values for the various binary interaction parameters was used.

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## **1.** INTRODUCTION

#### 1.1. SuperCritical Water Oxidation

The phase behavior of near-critical aqueous systems comprising light organic compounds is very important in the design of SuperCritical Water Oxidation (SCWO) processes [1].

SCWO is a promising method to destruct all sorts of toxic wastes, such as explosives, propellants, agents for chemical weapons and polychlorinated biphenyls (PCB's). In principle, SCWO is based on the fact that at critical conditions, water behaves as a non-polar solvent.

Most properties of a fluid depend strongly on the density and as a result on the temperature. One of the most important properties for predicting the solubility in a fluid, is the dielectric constant,  $\epsilon$ . The dielectric constant of water at ambient conditions (T=273 K,  $\rho$ =1000 kg/m<sup>3</sup>) equals to  $\epsilon$ =90. In the critical point (T=647 K,  $\rho$ =300 kg/m<sup>3</sup>), however,  $\epsilon$ =6, so the dielectric constant of water decreases with increasing temperature [2]. This decrease in  $\epsilon$  and the fact that in dense supercritical water the intermolecular association is considerably reduced [3], transforms water gradually from a polar into a non-polar solvent at higher temperatures. Because of these effects the solubility of non-polar organics in supercritical water increases dramatically.

In the resulting homogeneous phase, the organic compounds can be oxidized both by flameless oxidation or by flaming combustion [4]. In case of flameless oxidation, the oxidizing agent (e.g.  $H_2O_2$ ) is added to the feed. With flaming combustion, the oxidizing agent ( $O_2$ ) is mixed with the organic compound just before they enter the flame inside the reactor.

Oxidation in supercritical water has, in general, an efficiency of over 99.9 % [1].

SCWO processes have some advantages over the traditionally used incineration. Due to processing in a closed system, there is no emission to the atmosphere. The process temperatures are lower than that in incineration. In SCWO, no formation of nitrogen oxides and sulphur dioxide occurs. Finally, SCWO is energy sufficient if the carbon content is 10 %, as compared to 30 % in incineration [4].

A disadvantage is that due to the fact that supercritical water is highly corrosive, special alloys are to be used in the reactor design and consequently high investment costs are required. This is one of the main reasons that until now, SCWO has not been widely introduced. Another reason is the high critical pressure of water, which is difficult to maintain during the reaction. Finally there was no real need for companies to use SCWO, because the environmental standards were not so high.

Introduction

Protocol eliminate ratification of the Montreal to Since the chlorofluorocarbohydrates (CFC's), the interest in SCWO processes as a method to destruct these CFC's has increased again [5]. The destruction of light organic compounds containing chlorine and/or fluorine (freons) is an important factor in the protection of the environment, and in particular the ozone layer. These compounds can be effectively destroyed by means of SCWO, with efficiencies of 99.99 % [4]. The main reaction products in the SCWO of halogenated organic compounds are water, carbon dioxide and acids. In order to neutralize these acids, sodium hydroxide can be injected into the reactor. Thus resulting in the presence of sodium fluoride and/or sodium chloride, depending on the kind of halogens present in the organic compound. These salts can cause serious processing problems, such as plugging of the pipes and/or the reactor. This shows that both binary freon - water and ternary freon - water - salt system are very important in the design of SCWO processes.

The development of SCWO processes requires an accurate equation of state. The ever increasing progress in computer technology allows to handle more complex calculations, and as a result more complex equations of state can be used in the prediction of fluid phase behavior. Equations of state that are based on statistical mechanics are being developed. They account for physical and theoretical concepts and are in general more accurate than the cubic equations of state. Due to the unique behavior of water, e.g. its ability to form hydrogen bonds, the prediction of high pressure phase behavior of aqueous systems is very complicated. For these kind of systems, the Statistical Associating Fluid Theory (SAFT) [6,7] and the Associated-Perturbed-Anisotropic-Chain Theory (APACT) [8,9] can be used. They are specifically designed with association models to account for hydrogen bond formation.

APACT, has proven to be very reliable for pure water from 2.5 to 25000 MPa and from 473.15 to 1273.15 K, except the region close to the critical point [10]. In order to extend the APACT equation of state to relevant multi-component systems, there is a need for experimental data of both binary freon - water and ternary freon - water - salt systems at high pressures and temperatures.

#### 1.2. Objective of this study

Since no high pressure, high temperature experimental data on the phase behavior of freon - water or freon - water - salt systems are available in literature [11], this study was an attempt to fill this gap. For that purpose, the phase behavior of the systems  $CF_4 - H_2O$  and  $CF_4 - H_2O$  - NaCl was determined experimentally up to 200 MPa and 673 K.

In addition, also some preliminary experiments were performed for the systems  $CCIF_3 - H_2O$  and  $CHF_3 - H_2O$  and compared with the  $CF_4 - H_2O$  system.

Due to the good agreement of the APACT equation of state with experimental data of pure water at high pressures and temperatures [10], this equation was also applied to describe the experimental data obtained in this study.

The objective of this study was the investigation of the underlying phase behavior of model systems for SCWO processes.



Figure 2.1: The evolution of the phase behavior of binary mixtures due to increasing molecular dissimilarities between the components 1 and 2 [13]

# 2. THEORY

#### 2.1. Classification of fluid phase equilibria

#### 2.1.1. Introduction

*Van Konynenburg and Scott* [12] classified the fluid phase behavior and the location of critical curves in binary mixtures into five types by means of the van der Waals equation of state. This classification is based on the course of the various critical loci, three-phase lines, and their mutual interrelationship.

The five types of phase behavior can be divided into two classes. Mixtures in which the critical points of the pure components are connected by a continuous critical curve, belong to class 1. If there is no continuous critical curve connecting the critical points of the pure components, the mixture belongs to class 2.

#### 2.1.2. Transitions between the different types of fluid phase behavior

The five types of fluid phase behavior are discussed as they evolve due to increasing dissimilarities between the molecules, such as size and interaction [13]. This evolution of the types of phase behavior is shown in Figure 2.1 and described in detail by *Van Pelt* [13].

If the two components in the mixture are chemically similar or have comparable critical properties, type-I phase behavior occurs. Type-I shows a continuous Ig-critical curve, that connects both critical points of the pure components. There is no Ilg-three-phase equilibrium present in the p,T-projection, although this can be hidden by the occurrence of crystallization of one or both of the components.

As the dissimilarities between the molecules increase, a llg-three-phase line appears in one of two possibilities. If the size difference between the molecules increases moderately, type-V phase behavior occurs. Here, the llg-three-phase line appears as an interruption on the lg-critical curve, with a LCEP and a lg-UCEP. The critical curve is divided into two parts. The first connects the critical point of the less volatile component (2) to the LCEP. The second originates in the critical point of the most volatile component (1) and ends in the lg-UCEP. If the interactions between the molecules increases gradually, type-II phase behavior occurs. Besides the continuous lg-critical curve, a llg-three-phase line appears that intersects with a ll-critical curve in a ll-UCEP. In the p,T-diagram, the llg-three-phase line can be located in between the vapor pressure curves of both pure components. For type-II mixtures the llg-three-

- 4 -



Figure 2.2: Four possibilities of Type VI phase behavior [13]

phase line can also be located above the vapor pressure curve of the most volatile component (1). As a consequence heteroazeotropy occurs, which is called type-II-HA. This type of phase behavior is found if two liquids of almost coinciding vapor pressure curves are only partially miscible.

As the dissimilarities between the components increase even further, type-IV phase behavior appears as a superposition of the types II and V. The Ilg-three-phase line is interrupted and consists of two parts. One part at low temperatures (Type-II) and one at high temperatures (Type-V). Three critical curves can be distinguished. The first is a Il-critical curve that runs from a Il-UCEP to high pressures. The second one connects the critical point of the most volatile component (1) and the Ig-UCEP at the highest temperature. The third critical curve connects the critical point of the less volatile component (2) and the LCEP of the high temperature Ilg-three-phase line.

Finally, the LCEP and the II-UCEP of type-IV coincide and type-III is formed. The II-critical curve and the Ig-critical curve, that connects the critical point of component 2 and the LCEP, converge to a single (II+Ig)-critical curve. The second branch of the Ig-critical curve connects the critical point of component 1 and the Ig-UCEP. Type-III phase behavior will be discussed more extensively in section 2.1.3.

From this it can be seen that types I and II of fluid phase behavior belong to class 1, whereas types III, IV and V belong to class 2.

Besides these five types, which were derived from the van der Waals equation of state, there exists a type-VI phase behavior that can not be derived from the van der Waals equation of state. Type-VI can be observed experimentally and can be derived with other equations of state, such as the SPHCT [13]. Type-VI is characterized by a continuous Ig-critical curve connecting the critical points of both pure components and a closed II-critical curve. The II-critical curve starts on the IIgthree-phase line in a LCEP and ends on the same IIg-three-phase line in a II-UCEP. Figure 2.2 shows a number of possibilities for type-VI phase behavior. For details one is referred to *Van Pelt* [13].

![](_page_13_Figure_0.jpeg)

Figure 2.3: Four possible types of critical curves in Type III phase behavior [13]

![](_page_13_Figure_2.jpeg)

Figure 2.4: T,x-projection of heteroazeotropy [15]

#### 2.1.3. Fluid phase behavior of Type-III

Since aqueous systems of organic compounds usually exhibit type-III phase behavior [14], a more extensive treatment of this type will be given.

Type-III phase behavior is characterized by two separate critical curves. The low temperature critical curve begins in the critical point of the most volatile component (1) and ends in a Ig-UCEP of the Ilg-three-phase line. The high temperature critical curve begins in the critical point of the less volatile component (2) and extends to high pressures.

As shown in Figure 2.1, the two llg-three-phase lines of type-IV coincide to form type-III. The high temperature critical curve may have a pressure maximum as well as a pressure minimum and is indicated by type-III<sub>m</sub> (Figure 2.3, *curve a*). With increasing dissimilarities between the components, the pressure maximum and minimum may become less pronounced and even may vanish. Figure 2.3 also shows other possibilities of the course of this critical curve. In the case of *curve d* where the critical curve proceeds to high pressures and high temperatures as well, this is referred to as (gas+gas) immiscibility of the first kind. If the critical curve goes through a temperature minimum while going to high pressures (*curve c*), (gas+gas) immiscibility of the second kind applies.

Similar to type-II mixtures, the llg-three-phase line can be located above or below the saturated vapor pressure curves of components 1. The first situation refers to heteroazeotropy, type-III-HA. This means that three phases coexist in the sequence  $L_2VL_1$  (normal  $L_1L_2V$ ) at a lower temperature than the boiling temperature of both pure components. This is shown graphically in Figure 2.4. [15]

#### 2.2. The Associated-Perturbed-Anisotropic-Chain Theory

The Associated-Perturbed-Anisotropic-Chain Theory (APACT) has been introduced by *Ikonomou and Donohue* in 1986 [8,16]. It is an equation of state specifically designed for molecules differing in size and shape. Moreover, the APACT equation of state also takes directional forces like molecular interactions into account.

APACT is an extension of the Perturbed-Anisotropic-Chain Theory (PACT). PACT is a three-parameter equation of state. These parameters are: the shape factor c, the characteristic size parameter v, and the characteristic energy parameter T<sup>\*</sup>. PACT takes into account molecular motions due to rotational, vibrational, and translational degrees of freedom. The anisotropic forces due to dipoles and quadrupoles as well as induced polar forces are accounted for by the perturbation theory of *Gubbins and Twu* [17]. The mixing rules for the isotropic as well as the anisotropic terms, are derived by a lattice theory model [18].

In order to treat systems which include components that associate through hydrogen bonding, an association model has been superimposed on PACT by means of the Heidemann and Prausnitz approach [19] resulting in the APACT equation of state. A number of different association models have been developed; e.g. monomerdimer model, two-site model, and three-site model.

Even though water has four hydrogen bonding sites per molecule, only three of these four sites participate in hydrogen bonding [20]. Therefore, the three-site model is used for systems of water and hydrocarbons.

The APACT equation of state can be written in terms of the compressibility factor Z, and can be expressed as the sum of the various contributions.

 $Z = 1 + Z^{assoc} + Z^{rep} + Z^{attr}$ (2.1)

The association term,  $Z^{assoc}$ , is given by *Ikonomou and Donohue* [8] and by *Economou and Donohue* [9]. Associating components are considered to form n-mers as a result of hydrogen bonding. The extent of association is defined as the ratio of the total number of moles of n-mers,  $n_T$ , divided by the number of moles that would be present without hydrogen bonding,  $n_0$ . If no hydrogen bonding occurs, this ratio equals unity. On the other hand, the ratio approaches zero if the substance has a strong tendency for hydrogen bonding. Besides pressure, temperature and volume, this ratio is also influenced by the equilibrium constant K for hydrogen bonding molecules.

Theory

(2.3)

The addition of an association term in the equation of state, implies that the number of parameters increases from three to five. Besides c,  $v^*$ , and  $T^*$  also two parameters that account for the hydrogen bonding are introduced. By expressing the chemical equilibrium constant as:

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$
(2.2)

the two parameters are the standard enthalpy and the entropy of hydrogen bond formation,  $\Delta H_0$  and  $\Delta S_0$ .

All parameters are determined by fitting the equation of state to experimental liquid density and vapor pressure data.

Both the repulsive, Z<sup>rep</sup> and the attractive, Z<sup>attr</sup> term are defined by *Vimalchand* [21,22]. The repulsive term is the Carnahan-Starling equation of state for hard spheres.

The attractive term, due to Lennard-Jones attraction, is obtained from the Perturbed-Soft-Chain Theory (PSCT). The attractive terms are calculated by extending the perturbation expansion of Barker and Henderson [23] for spherical molecules to that of chainlike molecules.

$$Z^{attr} = Z^{LJ} + Z^{\mu ind\mu} + Z^{ani}$$

Ν

The anisotropic attractions, due to multipolar interactions, are calculated with the perturbation expansion of *Gubbins and Twu* [17]. Here the multipolar forces are treated as a perturbation over the isotropic Lennard-Jones forces.

The mixing rules for APACT as given by Vimalchand and Donohue [21] are:

$$\langle c \rangle = \sum_{i=1}^{N} x_i c_i$$

$$\langle T^* \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} x_j x_j \frac{\epsilon_{ij} q_i}{k c_i}$$
(2.4)
(2.5)

Theory

where:

$$\epsilon_{ii} = (1 - k_{ii}) \sqrt{\epsilon_i \epsilon_i} \tag{2.6}$$

$$q_i = \frac{T^*_i c_i k}{\epsilon_i}$$
(2.7)

$$<_{V}^{*}> = \sum_{i=1}^{N} \sum_{j=1}^{N} x_{j} x_{j} \frac{N_{A} r_{i} \sigma_{ij}^{3}}{\sqrt{2}}$$
 (2.8)

with:

$$r_i = \frac{V_i^*}{8.667 \cdot 10^{-2}} \tag{2.9}$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$
(2.10)

#### 2.3. The Peng-Robinson equation of state

In 1976 *Peng and Robinson* [24] introduced a semi-empirical, two constants equation of state that is a modification of the van der Waals equation of state.

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) - b(v-b)}$$
(2.11)

This equation of state requires three input parameters for every component. These are the critical pressure( $p_c$ ), the critical temperature( $T_c$ ), and the acentric factor( $\omega$ ).

The two constants a(T) and b are given by:

$$a(T) = a \cdot \alpha(T_r, \omega) \tag{2.12}$$

$$a = 0.45724 \cdot \frac{R^2 T_c^2}{p_c} \tag{2.13}$$

$$\alpha (T_r, \omega) = \left[ 1 + (0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2) \cdot \sqrt{1 - T_r} \right]^2$$
(2.14)

$$b = 0.07780 \cdot \frac{RT_c}{p_c}$$
(2.15)

The mixing rules for the Peng-Robinson equation of state are:

$$= \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j a_{ij}$$
 (2.16)

$$a_{ii} = (1 - k_{ii})\sqrt{a_i a_i}$$
(2.17)

$$\langle b \rangle = \sum_{i=1}^{N} x_i b_i$$
 (2.18)

# 3. EXPERIMENTAL

#### 3.1. Choice of compounds

In order to study the freon - water and freon - water - salt systems at high pressures and temperatures, a certain freon had to be chosen. This choice is mainly determined by the stability of the freon in water at these extreme conditions. If the freon is not stable it will decompose before the measurements are finished or even started.

Hagen and Elphingstone [25] studied the interaction of  $H_2O$  with  $CF_4$ ,  $CCIF_3$ ,  $CCI_2F_2$ ,  $CCI_3F$  and  $CCI_4$  in the pressure range of 1.01 to 405.30 MPa and the temperature range of 303.15 to 773.15 K.

Table 3.1: Non-reacting Systems [25]				
System	Temperature [K]	Pressure [MPa]		
H₂O - CF₄	773.15	405.30		
$H_2O - CCIF_3$	773.15	405.30		
$H_2O - CCI_2F_2$	373.15	405.30		
H <sub>2</sub> O - CCl <sub>2</sub> F <sub>2</sub>	573.15	1.01		
H <sub>2</sub> O - CCI <sub>3</sub> F	573.15	1.01		
H <sub>2</sub> O - CCI <sub>4</sub>	303.15	405.30		
$H_2O - CCI_4$	573.15	1.01		

They concluded that both  $CF_4$  and  $CCIF_3$  are stable in  $H_2O$  up to 773.15 K and 405.30 MPa.  $CCI_2F_2$ ,  $CCI_3F$  and  $CCI_4$  are not stable near the critical point of  $H_2O$ , and as a consequence not suitable for the purpose of this study. Apparently, only  $CF_4$  and  $CCIF_3$  are suitable for measurements.

In this study the main focus was on the  $CF_4 - H_2O$  system, whereas, only a small number of data points were measured of the  $CCIF_3 - H_2O$  system. Furthermore, one isopleth of the  $CHF_3 - H_2O$  system was determined.

It is interesting to note that the solubility of  $CF_4$  in  $H_2O$  at atmospheric pressure and in the temperature range of 273.15 to 323.15 K is remarkably low [26]. Therefore, it is very interesting to see the effect of high pressures and temperatures on the solubility of  $CF_4$  in  $H_2O$ . With respect to SCWO, it would be straightforward to choose NaF as a third component, since  $CF_4$  and  $H_2O$  may react to, among others, HF. Injection of NaOH into the system, in order to neutralize the acid formed, NaF is formed. However, as in almost all known literature dealing with ternary water - organic compound - salt systems the phase behavior is determined with NaCl. It was decided to use NaCl as the third component in this study.

#### 3.2. The chemicals used

For the experiments, ordinary laboratory double distilled H<sub>2</sub>O was used.

A summary of the other chemical compounds used in this study is given in Table 3.2, along with their synonyms, formula, origin and purity.

In Table 3.3, some properties of the used chemical compounds are given.

# Table 3.2: Synonyms, formula, origin and purity of the chemical compounds used

Compound	Synonyms	Formula	Origin	Purity [%-mole]
Tetrafluoromethane	Carbontetrafluoride Perfluoromethane R-14	CF4	Praxair N.V.	99.995
Chlorotrifluoromethane	R-13	CCIF3	Praxair N.V.	99.7
Trifluoromethane	Fluoroform R-23	CHF3	Praxair N.V.	99.995
Sodium Chloride		NaCl	MERCK	99.5

![](_page_21_Figure_0.jpeg)

Figure 3.1: Optical high pressure autoclave. 1: Air exhaust, 2: air cooling, 3: electromagnet, 4: cooling coil, 5: Pt thermometer, 6: soft iron cover, 7: closing plug, 8: copper coated mild steel ring, 9: silicone oil, 10: stirrers, 11: top of measuring cell (sapphire), 12: sapphire window, 13: measuring cell, 14: container, 15: mercury, 16: silicone oil, 17: water cooling, 18: screwed rod

Table 3.3: Properties of the used chemical compounds [27]					
		H <sub>2</sub> O	CF₄	CCIF <sub>3</sub>	CHF <sub>3</sub>
M,	[g/mole]	18.015	88.005	104.459	70.013
т.р.	[K]	273.15	86.4	92.0	110
b.p.	[K]	373.15	145.1	193.2	191
v	[m3/mole]	18.1 <b>·</b> 10 <sup>-6</sup>	54.8·10 <sup>-6</sup>	68.6·10 <sup>-6</sup>	48.6·10 <sup>-6</sup>
p,	[MPa]	22.12	3.74	3.87	4.86
T_	[K]	647.35	227.6	302.0	299.30
V	[m3/mole]	63.5 <b>·</b> 10 <sup>-6</sup>	139.6 <b>·</b> 10 <sup>-6</sup>	180.4·10 <sup>-6</sup>	132.7·10 <sup>-6</sup>
ω	[-]	0.344	0.177	0.198	0.26
μ	[Debye]	1.85	0	0.5	1.6

#### 3.3. Experimental set-up

The experiments were performed according to the so called synthetic method, which involved the visual observation of phase boundaries for mixtures of constant and known composition.

The measurements were performed in a stainless steel optical high pressure autoclave, designed for temperatures up to 673 K and pressures as high as 200 MPa. A schematic design of the autoclave is given in Figure 3.1.

The high temperatures were obtained by two electrical heating coils, which were controlled by a Shimaden type SR20 PID temperature controller. The temperature stability was approximately 0.1 K. A platinum resistance thermometer was inserted in a shaft in the closing plug of the autoclave, and was used to measure the temperature. The platinum thermometer was connected to a Bleeker type 53421 resistance bridge. The measurements of the temperature were accurate to approximately 0.01 K.

A dead weight pressure gauge of Tradinco Instruments was used to measure and to maintain the pressure. The maximum error in the pressure measurements was 0.008 MPa (0.04 % at 250 MPa). A high pressure bench was connected to the autoclave, by a silicone oil - mercury - hydraulic oil separator. As hydraulic oil, Shell Tellus 22 was used. The silicone oil functioned as a heat transfer medium, Dow Corning<sup>®</sup> 200 Fluid, 5CS and 10 CS was used. The use of 10 CS oil resulted in some problems. At high temperatures the oil appeared to be very sensitive to sudden and large pressure changes, leading to a deterioration in transparency.

![](_page_23_Figure_0.jpeg)

Figure 3.2: Schematic presentation of the gas-rack

Stirring was obtained by means of two magnets, that were activated by an electromagnet. The two magnets activated a magnetic stirrer inside the measuring cell. The measuring cell could move vertically, in front of the sapphire windows, by means of a screwed rod and was lighted by a lamp which was positioned at an angle of 139°.

#### 3.4. Filling procedure

#### 3.4.1. Binary mixtures

The mixtures were prepared using a specifically designed gas-rack, which is schematically shown in Figure 3.2.

An asbestos string of rope was wound around a sapphire tube, which was inserted in a steel sample holder. Sapphire was used because of the extreme corrosiveness of  $H_2O$  at near-critical conditions. The sapphire tube functioned as the measuring cell, and was kept in place by a screw. A small magnetic stainless steel stirrer was inserted into the measuring cell, after which a glass bulb was connected to the measuring cell.

 $H_2O$  was dosed by means of a micrometer syringe. The exact amount of  $H_2O$  added was determined by the weight of the filled sample.

A glass support was used to connect the sample to the gas rack. Since air is dissolved in  $H_2O$ , the air had to be removed by degassing. For that purpose, the  $H_2O$  was frozen with a cooling jacket containing liquid nitrogen. Next, the sample was evacuated by means of a high vacuum turbo pump. Then the  $H_2O$  was melted and the vacuum forced the air out of the  $H_2O$ . The above described procedure was repeated until all the air was removed from the  $H_2O$ . This was determined by both visual observation and with a manometer.

In order to fill the sample-tube with  $CF_4$  the sample was turned upwards, while cooling with liquid nitrogen continued. A volumetrically determined amount of  $CF_4$  was added to the frozen and degassed  $H_2O$  in the following manner. The gas rack was filled with  $CF_4$ , which was pressed into the measuring cell by means of the displacement of mercury. The mercury displacement was caused by nitrogen pressure. The amount of added  $CF_4$  was determined by the pressure, temperature and a volumetrically calibrated volume. The mercury was inserted further into the measuring cell, where it was partly frozen. The maximum error in the mole fraction was estimated to be approximately 0.0002 [28]. The vessel with the sample was taken from the gas rack and the glass support was removed from the sample under mercury, so the sample could not be contaminated with air. During this procedure cooling with liquid nitrogen was continued. The cooling was stopped and the container was inserted in the closing plug of the autoclave. The closing plug with the container was inserted in the autoclave, with in between a copper coated mild steel ring to achieve good sealing. A big nut was used to close the system, after which the pressure in the autoclave was quickly raised to approximately 20 MPa by means of a low pressure bench.

For the  $CHF_3 - H_2O$  mixture, the same procedure was followed. However, due to its low purity, the  $CCIF_3$  had to be degassed as well before dosing the sample into the vessel. As will be discussed later, the degassing of the  $CCIF_3$  did not have the desired effect.

#### 3.4.2 Ternary mixtures

In case of the ternary systems, the same procedure was followed, be it with some minor adjustments. A certain NaCl solution was prepared by dissolving a weight amount of NaCl in a 300 ml flask, which was filled with  $H_2O$ . This solution was dosed, into the measuring cell in the same manner as the  $H_2O$  in the binary system. The mass ratio of NaCl to  $H_2O$  is defined by:

$$\frac{M_{NaCl}}{M_{H_2O}} = \frac{m_{NaCl}}{\rho_{H_2O} \cdot \left[300 - \frac{m_{NaCl}}{\rho_{NaCl}}\right]} = K_{NaCl}$$
(3.1)

Since the NaCI did not dissolve spontaneously but after rigorous shaking, this method gives acceptable results.

From the mass ratio, the NaCl concentration was determined in weight percent.

$$wt\% = \frac{M_{NaCl}}{M_{H_2O} + M_{NaCl}} \cdot 100\% = \frac{K_{NaCl}}{K_{NaCl} + 1} \cdot 100\%$$
(3.2)

The density of  $H_2O$  was taken as 1 g·ml<sup>-1</sup> and that of NaCl as 2.16 g·ml<sup>-1</sup>.

![](_page_26_Figure_0.jpeg)

Figure 3.3: The second virial coefficient (B) of CF<sub>4</sub>, as a function of temperature

![](_page_26_Figure_2.jpeg)

Figure 3.4: The second virial coefficient (B) of  $CCIF_3$ , as a function of temperature

#### 3.5. Calculation of the composition

#### 3.5.1. Binary mixtures

The amount of  $H_2O$  in the samples is determined by the weight of the added  $H_2O$  and by its molecular weight.

$$n_{H_2O} = \frac{M_{H_2O}}{M_{w,H_2O}}$$
(3.3)

The amount of gas is determined by the virial equation.

$$Z = \frac{p \cdot v}{R \cdot T} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3}$$
(3.4)

At a low pressure and temperature, the second order of the virial equation is used. The higher order terms, of the virial equation, are negligible at the filling conditions.

First the gas pressure during filling  $(p_1)$  is corrected for a pressure deviation on the gas rack.

$$\Delta p = p_1 \cdot 4.8031 \cdot 10^{-4} - 0.38828 \tag{3.5}$$

Next the pressure is transformed from millibar (mbar) to pascal (Pa).

$$p_2 = (p_1 + \Delta p) \cdot 10^2 \tag{3.6}$$

Finally, the amount of gas is calculated using the second order virial equation, which can be rewritten into:

$$n_{gas} = \frac{p_2 \cdot V}{R \cdot T + B_{gas} \cdot p_2}$$
(3.7)

The second virial coefficient (B), for the gases, are taken from *Dymond and Smith* [29]. Figures 3.3 to 3.5 show the second virial coefficient of the gases  $CF_4$ ,  $CCIF_3$ ,

![](_page_28_Figure_0.jpeg)

Figure 3.5: The second virial coefficient (B) of  $CHF_3$ , as a function of temperature

and  $CHF_3$ , as a function of the temperature. From these figures polynomial functions have been calculated, which are valid only within the region of the data points. The coefficients of the polynomials are given in Table 3.4.

$$B_{gas} = C_0 + C_1 \cdot T + C_2 \cdot T^2 + C_3 \cdot T^3 + C_4 \cdot T^4$$
(3.8)

# Table 3.4: Polynomial coefficients for the second virial coefficient of the gases used in the experiments

gas	CF₄	CCIF <sub>3</sub>	CHF3	
C <sub>0</sub> C <sub>1</sub>	-8.56249.10 <sup>2</sup> 5.22096	-3.0446 10 <sup>3</sup> 2.1840 10 <sup>1</sup> 5.777 10 <sup>-2</sup>	$-2.3871 \cdot 10^{3}$ 1.7474 \cdot 10^{1}	
$C_2$ $C_3$ $C_4$	-1.24604.10 <sup>-2</sup> 1.36793.10 <sup>-5</sup> -5.65695.10 <sup>-9</sup>	-5.777-10 <sup>-5</sup> -8.2622-10 <sup>-9</sup>	-4.727710 4.5340·10 <sup>-5</sup>	

Now the mole fractions can be determined, from the amounts of  $H_2O$  and gas.

Xua	=		(3.9)
ΛH <sub>2</sub> O	$n_{H_2O} + n_{gas}$		

$$X_{gas} = \frac{n_{gas}}{n_{H_2O} + n_{gas}}$$
(3.10)

#### 3.5.2. Ternary systems

The amounts of  $H_2O$  and NaCl are determined by the weight of the added solution, the weight percent NaCl.

$$M_{NaCl} = M_{solution} \cdot wt\%$$
(3.11)

![](_page_30_Figure_0.jpeg)

Figure 3.6: Resistance of the *BLEEKER type 53421* resistance bridge, as a function of temperature

 $n_{NaCl} = \frac{M_{NaCl}}{M_{w NaCl}}$ (3.12)

$$M_{H_2O} = M_{NaCl} \cdot \frac{1 - wt\%}{wt\%}$$
(3.13)

$$n_{H_2O} = \frac{M_{H_2O}}{M_{w,H_2O}}$$
(3.14)

The determination of the amount of gas is completely similar to the procedure as with the binary systems. So, the mole fractions are determined from the amounts of  $H_2O$ , gas and NaCl.

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{gas} + n_{NaCl}}$$
(3.15)

$$X_{gas} = \frac{n_{gas}}{n_{H_2O} + n_{gas} + n_{NaCl}}$$
(3.16)

$$X_{NaCl} = \frac{n_{NaCl}}{n_{H_2O} + n_{gas} + n_{NaCl}}$$
(3.17)

#### 3.6 Measuring procedure

At a certain pressure the temperature was set to just below the bubble point. The pressure was kept constant, while the temperature is slowly increased. The moment the gas phase disappears, the temperature was determined by neutralizing the resistance bridge. The resistance, as given by the resistance bridge, could be related to the temperature (Figure 3.6) by:

![](_page_32_Figure_0.jpeg)

Figure 3.7: Isopleth with isobaric and isothermal measurements,  $x_{CF4} = 0.0160$ 

![](_page_32_Figure_2.jpeg)

Figure 3.8: Schematic presentation of the barotropic effect (a) and (b), and of a measurement of a critical point (c)

(3.18)

$$R_{r.b.} = R_0 \cdot (1 + C_1 \cdot t + C_2 \cdot t^2)$$

with:  $R_0 = 99.98215$  $C_1 = 3.908145 \cdot 10^{-3}$  $C_2 = -5.736918 \cdot 10^{-7}$ 

Even though the autoclave is not designed for isobaric measurements, the error made compared to isothermal measurements is negligible. This is illustrated in Figure 3.7 where for the mixture with a  $CF_4$  mole fraction of 0.0160, three isothermal measurements were performed. These data points do not deviate from the isobaric determined data points. Therefore, it can be concluded that both measuring procedures can be used, providing small temperature increases are used with the isobaric measurements. Especially in the high pressure region the isobaric measurements are preferred, because of the steep slope of the isopleths. Isothermal measurements in this region could result in larger errors in the measurements.

The systems investigated showed barotropy, which is an inversion of phases in the gravitational field caused by a change in density. At low pressures the density of the gas phase is smaller than that of the liquid phase, so the gas phase is situated in the top of the measuring cell (Figure 3.8a). At high pressures the density of the gas phase is larger than that of the liquid phase, so the gas phase is situated on the bottom of the measuring cell (Figure 3.8b). For each temperature, there is one unique pressure at which the densities of the phases become identical. All other properties, such as interfacial tension are still different, which distinguishes a barotropic inversion point from a critical point.

Critical points were determined by visual observation of the disappearance of the phase boundary. If the liquid-vapor mixture is slowly heated, there are three possibilities. If the pressure is smaller than the critical pressure, the meniscus will fall and all the liquid will evaporate. If the pressure is greater than the critical pressure, the meniscus will rise and all the vapor will condense. If the pressure is equal to the critical pressure, the meniscus will become flat, fainter, and eventually will vanish at the critical temperature (Figure 3.8c).

For measuring a critical point, a pressure in the range of the critical point is sufficient. The meniscus will move up or down to a height in the measuring cell where the local pressure is equal to the critical pressure. This method determines the critical temperature. Next the temperature is set constant to this critical temperature and the pressure is varied until the meniscus vanishes in the middle of the measuring cell. The upper boundary of the pressure and temperature range that could be investigated were restricted by the specifications of the autoclave. The low pressure boundary was restricted by the fact that the isothermal compressibility of  $H_2O$  increases upon approaching its critical pressure. The minimum pressure of each mixture was reached when the volume of the mixture became larger than the measuring cell. The minimum  $CF_4$  mole fraction is that mixture at which the gas phase was just visible in the measuring cell. The maximum  $CF_4$  mole fraction was determined by the maximum allowable operation temperature of the autoclave. The isopleth shifts to higher temperatures with increasing  $CF_4$  mole fractions, ultimately exceeding 673 K.

#### 3.7. Calculation of the exact pressure

Since the pressure and temperature are high, the partial pressure of mercury contributes significantly to the pressure in the measuring tube. At high pressures and temperatures this contribution of the partial pressure of mercury is not only determined by the saturation pressure.

To calculate the fugacity at pressure p and temperature T, the generally applicable fugacity integral is separated into two parts [30].

$$R \cdot T \cdot \ln\left(\frac{f}{p}\right)_{pure \ i} = \int_{0}^{p} \left(v_{i} - \frac{R \cdot T}{p}\right) dp$$
(3.19)

$$R \cdot T \cdot \ln\left(\frac{f_i}{p}\right) = \int_0^{p_i^s} (v_i - \frac{R \cdot T}{p}) \, dp + \int_{p_i^s}^p (v_i - \frac{R \cdot T}{p}) \, dp \tag{3.20}$$

The first part gives the fugacity of the saturated vapor at temperature T and at the saturation pressure p<sup>s</sup>. The second part gives the correction due to the compression of the liquid phase to the pressure p.

At the saturation pressure, the fugacity of the vapor phase equals that of the liquid phase.

![](_page_35_Figure_0.jpeg)

Figure 3.9: The saturation pressure of Mercury as a function of temperature
$$R \cdot T \cdot \ln\left(\frac{f_i}{p}\right) = R \cdot T \cdot \ln\left(\frac{f_i^s}{p_i^s}\right) + \int_{p_i^s}^p v_i dp - R \cdot T \cdot \ln\left(\frac{p}{p_i^s}\right)$$
(3.21)

which is rearranged to:

$$f_{i} = p_{i}^{s} \cdot \phi_{i}^{s} \cdot \exp\left[\int_{p_{i}^{s}}^{p} \frac{V_{i}}{RT} dp\right]$$

$$with \quad \phi_{i}^{s} = \frac{f_{i}^{s}}{p_{i}^{s}}$$
(3.22)

This derivation shows that the fugacity of the liquid is not only determined by the saturation pressure. Deviations of the saturated vapor from ideal gas behavior are accounted for by the fugacity coefficient,  $\Phi_i^s$ . The exponential factor, also known as the Poynting correction, takes into account the fact that the liquid is at a different pressure than the saturation pressure.

The experimental saturated vapor pressure data of mercury of *Smith and Menzies* as summarized by *Nesmeyanov* [31] were fitted to a polynomial (Figure 3.9):

$$p_{H_{a}}^{s} = C_{0} + C_{1} \cdot T + C_{2} \cdot T^{2} + C_{3} \cdot T^{3} + C_{4} \cdot T^{4}$$
(3.23)

with the following constants:

 $C_0=2.71921372423276 \cdot 10^6$   $C_1=-2.37758478284464 \cdot 10^4$   $C_2=78.328175330613$   $C_3=-1.15452169709569 \cdot 10^{-1}$  $C_4=6.4378760641348 \cdot 10^{-5}$ 

The critical temperature of mercury equals  $T_c=1735$  K, so the highest possible reduced temperature is  $T_r=673.15/1735=0.39$ . At these temperatures the fugacity coefficient is assumed to be equal to unity.

In general the volume of the liquid is a function of both pressure and temperature, but at conditions well below the critical point the liquid phase may be regarded as incompressible. Therefore, the Poynting correction is simplified to:

$$\exp\left[\int_{p_i^s}^{p} \frac{v_i}{RT} dp\right] = \exp\left[\frac{v_i^{\ l} \cdot (p - p_i^{\ s})}{R \cdot T}\right]$$
(3.24)

The liquid molar volume of mercury equals,  $v_{Hg}^{I} = 14.9 \cdot 10^{-6} \text{ m}^{3} \cdot \text{mole}^{-1}$  [32].

So the contribution of mercury to the pressure can be written as:

$$p_{Hg} = p_{Hg}^{s} \cdot \exp\left[\frac{v' \cdot (p_{measured} \cdot 10^{5} - p_{Hg}^{s})}{R \cdot T_{measured}}\right]$$
(3.25)

Since the pressure gauge measures the absolute pressure, the pressure also has to be corrected for the atmospheric pressure, resulting in equation 3.26.

$$p_{corrected} = p_{measured} \cdot 10^{-1} + p_{atmospheric} - p_{Hg} \cdot 10^{-6}$$
(3.26)



Figure 4.1: Ten isopleths of the  $CF_4 - H_2O$  system, with  $CF_4$  mole fractions of: 0.0121 (1), 0.0160 (2), 0.0172 (3), 0.0222 (4), 0.0249 (5), 0.0274 (6), 0.0324 (7), 0.0366 (8), 0.0442 (9), and 0.0583 (10)



Figure 4.2: Isobaric T,x-projections of the  $CF_4$  -  $H_2O$  system at pressures of 40, 100, and 200 MPa

## 4. RESULTS AND DISCUSSION

#### 4.1. Results of the measurements

#### 4.1.1. The system $CF_4 - H_2O$

The experimental results for the binary  $CF_4 - H_2O$  system are given in Appendix A, Table A.1. Figure 4.1 shows the isopleths, which are p,T-curves at constant composition. Isopleths are the border lines between the two-phase region and the one-phase region. The two-phase region is always on the low temperature side of the isopleth.

Two critical points could be measured, and are denoted by (cp) in Table A.1 (Appendix A). Figure 4.2 presents isobaric T,x-sections of the isopleths.

All isopleths measured show a temperature minimum between 60 and 100 MPa. This temperature minimum shifts to higher temperatures with increasing  $CF_4$  mole fractions.

All the mixtures investigated exhibit barotropy in the pressure interval between 80 and 100 MPa. At pressures of 100 MPa and higher, the density of the gas phase is larger than that of the liquid phase. As a consequence, the gas phase is situated on the bottom of the measuring cell. However, at pressures of 80 MPa and lower, the density of the gas phase is smaller than that of the liquid phase. Consequently, the coexisting phases change position.

Figure 4.3 shows the two critical points that were determined, together with a part of the critical curve of the  $CH_4 - H_2O$  system. From the two measured critical points, it can be concluded that the critical curve of the  $CF_4 - H_2O$  system has a negative slope near the critical point of  $H_2O$ . As a consequence, the  $CF_4 - H_2O$  system exhibits (gas+gas) immiscibility of the second kind. The critical curve of the  $CF_4 - H_2O$  system is situated at higher temperatures than the critical curve of the  $CH_4 - H_2O$  system.

### 4.1.2. The systems CCIF<sub>3</sub> - $H_2O$ and CHF<sub>3</sub> - $H_2O$

The experimental results for the binary systems  $CCIF_3 - H_2O$  and  $CHF_3 - H_2O$  are given in Appendix B, Table B.1 and B.2, respectively. Graphical presentations of the isopleths of these systems are given in Figures 4.4 and 4.5, respectively.

A small number of measurements were performed for the  $CCIF_3 - H_2O$  system, because of the fact that a reaction of the investigated system deteriorated the



Figure 4.3: p,T-projection of the two critical points of the  $CF_4 - H_2O$  system (1), together with a small part of the critical curve of the  $CH_4 - H_2O$  system (2). (Source: *Brunner* [14])



Figure 4.4: Some data points of the  $CCIF_3$  -  $H_2O$  system, with  $CCIF_3$  mole fractions of 0.0306 and 0.0320

transparency of the system. The impurity of the  $CCIF_3$  may have played an important role. Even after degassing the  $CCIF_3$ , before preparing the sample, the problems described above could not be solved.

Therefore, it may be concluded that the measurements of the  $CCIF_3 - H_2O$  system are not reliable. However, at least it gives some indication of the effect of the substitution of one fluorine by a chlorine atom. The immiscibility region is located at temperatures that are approximately 20 K lower, compared to the same composition of the  $CF_4 - H_2O$  system.

Barotropy in the CCIF<sub>3</sub> -  $H_2O$  system occurred in the same pressure interval as in the CF<sub>4</sub> -  $H_2O$  system, i.e. between 70 and 80 MPa.

One isopleth has been measured for the  $CHF_3 - H_2O$  system. As can be seen in Figure 4.5, the shape of the isopleth is different from the  $CF_4 - H_2O$  system. A temperature minimum could not be observed even up to 200 MPa.

The effect of the substitution of one fluorine by a hydrogen atom is clear. The immiscibility region is located at temperatures that are more than 100 K lower, compared to the same composition of the  $CF_4$  -  $H_2O$  system.

This system is well suited for future work. A larger composition range can be investigated before the experimental temperature boundary is exceeded.

Barotropy occurred in the pressure interval between 80 and 90 MPa.

4.1.3. The system  $CF_4 - H_2O - NaCI$ 

The experimental results for the ternary system  $CF_4 - H_2O - NaCl$ , with 0.5, 1.1, 2.1 and 3.3 weight percent NaCl (relative to water) are given in Appendix C, Table C.1 to C.4, respectively. Graphical presentations of the isopleths of this system are given in Figures 4.6 to 4.9. Figures 4.10 to 4.12 present isobaric T,x-sections of the isopleths at 40, 100 and 200 MPa.

Since the effect of 0.5 weight percent NaCl is almost negligible, only one isopleth has been measured with this NaCl concentration. The effect of the three other NaCl concentrations are more pronounced. The mixtures with 1.1, 2.1, 3.3 weight percent NaCl shift the immiscibility region to higher temperatures by approximately 5, 15 and 20 K, respectively.

As was the case for the binary  $CF_4 - H_2O$  system, all measured isopleths show a temperature minimum between 60 and 100 MPa.

For all ternary mixtures, barotropy occurred between 80 and 100 MPa.



Figure 4.5: One isopleth of the  $CHF_3 - H_2O$  system, with a  $CHF_3$  mole fraction of 0.0499



Figure 4.6: One isopleth of the  $CF_4 - H_2O - NaCl$  system, with 0.5 weight percent NaCl and with a  $CF_4$  mole fraction of 0.0198



Figure 4.7: Three isopleths of the  $CF_4 - H_2O$  - NaCl system, with 1.1 weight percent NaCl and with  $CF_4$  mole fractions of 0.0176 (1), 0.0234 (2), and 0.0325 (3)



Figure 4.8: Three isopleths of the  $CF_4 - H_2O - NaCl$  system, with 2.1 weight percent NaCl and with  $CF_4$  mole fractions of 0.0173 (1), 0.0234 (2), and 0.0325 (3)



Figure 4.9: Four isopleths of the  $CF_4 - H_2O$  - NaCl system, with 3.3 weight percent NaCl and with  $CF_4$  mole fractions of 0.0076 (1), 0.0180 (2), 0.0233 (3), and 0.0325 (4)



Figure 4.10: Isobaric T,x-projection at 40 MPa, for the  $CF_4$  -  $H_2O$  and the  $CF_4$  -  $H_2O$  - NaCl systems



Figure 4.11: Isobaric T,x-projection at 100 MPa, for the  $CF_4$  -  $H_2O$  and the  $CF_4$  -  $H_2O$  - NaCI systems



Figure 4.12: Isobaric T,x-projection at 200 MPa, for the  $CF_4$  -  $H_2O$  and the  $CF_4$  -  $H_2O$  - NaCI systems

#### 4.2. Results of the modelling

#### 4.2.1. Fitting of the CF₄ parameters with PACT

The five molecular parameters for the three-site APACT model for  $H_2O$  were taken from *Smits et al.* [10].

Since  $CF_4$  does not associate, the three molecular parameters (c, v, and T) of PACT were determined without an association model. The parameters for  $CF_4$  were determined by fitting to experimental liquid density data from 133.15 K and 0.04 MPa up to its critical point [33]. The experimental saturated vapor pressure data ranged from 90 K up to its critical temperature [32]. The liquid density and saturated vapor pressure data are given in Appendix D.

Table 4.1 presents the fitted parameters for  $CF_4$ , along with the used parameters for the three-site model of  $H_2O$ . The % AAD means percentage Absolute Average Deviation, and is defined as:

$$\% AAD = \frac{100}{K} \sum_{i=1}^{K} \frac{|M_i^{calc} - M_i^{exp}|}{M_i^{exp}}$$
(4.1)

Where M is the fitted thermodynamic property. K is the number of experimental data points.

Table 4.1: Molecular parameters for CF <sub>4</sub> and H <sub>2</sub> O (the three-site model)	and	the
% AAD in Liquid Molar Volume and Vapor Pressure <sup>a</sup>		

	Т	v	С	ΔH₀	∆S₀/R	<i>€</i> /k	μ	α	% A p <sup>sat</sup> (28)	AD v <sup>liq</sup> (70)
	[K]	[cm <sup>3</sup> /mole]		[kJ/mole]			[D]	[Å <sup>3</sup> ]		
CF₄ H₂O <sup>b</sup>	157.2 183.8	2 30.09 3 11.64	1.411 1.000	4 0 -20.10	-10.97	105 350	0 1.75	3.838 1.59	2.001	1.827

<sup>a</sup> Number of data points used to fit the parameters are shown in parentheses.

<sup>b</sup> Three-site model.



Figure 4.13: Results of binary flash calculations in APACT, with an average value of 0.000 for the binary interaction parameter ( $k_{ij}^{avg}$ ) at 40 MPa



Figure 4.14: Results of binary flash calculations in APACT, with an average value of 0.000 for the binary interaction parameter ( $k_{ij}^{avg}$ ) at 100 MPa

### 4.2.2. Modelling of the system $CF_4$ - $H_2O$ with APACT

With the previously determined molecular parameters the binary system was modelled. All calculations with APACT were performed as flash calculations. Since there are a number of series of T,x data at constant pressure, the following procedure was followed.

First the binary interaction parameter  $k_{ij}$  was optimized for a number of different pressures, by minimizing the % AAD in the CF<sub>4</sub> composition (x<sub>1</sub>). Next the optimized binary interaction parameters  $k_{ij}^{opt}$ , for the different pressures, have been averaged. The average binary interaction parameter equals,  $k_{ij}^{avg} = 0.000$ . With this average binary interaction parameter  $k_{ij}^{avg}$ , the entire system was remodelled. These results are presented in Table 4.2. Graphical presentations are shown in Figures 4.13 to 4.15, for pressures of 40, 100, and 200 MPa, respectively.

Table 4.	2: Opt	imization of the	binary interaction	on parameter k	ij
p [MPa]	N	k <sub>ij</sub> opt	% AAD in x <sub>1</sub> with k <sub>ij</sub> <sup>opt</sup>	% AAD in x <sub>1</sub> with k <sub>ij</sub> <sup>avg</sup>	% AAD in $x_2$ with $k_{ij}^{avg}$
40	10	-0.069	27.1	36.1	1.37
60	10	-0.029	22.3	24.6	0.982
80	10	-0.010	20.0	21.0	0.785
100	9	-0.002	17.2	17.2	0.675
120	9	0.009	16.4	17.3	0.609
140	9	0.017	15.9	18.5	0.584
160	9	0.023	15.3	20.0	0.583
180	9	0.027	14.7	22.0	0.604
200	9	0.031	14.4	24.8	0.675

These Figures show that the modelling of this system with one constant binary interaction parameter is not accurate. The fact that the average value of the binary interaction parameter equals zero does not mean that it has no influence. At low pressures the value for  $k_{ij}^{opt}$  is negative, whereas, at high pressures it is positive. This causes the average value to be zero, which is highly unlikely.

However, from Figure 4.16 it can be concluded that it is not the change of  $k_{ij}$  with pressure that causes the bad results. Figure 4.16 shows the results of APACT with the optimized  $k_{ij}$  value for 40 MPa. It is clear that the results of APACT are only shifted in the composition direction, when taking a different constant value for the binary interaction parameter. A constant binary interaction parameter does not accurately describe the shape of the experimental T,x-curve.



Figure 4.15: Results of binary flash calculations in APACT, with an average value of 0.000 for the binary interaction parameter ( $k_{ij}^{avg}$ ) at 200 MPa



Figure 4.16: Results of binary flash calculations in APACT, with the optimum value of -0.069 for the binary interaction parameter ( $k_{ij}^{opt}$ ) at 40 MPa

(4.2)

Therefore, it was attempted to model the system  $CF_4 - H_2O$  with a temperature dependent binary interaction parameter. For 40, 100, and 200 MPa, the temperature dependence of the binary interaction parameter was determined. The results are given in Table 4.3 and in Figure 4.17.

Table	4.3:	Temperature	dependence	of	the	optimized	binary	interaction
param	eter I	<b>K</b> <sub>ii</sub>						

p = 40	MPa	p = 1(	00 MPa	p = 2	00 MPa	
T [K]	k <sub>ij</sub> <sup>opt</sup>	T [K]	k <sub>ij</sub> <sup>opt</sup>	T [K]	k <sub>ij</sub> <sup>opt</sup>	
	0.004	500.05	0.000	COF CF	0.052	
602.88	-0.001	599.85	0.028	605.65	0.052	
614.74	-0.029	606.99	0.029	614.63	0.055	
621.61	-0.030	614.52	0.004	623.77	0.033	
626.97	-0.068	622.23	-0.001	633.80	0.032	
632.40	-0.081	626.77	-0.008	641.31	0.029	
634.33	-0.096	633.15	-0.022	647.89	0.015	
638.16	-0.122	638.64	-0.032	654.37	0.008	
640.41	-0.143	643.87	-0.051	662.45	-0.007	
642.12	-0.176	648.12	-0.085	664.24	-0.042	
643.18	-0.229					

From Figure 4.17 it can be seen that the temperature dependence at 100 MPa is approximately the average fit over the entire pressure range. Therefore the entire system was remodelled with that temperature dependent binary interaction parameter.

$$k_{ii} = C_0 + C_1 \cdot T + C_2 \cdot T^2$$

with:

 $C_0 = -13.47051485$   $C_1 = 4.52630675 \cdot 10^{-2}$  $C_2 = -3.79460349 \cdot 10^{-5}$ 

The results of APACT with a temperature dependent binary interaction parameter are given in Table 4.4 and in Figures 4.18 to 4.20



Figure 4.17: Temperature dependence of the optimized binary interaction parameter ( $k_{ij}^{opt}$ ) at 40, 100, and 200 MPa



Figure 4.18: Results of binary flash calculations in APACT, with a temperature dependent binary interaction parameter ( $k_{ij}(T)$ ) at 40 MPa

p [MPa]	Ν	% AAD in x <sub>1</sub>	% AAD in $x_2$
40	10	31.6	1.14
60	10	20.0	0.746
80	10	11.0	0.399
100	9	3.75	0.138
120	9	13.2	0.496
140	9	27.2	1.06
160	9	44.2	1.78
180	9	66.5	2.75
200	9	85.5	3.41

Table 4.4: Modelling of the binary system with the temperature dependent binary interaction parameter  $k_{ii}$ 

The results obtained with a temperature dependent binary interaction parameter are not satisfactory. Since the temperature dependent binary interaction parameter used was obtained at 100 MPa, it is not surprising that this pressure gives good results. However, at 40 and 200 MPa APACT is very inaccurate, especially at the higher temperatures. This can be explained by examining Figure 4.17. At the lower temperatures, the binary interaction parameters for 40 and 200 MPa do not deviate much from the fit at 100 MPa. Whereas, at higher temperatures an increasing deviation occurs between the optimized binary interaction parameter and the value obtained from the fit at 100 MPa.



Figure 4.19: Results of binary flash calculations in APACT, with a temperature dependent binary interaction parameter ( $k_{ij}(T)$ ) at 100 MPa



Figure 4.20: Results of binary flash calculations in APACT, with a temperature dependent binary interaction parameter ( $k_{ii}(T)$ ) at 200 MPa

4.2.3. Modelling of the system  $CF_4$  -  $H_2O$  with the Peng-Robinson equation of state

Since it was not possible to model the binary  $CF_4 - H_2O$  system with satisfactory results using APACT, it was attempted to use the Peng-Robinson (PR) equation of state.

The PR equation of state requires three input parameters for each component: the critical pressure ( $p_c$ ), the critical temperature ( $T_c$ ), and the acentric factor ( $\omega$ ). These parameters for CF<sub>4</sub> and H<sub>2</sub>O are given in Table 4.5, together with the parameters for NaCl that will be treated in section 4.2.4.

Table 4.5:	The input parameters	for the Peng-Rob	oinson equation of sta	te [27,
34]				
component	p <sub>c</sub> [MPa]	T <sub>c</sub> [K]	ω [-]	
CF.	3.74	227.6	0.177	
H <sub>2</sub> O	22.12	647.3	0.344	
NaCl	26	3873	-0.294	

The modelling was similar as the procedure applied for APACT. All calculations with the PR equation of state were performed as flash calculations.

First the binary interaction parameter  $k_{ij}$  was optimized for a number of different pressures, by minimizing the % AAD in the CF<sub>4</sub> composition (x<sub>1</sub>). Next the optimized binary interaction parameters  $k_{ij}^{opt}$ , for the different pressures, have been averaged. The average binary interaction parameter equals,  $k_{ij}^{avg} = 0.222$ . With this average binary interaction parameter  $k_{ij}^{avg}$ , the entire system was remodelled. These results are presented in Table 4.6. Graphical presentations are shown in Figures 4.21 to 4.23, for pressures of 40, 100, and 200 MPa.

These Figures show an acceptable agreement between the experimental data and the values predicted with the PR equation of state. The fact that the results are obtained with one average value for the binary interaction parameter, illustrates that the PR equation of state performs much better for this system than APACT, in the composition range and at the conditions investigated.



Figure 4.21: Results of binary flash calculations in the Peng-Robinson (PR) equation of state, with an average value of 0.222 for the binary interaction parameter ( $k_{ij}^{avg}$ ) at 40 MPa



Figure 4.22: Results of binary flash calculations in the Peng-Robinson (PR) equation of state, with an average value of 0.222 for the binary interaction parameter ( $k_{ii}^{avg}$ ) at 100 MPa

Table 4.	6: Opti	mization of the	e binary interacti	on parameter k	ij
p [MPa]	N	K <sub>ij</sub> opt	% AAD in x <sub>1</sub> with k <sub>ij</sub> <sup>opt</sup>	% AAD in x <sub>1</sub> with k <sub>ij</sub> <sup>avg</sup>	% AAD in x <sub>2</sub> with k <sub>ij</sub> <sup>avg</sup>
40	9	0.197	9.930	9.322	0.429
60	10	0.210	5.936	6.934	0.289
80	10	0.210	5.337	5.749	0.232
100	9	0.221	4.557	4.581	0.200
120	9	0.223	4.311	4.345	0.176
140	9	0.228	4.213	4.508	0.169
160	9	0.230	4.421	5.113	0.182
180	9	0.238	4.244	5.759	0.200
200	9	0.240	5.414	7.639	0.288

# 4.2.4. Modelling of the system $CF_4 - H_2O - NaCl$ with the Peng-Robinson equation of state

Since APACT could not describe the  $CF_4 - H_2O$  system adequately, it was not attempted to model the ternary  $CF_4 - H_2O$  - NaCl system with APACT. The PR equation of state, however, could be used to describe the  $CF_4 - H_2O$  system. Therefore, it was attempted to model the  $CF_4 - H_2O$  - NaCl system with the PR equation of state.

First the three input parameters for NaCl had to be found. *Bischoff and Pitzer* [34] estimated the critical pressure and temperature to be 26 MPa and 3873 K. The acentric factor had to be calculated using:

$$\omega = -\log p_{VP_r}(T_r = 0.7) - 1.000 \tag{4.3}$$

*Barton and Bloom* [35] correlated the vapor pressure of NaCl in the temperature range from 1250 to 1740 K, in the following way:

$$\log p_{VP} = -11495 \cdot T^{-1} - 3.526 \cdot \log T + 20929 \tag{4.4}$$

Applying equation 4.4 to a temperature of 2711 K ( $0.7 \cdot T_c$ ), the value for the vapor pressure of NaCl was 5.11 MPa. Even though the temperature is out of the region of



Figure 4.23: Results of binary flash calculations in the Peng-Robinson (PR) equation of state, with an average value of 0.222 for the binary interaction parameter ( $k_{ij}^{avg}$ ) at 200 MPa

correlation, an extrapolation was used to determine an estimation for the vapor pressure of NaCI. The above mentioned procedure resulted in a value for the acentric factor of,  $\omega$ =-0.294. This value must be regarded as an estimation with a large degree of uncertainty.

For the modelling, the same procedure as described before was performed. The calculations were performed as flash calculations. All data points at 40, 60, 80, 100, 120, 160, and 200 MPa were optimized simultaneously. The optimum  $CF_4 - H_2O$  interaction parameter was 0.222. The binary interaction parameters for  $CF_4$  - NaCl ( $k_{13}$ ) and  $H_2O$  - NaCl ( $k_{23}$ ) were optimized. The optimized values for the binary interaction parameters were:

 $k_{12} = 0.222$  $k_{13} = 0.200$  $k_{23} = -0.300$ 

A more negative value for  $k_{23}$  and a more positive value for  $k_{13}$ , increased the % AAD in the mole fractions. However, a less negative value for  $k_{23}$  and a less positive value for  $k_{13}$  resulted in convergence problems in the calculations.

The entire system was modelled with the three constant binary interaction parameters. This resulted in % AAD in the  $CF_4$ ,  $H_2O$  and NaCl mole fractions of 16.9, 0.420 and 1.012 %, respectively.

Figure 4.24 to 4.27 give graphical presentations of the modeled system. These figures show that the PR equation of state does not describe the ternary  $CF_4 - H_2O - NaCI$  system satisfactory. Especially the results at 80 MPa are poor. At 200 MPa only the 1.1 and 2.1 weight percent NaCI give reasonable results, but the 3.3 weight percent NaCI deviates significantly.



Figure 4.24: Results of ternary flash calculations in the Peng-Robinson (PR) equation of state, with a constant set of binary interaction parameters ( $k_{12} = 0.222$ ,  $k_{13} = 0.200$ , and  $k_{23} = -0.300$ ) at 80 MPa, for 0.5 and 2.1 weight percent NaCl



Figure 4.25: Results of ternary flash calculations in the Peng-Robinson (PR) equation of state, with a constant set of binary interaction parameters ( $k_{12} = 0.222$ ,  $k_{13} = 0.200$ , and  $k_{23} = -0.300$ ) at 80 MPa, for 1.1 and 3.3 weight percent NaCl



Figure 4.26: Results of ternary flash calculations in the Peng-Robinson (PR) equation of state, with a constant set of binary interaction parameters ( $k_{12} = 0.222$ ,  $k_{13} = 0.200$ , and  $k_{23} = -0.300$ ) at 200 MPa, for 2.1 weight percent NaCl



Figure 4.27: Results of ternary flash calculations in the Peng-Robinson (PR) equation of state, with a constant set of binary interaction parameters ( $k_{12} = 0.222$ ,  $k_{13} = 0.200$ , and  $k_{23} = -0.300$ ) at 200 MPa, for 1.1 and 3.3 weight percent NaCl

### 5. CONCLUSIONS AND RECOMMENDATIONS

The measurements were in general performed without serious problems.

The measurements of the  $CF_4$  -  $H_2O$  system gave accurate results.

With the measurements of the  $CCIF_3 - H_2O$  system problems were encountered, and consequently the results were not reliable. After measuring a few data points the vision deteriorated, which was caused by undesired reactions of the system. As  $CCIF_3$  is supposed to be stable in  $H_2O$  up to 773 K and 400 MPa, the reactions were probably due to impurities in the  $CCIF_3$ .

The measurements of the  $CHF_3 - H_2O$  system provided good results. The immiscibility region is located at temperatures that are 100 K lower, with respect to the  $CF_4 - H_2O$  system. Therefore, the  $CHF_3 - H_2O$  system is well suited for future work. A larger composition range can be investigated before the experimental temperature boundary is exceeded.

As with the  $\rm CF_4$  -  $\rm H_2O$  system, the results for the  $\rm CF_4$  -  $\rm H_2O$  - NaCl measurements were accurate.

The Associated-Perturbed-Anisotropic-Chain Theory (APACT) can not be used to describe the experimental data of the  $CF_4$  -  $H_2O$  system with satisfactory accuracy.

The Peng-Robinson equation of state with a constant value for the binary interaction parameter gives satisfactory results for the  $CF_4 - H_2O$  system.

The  $CF_4 - H_2O$  - NaCl system was modelled using the Peng-Robinson equation of state with a constant set of binary interaction parameters. These calculations provided less satisfactory results than for the  $CF_4 - H_2O$  system.

# 6. REFERENCES

- Tedder, D.W., Pohland, F.G. (ed.), <u>Emerging Technologies in Hazardous</u> <u>Waste Management III</u>, ACS Symposium Series no. 518, American Chemical Society; Washington DC, 1993.
- 2. Tödheide, K., <u>Hydrothermal Solutions</u>, *Ber. Bunsenges. Phys. Chem.*, **86**, 1005(1982).
- 3. Franck, E.U., In Findenegg, G.H. (ed.), <u>Chemical Thermodynamics-III</u>, Baden bei Wien, Austria, 3-7 September 1973, p 456.
- 4. Shaw, R.W., Brill, T.B., Clifford, A.A., Eckert, C.A., Franck, E.U., <u>Super-critical Water, A Medium for Chemistry.</u>, <u>Special Report.</u>, *C&EN*, 23 December 1991, p 26-39.
- 5. Institut. International du Froid (org), <u>Les Actes de XVIII-e Congres Intern.</u> <u>du Froid</u> Montreal, 1991.
- Chapman, W.G., Gubbins, K.E., Jackson, G., Radosz, M., <u>SAFT: Equation-of-State Solution Model for Associating Fluids</u>, *Fluid Phase Equilibria*, **52**, 31(1989).
- 7. Huang, S.H., Radosz, M., <u>Equation of State for Small, Large, Polydisperse,</u> <u>and Associating Molecules</u>, *Ind. Eng. Chem. Res.*, **29**, 2284(1990).
- 8. Ikonomou, G.D., Donohue, M.D., <u>Thermodynamics of Hydrogen-Bonded</u> <u>Molecules: The Associated Perturbed Anisotropic Chain Theory</u>, *AIChE Journal*, **32**, 1716(1986).
- Economou, I.G., Donohue, M.D., <u>Equation of State with Multiple Associating</u> <u>Sites for Water and Water-Hydrocarbon Mixtures</u>, *Ind. Eng. Chem. Res.*, **31**, 2388(1992).
- Smits, P.J., Economou, I.G., Peters, C.J., de Swaan Arons, J., <u>Equation of State of Thermodynamic Properties of Near-critical and Supercritical Water</u>, *J. Phys. Chem.*, **98**, 12080(1994).
- 11. Smits, R.J.A., <u>High Pressure Phase Behavior of Binary Water Light</u> <u>Organic and Ternary Water - Light Organic - Salt Systems; a literature</u> <u>review, and a theoretical treatment of the salt effect</u>, December 1995.
- 12. van Konynenburg, P.H., Scott, R.L., <u>Critical Lines and Phase Equilibria in</u> <u>Binary van der Waals Mixtures</u>, *Phil. Trans. A*, **298**, 495(1980).
- Pelt, A van, <u>Critical Phenomena in Binary Fluid Mixtures; Classification of</u> <u>Phase Equilibria with the Simplified-Perturbed-Hard-Chain-Theory</u>, Dissertation, Rotterdam, 1992.

- Brunner, E., <u>Fluid Mixtures at High Pressures</u>; IX. Phase Separation and <u>Critical Phenomena in 23(n-alkane + water) mixtures</u>, J. Chem. Thermodynamics, **22**, 335(1990).
- 15. McGlashan, M.L., <u>Phase equilibria in fluid mixtures</u>, *J. Chem Thermodynamics*, **17**, 301(1985).
- Ikonomou, G.D., Donohue, M.D., <u>Extension of the Associated Perturbed</u> <u>Anisotropic Chain Theory to Mixtures with More Than One Associating</u> <u>Component</u>, *Fluid Phase Equillib.*, **39**, 129(1988).
- 17. Gubbins, K.E., Twu, G.H., <u>Thermodynamics of Polyatomic Fluid Mixtures-I</u> <u>Theory</u>, *Chem. Eng. Sci.*, **33**, 863 (1978).
- Donohue, M.D., Prausnitz, J.M., <u>Perturbed Hard Chain Theory for Fluid</u> <u>Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and</u> <u>Petroleum Technology</u>, *AIChE J.*, **24**, 849 (1978).
- 19. Heidemann, R.A., Prausnitz, J.M., <u>Van der Waals-type Equation of State for</u> <u>Fluids with Associating Molecules</u>, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 1773(1976).
- Wei, S., Shi, Z., Castleman Jr., A.W., <u>Mixed Cluster lons as a Structure Probe:</u> <u>Experimental Evidence for Clathrate Structure of (H<sub>2</sub>O)<sub>20</sub> H<sup>+</sup> and (H<sub>2</sub>O)<sub>21</sub> H<sup>+</sup>. J. Chem. Phys., **94**, 3268(1991).
  </u>
- 21. Vimalchand, P., Donohue, M.D., <u>Thermodynamics of Quadrupolar</u> <u>Molecules: The Perturbed-Anisotropic-Chain Theory</u>, *Ind. Eng. Chem. Fundam.*, **24**, 246(1985).
- 22. Vimalchand, P., Celmins, I., Donohue, M.D., <u>VLE Calculations for Mixtures</u> <u>Containing Multipolar Compounds Using the Perturbed Anisotropic Chain</u> Theory, *AIChE J.*, **32**, 1735(1986).
- 23. Barker, J.A., Henderson, D., <u>Perturbation Theory and Equation of State for</u> <u>Fluids. II. A successful Theory of Liquids</u>, *J. Chem. Phys*, **47**, 4714(1967).
- 24. Peng, D.Y., Robinson, D.B., <u>A New Two-Constant Equation of State</u>, *Ind. Eng. Chem., Fundam.*, **15(1)**, 59(1976).
- 25. Hagen, A.P., Elphingstone, E.A., <u>The High Pressure Hydrolysis of CFCl<sub>3</sub></u> and CF<sub>2</sub>Cl<sub>2</sub>, J. Inorg. Nucl. Chem., **36**, 509(1974).
- Ashton, J.T., Dawe, R.A., Miller, K.W., Smith, E.B., Stickings, B.J., <u>The</u> <u>Solubility of Certain Gaseous Fluorine Compounds in Water</u>, *J. Chem. Soc.* (A), 1793(1986).
- 27. Reid, R.C., Prausnitz, J.M., Poling, B.E., <u>The Properties of Gases and Liquids</u>, 4<sup>th</sup> Edition, McGraw-Hill Book Company, 1988.
- 28. Penders, W.G., <u>Gas-Gas-Ontmenging in het Systeem n-Hexaan Water</u>, stageverslag, 1980.

- 29. Dymond, J.H., Smith, E.B., <u>The Virial Coefficients of Pure Gases and</u> <u>Mixtures, A Critical Compilation</u>, Clarenden Press, Oxford, 1980.
- Prausnitz, J.M., Lichtenthaler, R.N., Gomes de Azevedo, E., <u>Molecular</u> <u>Thermodynamics of Fluid Phase Equilibria, 2e ed</u>, Prentice-Hall Inc., Englewood Cliffs, N.J. 07632, 1986.
- 31. Nesmeyanov, A.N. (ed.), <u>Vapor Pressure of the Chemical Elements</u>, Elsevier Publishing Company, Amsterdam/London/New York, 1963.
- 32. Lide, D.R. (ed.), Handbook of Chemistry and Physics, Boca Raton, 1995
- 33. 1993 ASHRAE Handbook fundamentals, S.I. Edition, Atlanta, 1993
- Bischoff, J.L., Pitzer, K.S., <u>Liquid-Vapor Relations for the System NaCl -</u> <u>H<sub>2</sub>O: Summary of the P-T-x Surface from 300° to 500°C</u>, *Am. J. Sci.*, 289, 217(1989).
- 35. Barton, J.L., Bloom, H., <u>A Boiling Point Method for Determination of Vapor</u> Pressures of Molten Salts, J. Phys. Chem., **60**, 1413(1956).

## 7. LIST OF SYMBOLS

Latin:

а	Attraction parameter	m <sup>6</sup> ·Pa·mole <sup>-2</sup>
a(T)	Attraction parameter	m <sup>6</sup> ·Pa·mole <sup>-2</sup>
В	Second virial coefficient	m³⋅mole <sup>-1</sup>
b	Van der Waals covolume	m³ •mole <sup>-1</sup>
b.p.	Boiling point	K
С	Third virial coefficient	m <sup>6</sup> ·mole <sup>-2</sup>
Ci	Constants, with j = 0, 1, 2, 3,	-
c	Shape factor	-
D	Fourth virial coefficient	m <sup>9</sup> ·mole⁻ <sup>3</sup>
f	Fugacity	Pa
fs	Saturation fugacity	Pa
ΔH°	Standard enthalpy of hydrogen bond formation	kJ•mole <sup>-1</sup>
К	Equilibrium constant for hydrogen bond formation	-
K <sub>NaCl</sub>	Mass ratio of NaCl to H <sub>2</sub> O	-
k	Boltzmann's constant	J⋅K-1
k <sub>ii</sub>	Binary interaction parameter	-
k <sub>ij</sub> <sup>avg</sup>	Averaged binary interaction parameter	-
k <sub>ii</sub> <sup>opt</sup>	Optimized binary interaction parameter	-
k <sub>12</sub>	Binary interaction parameter of $CF_4$ and $H_2O$	-
k <sub>13</sub>	Binary interaction parameter of CF <sub>4</sub> and NaCl	-
k <sub>23</sub>	Binary interaction parameter of H <sub>2</sub> O and NaCI	-
Μ	Mass	g
M <sub>w</sub>	Molecular weight	g•mole <sup>-1</sup>
M <sup>calc</sup>	Calculated thermodynamic property	
$M^{exp}$	Experimental thermodynamic property	
m	Predetermined mass	g
m.p.	Melting point	K
Ν	Number of data points	-
N <sub>A</sub>	Avogadro's number	mole <sup>-1</sup>
n	Number of moles	mole
р	Pressure	Pa
Patmospheric	Atmospheric pressure	MPa
Pcorrected	Corrected pressure	MPa
$p_{Hg}$	Pressure contribution due to mercury	Pa

List of symbols

D	Measured pressure	bar
D <sub>1</sub>	Gas pressure during filling	mbar
p2	Transformed pressure	Pa
D <sub>VD</sub>	Vapor pressure	mm Hg
p <sup>s</sup>	Saturation pressure	Pa
p <sup>sat</sup>	Saturation pressure	bar
Δp	Pressure deviation on the gas rack	mbar
q	Normalized surface area per molecule (relative to the	
,	surface area of sphere of the size of a segment)	-
R	Universal gas constant	J·mole <sup>-1</sup> ·K <sup>-1</sup>
R.	Resistance on the resistance bridge	Ω
R <sub>o</sub>	Resistance at 0 °C	Ω
r	Number of segments per molecule	-
ΔS <sup>o</sup>	Standard entropy of hydrogen bond formation	J·mole <sup>-1</sup> ·K <sup>-1</sup>
Т	Temperature	К
Tmassured	Measured temperature	K
T*	Characteristic energy parameter	K
t	Temperature	°C
V	Volume	m³
V	Molar volume	m³ •mole <sup>-1</sup>
$v^{i}$	Liquid molar volume	m <sup>3</sup> ·mole <sup>-1</sup>
V <sup>liq</sup>	Liquid molar volume	cm³ •mole <sup>-1</sup>
v	Characteristic size parameter	cm³ •mole <sup>-1</sup>
wt%	Weight percent of NaCl	%
Х	Mole fraction	-
Z	Compressibility factor	-
Z <sup>ani</sup>	Compressibility factor due to anisotropic attraction	-
Z <sup>assoc</sup>	Compressibility factor due to association	-
Z <sup>attr</sup>	Compressibility factor due to attraction	-
Z <sup>lj</sup>	Compressibility factor due to Lennard-Jones attraction	
Z <sup>rep</sup>	Compressibility factor due to repulsion	-
$Z^{\mu \text{ ind } \mu}$	Compressibility factor due to dipole - induced dipole attra	action -
%AAD	Percentage Absolute Average Deviation	%

Greek:

α	Polarizibility	ų
$\alpha(\top_{r},\omega)$	Scaling factor	-
E	Dielectric constant	-
e	Caracteristic energy per unit surface area of a molecule	J∙m²
μ	Dipole moment	Debye
ρ	Density	kg •m⁻³
$ ho_{i}$	Density of component i	g∙ml⁻¹
σ	Soft-core diameter of a segment	m
$\phi^{s}$	Fugacity coefficient	-
ω	Acentric factor	-

Subscripts:

С	Critical property
i	Component identification
j	Component identification
r	Reduced property

# APPENDIX A

Table A.1: Experimental results for the system CF <sub>4</sub> - H <sub>2</sub> O									
p [MPa]	Т [К]	p [MPa]	Т [К]	p [MPa]	T[K]	p [MPa]	T [K]		
			× <sub>CF4</sub> =0	.0121					
80.05	587.19	60.04	590.80	45.04	598.23	30.01	619.38		
70.05	588.97	55.04	592.38	40.03	602.88				
65.05	589.50	50.04	594.87	35.03	608.72				
			× <sub>cf4</sub> =0	.0160					
199.99	605.65	100.02	599.85	60.03	603.27	34.20	623.15		
180.00	604.15	90.03	599.53	55.03	604.92	29.99	630.69		
160.00	602.76	80.03	599.73	50.03	607.10				
140.01	601.60	70.03	600.64	45.02	610.54				
120.02	600.70	65.03	601.94	40.02	614.74				
			X <sub>CE4</sub> =C	0.0172					
199.97	614.63	100.01	606.99	42.21	619.73	31.87	638.17		
179.98	613.09	80.02	606.11	40.00	621.61	29.76	643.29		
159.99	611.59	63.32	609.34	39.10	623.67	25.76	647.08		
140.00	609.77	60.02	610.73	37.19	628.07				
120.01	607.95	50.71	614.15	34.58	632.97				
			x <sub>cr4</sub> =0	0.0222		2			
			014						
199.94	623.77	139.98	616.65	80.01	614.37	39.99	626.97		
179.96	620.75	119.99	614.86	60.01	617.82	34.98	632.97		
159.97	618.36	100.00	614.53	50.00	620.98	29.97	641.54		
			×=(	0249					
			ACE4						
199.91	633.80	119.97	624.00	69.99	622.86	44.99	628.87		
179.93	631.14	99.98	622.23	59.99	624.23	39.98	632.40		
159.95	628.60	89.99	621.83	54.99	625.29	34.98	636.87		
139.96	626.20	79.99	622.06	49.99	626.51	29.97	642.14		

Appendix A

Table A	.1 - contin	ued					
p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]	T[K]	p [MPa]	T [K]
			× <sub>CF4</sub> =0	.0274			
199.89	641.31	119.96	628.43	49.98	631.17	27.96	643.98
179.91	636.52	99.98	626.77	39.98	634.33		
159.93	633.28	79.98	627.23	34.97	637.98		
139.95	630.68	59.98	628.66	29.96	643.06		
			× -0	0224			
			X <sub>CF4</sub> =U	0.0324			
199.86	647.89	119.95	635.15	59.98	632.14	39.97	638.16
179.89	644.44	99.96	633.15	54.98	632.89	34.97	641.23
159.91	641.34	79.97	631.43	49.98	634.12	28.46 <sup>ср</sup>	644.21
139.93	638.10	69.98	631.29	44.97	635.78		
			× <sub>cf4</sub> =0	0.0366			
100.82	654 27	120.01	642.67	70.06	637 30	29.96	643 87
199.03	650.82	139.91	641.00	59.90	637.01	26.45	647 47
159.89	647.00	99.95	638.64	39.97	640.14	20.40	017.17
				0.440			
			X <sub>CF4</sub> =(	).0442			
199.80	662.45	99.93	643.87	54.96	640.25	31.56	643.44
179.83	658.52	79.95	641.34	49.96	640.62	29.96 <sup>cp</sup>	643.92
159.86	654.57	69.95	640.39	44.96	641.34		
139.89	650.85	64.96	640.22	39.96	642.12		
119.91	647.32	59.96	640.08	34.96	642.95		
			Х <sub>СЕ4</sub> =(	0.0583			
			014				
199.77	669.24	139.87	656.33	79.94	644.70	39.96	643.18
179.78	664.85	119.89	652.29	59.95	642.58	34.96	643.58
159.84	660.48	99.92	648.12	49.96	642.40	29.96	644.20

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## APPENDIX B

Table B.1: Experimental results for the system CCIF <sub>3</sub> - H <sub>2</sub> O									
p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]	T[K]	p [MPa]	T [K]		
			× <sub>CCIF3</sub> =	0.0306					
45.01	615.63	40.01	619.04	35.00	625.26				
			X <sub>CCIF3</sub> =	0.0320			*		
80.01	611.28	70.01	611.99	50.01	614.03				

Table B.2: Experimental results for the system CHF <sub>3</sub> - H <sub>2</sub> O									
p [MPa]	T [K]	p [MPa]	Т [К]	p [MPa]	T[K]	p [MPa]	T [K]		
			X <sub>CHF3</sub> =(	0.0499					
200.08 180.08	496.61 497.79	100.09 90.09	507.48 510.09	60.09 55.09	523.35 526.30	40.08 37.98	545.13 550.90		
160.09 140.09 120.09	499.05 501.11 503.63	80.09 70.09 65.09	513.36 517.36 520.56	50.09 46.69 42.78	531.26 535.16 540.91	34.08 33.07	559.18 565.28		

# APPENDIX C

Table C.1: Experimental results for the system  $CF_4 - H_2O - NaCl$ , with 0.5 weight percent NaCl

p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]	T[K]	p [MPa]	T [K]
			x <sub>CF4</sub> = x <sub>NaCI</sub> =	0.0198 0.0015			
100.01 80.01	611.30 612.91	60.01 50.01	615.68 619.50	39.99 34.98	626.66 633.55	29.96	644.81

# Table C.2: Experimental results for the system $H_2O - CF_4 - NaCl$ , with 1.1 weight percent NaCl

p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]	T[K]	p [MPa]	T [K]
				0470			
			$X_{CF4} = 0$	0.0176			
			X <sub>NaCI</sub> =U	).0032			
199.96	616.82	139.99	611.64	90.01	610.37	65.01	613.52
179.97	614.89	120.02	610.25	80.01	610.99		
159.98	613.07	100.01	609.88	70.01	612.38		
			X <sub>CF4</sub> =(	0.0234			
			X <sub>NaCl</sub> =(	0.0032			
100.00	636 18	130.05	628 88	89 98	625 69	64 98	628 34
170 02	633.55	119 97	627.06	79.98	626.40	0 1.00	020101
159.94	631.20	99.96	625.89	69.98	627.54		
			×=(	0 0325			
			×CF4	0.0020			
			^NaCl	0.0002			
199.85	651.60	119.93	640.37	64.96	637.93	44.95	644.01
179.87	648.70	99.94	638.70	59.96	638.62		
159.89	645.53	79.96	637.24	54.96	639.85		
139.91	642.58	69.96	637.13	49.96	641.43		
Appendix C

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p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]	T[K]	p [MPa]	T [K]
				0472			
			X <sub>CF4</sub> = l	J.0173			
			X <sub>NaCI</sub> =(	0.0064			
199.95	621.02	119.99	615.20	70.00	618.33	49.99	625.66
179.96	619.18	100.00	614.86	65.00	619.27	44.99	629.77
159.97	617.53	90.00	615.57	60.00	620.38	39.98	636.15
139.98	616.19	80.00	616.88	55.00	622.75	34.94	649.88
			X <sub>CE4</sub> =(	0.0234			
			X <sub>NaCI</sub> =(	0.0063			
199 88	642.89	119.95	633.66	69.97	633.95	49.96	640.65
179.90	639.96	99.96	632.60	64.97	634.98	44.95	644.27
159.92	637.33	89.97	632.23	59.97	636.21	39.94	650.20
139.94	635.03	79.97	632.74	54.96	638.21	37.13	655.03
			X <sub>CF4</sub> =	0.0325			
			X <sub>NaCI</sub> =	0.0063			
199.80	661.18	139.88	652.03	89.93	647.00	69.93	648.75
179.83	657.91	119.90	649.39	79.93	646.86	59.93	650.82
159.86	654.94	99.92	647.69	74.93	647.66		

Table C.3: Experimental results for the system  $H_2O - CF_4 - NaCl$ , with 2.1 weight percent NaCl

p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]	T[K]	p [MPa]	T [K]
			x =(	0076			
			X <sub>CF4</sub> =(	0.0103			
80.05	585.81	60.05	590.55	50.04	598.06	40.03	605.85
65.05	588.94	55.04	594.30	45.03	601.52		
			×=(	0180			
			× <sub>CF4</sub> × <sub>NaCl</sub> =(	0.0102			
199.94	623.75	119.98	619.18	64.99	623.63	44.98	635.38
179.95	622.23	99.99	619.27	59.99	625.60	39.96	643.87
159.97	621.04	79.99	620.61	54.99	628.03	35.92	658.32
139.98	619.98	69.99	622.23	49.98	631.17		
				0000			
			X <sub>CF4</sub> =(	0.0233			
			X <sub>NaCI</sub> -V	5.0101			
199.86	647.37	119.94	638.19	70.96	639.45	49.94	648.11
179.89	644.47	99.95	637.30	64.95	641.25	44.93	653.19
159.91	642.00	90.95	637.27	59.95	642.95	40.41	661.67
139.92	639.85	80.95	638.27	54.95	645.22		
			X <sub>CF4</sub> =(	0.0335			
			X <sub>NaCI</sub> =(	0.0100			
199.78	663.31	99.90	651.92	79.92	650.13	59.92	654.34
159.84 119.88	657.91 653.68	89.91	650.94	69.92	651.40	49.91	659.59

## Table C.4: Experimental results for the system $H_2O - CF_4 - NaCl$ , with 3.3 weight percent NaCl

## APPENDIX D

The experimental liquid density and vapor pressure data for  $CF_4$ , that were used in the determination of the pure component parameters of PACT, are given in Table D.1 and D.2.

Table D.1: Experimental liquid density data [32]			
T [K]	p [bar]	V [l/gmole]	
122 15	0 39440	0.0518286	
100.10	0.39440	0.0521511	
135.15	0.40740	0.0524808	
137.15	0.55080	0.0524808	
139.15	0.64560	0.0528148	
141.15	0.75280	0.0531592	
143.15	0.87370	0.0535115	
145.21	1.01320	0.0538817	
145.15	1.00930	0.0538718	
147.15	1.16070	0.0542404	
149.15	1.32930	0.0546174	
151.15	1.51620	0.0550066	
153.15	1.72270	0.0554048	
154.15	1.83380	0.0556043	
155.15	1.95010	0.0558124	
156.15	2.07210	0.0560185	
157.15	2.19980	0.0562332	
158.15	2.33330	0.0564460	
159.15	2.47290	0.0566641	
160.15	2.61880	0.0568838	
161.15	2.77100	0.0571090	
162.15	2.92980	0.0573360	
163.15	3.09530	0.0575648	
164.15	3.26770	0.0577992	
165.15	3.44720	0.0580355	
166.15	3.63400	0.0582776	
167.15	3.82820	0.0585217	
168.15	4.03000	0.0587719	
169.15	4,23960	0.0590241	
170.15	4.45720	0.0592826	
171 15	4 68290	0.0595433	
172 15	4 91690	0.0598104	
173 15	5 15940	0.0600840	
174 15	5 41060	0.0603601	
174.10	0.41000	0.0000001	

T [K]   p [bar]   V [l/gmole]     175.15   5.67070   0.0606387     176.15   5.93980   0.0609242     177.15   6.21810   0.0612166     178.15   6.50580   0.0615118     179.15   6.80310   0.0618143     180.15   7.11020   0.0621241     181.15   7.42730   0.0627621     183.15   8.09200   0.0630905     184.15   8.44010   0.0634270     185.15   8.79890   0.0637671
175.155.670700.0606387176.155.939800.0609242177.156.218100.0612166178.156.505800.0615118179.156.803100.0618143180.157.110200.0621241181.157.427300.0624415182.157.754500.0627621183.158.092000.0630905184.158.440100.0634270185.158.798900.0637671
175.155.670700.0600337176.155.939800.0609242177.156.218100.0612166178.156.505800.0615118179.156.803100.0618143180.157.110200.0621241181.157.427300.0624415182.157.754500.0627621183.158.092000.0630905184.158.440100.0634270185.158.798900.0637671
176.155.939800.0609242177.156.218100.0612166178.156.505800.0615118179.156.803100.0618143180.157.110200.0621241181.157.427300.0624415182.157.754500.0627621183.158.092000.0630905184.158.440100.0634270185.158.798900.0637671
177.156.218100.0612166178.156.505800.0615118179.156.803100.0618143180.157.110200.0621241181.157.427300.0624415182.157.754500.0627621183.158.092000.0630905184.158.440100.0634270185.158.798900.0637671
178.156.505800.0615118179.156.803100.0618143180.157.110200.0621241181.157.427300.0624415182.157.754500.0627621183.158.092000.0630905184.158.440100.0634270185.158.798900.0637671
179.156.803100.0618143180.157.110200.0621241181.157.427300.0624415182.157.754500.0627621183.158.092000.0630905184.158.440100.0634270185.158.798900.0637671
180.157.110200.0621241181.157.427300.0624415182.157.754500.0627621183.158.092000.0630905184.158.440100.0634270185.158.798900.0637671
181.157.427300.0624415182.157.754500.0627621183.158.092000.0630905184.158.440100.0634270185.158.798900.0637671
182.15   7.75450   0.0627621     183.15   8.09200   0.0630905     184.15   8.44010   0.0634270     185.15   8.79890   0.0637671
183.15   8.09200   0.0630905     184.15   8.44010   0.0634270     185.15   8.79890   0.0637671
184.15 8.44010 0.0634270   185.15 8.79890 0.0637671
185 15 8 79890 0 0637671
0.1000
186.15 9.16870 0.0641202
187.15 9.54950 0.0644772
188.15 9.94170 0.0648431
189.15 10.34500 0.065222
190.15 10.76100 0.065606
191.15 11.18800 0.0660004
192.15 11.62800 0.0664038
193.15 12.08000 0.0668223
195.15 13.02100 0.0676857
197.15 14.01500 0.0686038
199.15 15.06300 0.0695802
201.15 16.16700 0.0706187
203.15 17.33000 0.0717354
205.15 18.55300 0.0729363
207.15 19.83900 0.0742408
209.15 21.19100 0.0756642
211.15 22.61300 0.0772312
213.15 24.10700 0.0789849
215.15 25.67700 0.0809614
217.15 27.32900 0.0832513
219.15 29.06800 0.0859592
221.15 30.90100 0.0892908
223.15 32.83500 0.0936921
225.15 34.88100 0.1002792
227.15 37.05500 0.1163779
227.50 37.45000 0.1406505

## Appendix D

Table D.2: Experimental vapor pressure data [31]			
Т [К]	p <sub>vP</sub> [bar]		
	0.001		
90	0.001		
95	0.003		
100	0.008		
105	0.017		
110	0.034		
115	0.065		
120	0.115		
125	0.193		
130	0.308		
135	0.474		
140	0.702		
145	1.01		
150	1.41		
155	1.91		
160	2.54		
165	3.32		
170	4.25		
175	5.37		
180	6.69		
185	8.24		
190	10.05		
195	12.16		
200	14.60		
205	17.43		
210	20.73		
215	24.57		
220	29.07		
225	34.38		