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Measurement and Modeling of the Water Content of High Pressure Sweet and Acid Natural Gas Systems

by

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ABSTRACT

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This project culminated in the development of a new flow method and device for measuring the water contents of high pressure gases. This new flow method uses both an electrical resistance sensor and/or a chemical desiccant method to measure the water contents of methane, ethane and methane + carbon dioxide and ethane + carbon dioxide gas mixtures from 3.4 MPa to 110 MPa over a temperature range from 310 to 477 K. The resulting measurements have reduced uncertainty in the binary experimental results to between 2 to 7 percent, and give ternary results with an uncertainty between 5 and 14 percent.

The new experimental data are modeled using a hybrid method which combines the Peng-Robinson equation of state to calculate vapor phase fugacity coefficients with a highly accurate equation of state to calculate the fugacity of water. Gas solubilities in the aqueous phase are calculated using a Henry’s law coefficient, while aqueous fugacities are calculated using the NIST/ASME equation of state for water, while the effects of salts are incorporated using Pitzer correlations for the activity of brines. The new model is able to predict ternary
phase equilibria using interaction parameters fit to binary data. This allows predictive phase behavior calculations to be made for multiple components.

The related system methanol + alkanes, where the alkane was a member of the homologous series propane to decane was modeled using the Statistical Associating Fluid Theory (SAFT) equation of state for both liquid-vapor (VLE) and liquid-liquid equilibria (LLE). It was shown that the PC and CK-SAFT equations of state were capable of representing the phase behavior to within a few percent (generally 1-4%) of the experimental data using binary interaction parameters that were weak linear functions of temperature and alkane molecular weight. The binary interaction parameters were fit to the VLE data and then applied to the LLE data with excellent results for the methanol + alkane systems from 1 to 150 MPa. For alkanes longer than octane, systematic deviation was observed.
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1. Introduction

Accurate knowledge of the equilibrium water content of hydrocarbon gas mixtures is of vital importance to the energy industry. This information is necessary in order to prevent problems in transporting hydrocarbons in pipelines, such as hydrates, to prevent or mitigate corrosion in pipelines and processing equipment and to dehydrate the hydrocarbon streams for further processing in gas plants and refineries.

As global demand for oil and gas climbs, it becomes economical to produce deeper, higher pressure reservoirs that often have high percentages of carbon dioxide, hydrogen sulfide or sulfur dioxide. Gases that have these components present are usually referred to as ‘acid’ or ‘sour’ gases. These components present special problems for the oil and gas industries, as they will react with water to form acids, which can attack pipeline materials. They can also have a dramatic effect on the overall water content of the lighter hydrocarbon vapor phase, causing large deviations from the observed pure hydrocarbon behavior. If the data is not available, the models can not be fit to reproduce this phase behavior, and the industry is left with calculations that do not provide the desired level of accuracy. Calculations made with these sorts of models can lead to expensive de-bottlenecking processes, substantial plant down time or even equipment failure due to corrosion.
Existing data in the open literature for gas phase water contents of hydrocarbon systems only extends to 70 MPa. New exploration frequently encounters reservoir pressures in excess of 70 MPa, and can often exceed 100 MPa.

There is also scant data on ternary acid gas mixtures, at any pressure, let alone high pressure. It is the goal of the experimental section of this work to fill these gaps by extending water content data for pure methane, pure ethane and methane + carbon dioxide, ethane + carbon dioxide mixtures to 110 MPa over a temperature range from 300 to 477 K.

In addition to the experimental portion of this work, a new model has been developed that is capable of modeling not only the water content of the supercritical light hydrocarbon phase (known in industrial parlance as the ‘vapor’ phase) but also the gas content of the aqueous phase that is in equilibrium with the hydrocarbon phase. The model accurately predicts the changes of both phases due to due to compositional, pressure and salt effects.

As part of the development of an improved model, the SAFT equation of state was investigated as a potential candidate for dealing with these high pressure situations using the methanol + alkanes systems as a starting point.

The thesis is laid out in 9 chapters. Chapter 2 reviews the relevant literature for the experimental data and the models used in this thesis. In chapter 3 the modeling results with the CK-SAFT and PC-SAFT equations of state are presented. Chapter 4. presents the design, construction and operating
procedures of the experimental device. Chapter 5 details the experimental results. Chapter 6 describes the model, and how fugacities are calculated for both the liquid and vapor phases in the model. Chapter 7 presents the model results. Chapter 8 concludes the work, and in chapter 9 we propose some extensions for future work.
2. Literature Review

Experimental Literature

As early as 1888, Villiard\textsuperscript{1,2} noted that water and methane can combine to form an ice-like structure that is stable at temperatures above the normal freezing point of water. Scheffer\textsuperscript{3} (1913) performed the first studies of pressure, volume and temperature (PVT) relationships between water and hydrocarbons; he studied the water-pentane and water-hexane systems. These studies were limited in scope to conditions slightly above the room temperature vapor pressure of the pure hydrocarbons. However, Scheffer did discover the three-phase critical point, where the vapor phase and the lighter liquid phase have the same intensive properties.

Despite these warning flags that water and the light hydrocarbons have unusual properties that needed closer experimental and theoretical investigation, it was not until the early 1920’s that the first large scale experimental studies of water+ hydrocarbon equilibria were undertaken.

Bartlett\textsuperscript{4} measured the solubility of water in nitrogen and hydrogen. His is one of the first studies of compressed gas systems. For his investigation, two stainless steel cells were used in series. Gas flowed into the first cell, through a glass bead dispersion/anti-entrainment section and into a second saturation cell to ensure complete saturation. Bartlett’s analysis train consisted of a desiccant charged tube, a receiving bottle and several evacuated glass jars sealed with
septa. The amount of water was determined by weighing the desiccant charged tubes, while the volume of gas was determined by weighing the evacuated bottles after the run.

Clifford\textsuperscript{5, 6} used U-tubes packed with desiccant to measure the water content of gasoline. Repeated measurements of a 0.7 specific gravity gasoline at the same temperature and pressure showed a 25\% difference in the water content. Unfortunately, Clifford gives few details on the composition of the gasoline or the experimental method used to saturate the gasoline, so that the reason for the variance in the readings remains a mystery. However, Clifford’s idea of using a desiccant from a liquid hydrocarbon is novel because it allows a fast, easy way of removing water without having to worry about ‘freezing’ out the heavier hydrocarbons.

Hammerschmidt\textsuperscript{7} published some of the first systematic work on hydrate formation in natural gas pipelines. He showed that the water content of the natural gas was dramatically different than what would be expected using merely ideal gas behavior. It was not until the late 1930’s and early 1940’s that the solubility of water in the light hydrocarbons that make up natural gases was investigated over the broad range of reservoir conditions.

Olds et al.\textsuperscript{8} used a quasi-static type high pressure sampling technique to investigate the water content of methane gas from 1.3 MPa to 64.5 MPa from 310 to 510 K. Mercury from a pressure reservoir was pumped into the cell and used as a “confining fluid” to maintain the pressure in the containing cell while the
gas phase sample was withdrawn. The cell contents were mixed by means of a magnetically driven agitator in the containing cell. Olds et al. used gravimetric measurements for both the water removed from the gas phase and the mass of methane used during the experiment.

Reamer et al.\textsuperscript{9} used the same apparatus to measure the water content of ethane gases. The volume of dried gas was ascertained using an evacuated glass vessel of known volume immersed in a constant temperature oil bath. The change in pressure was noted as gas was introduced, and the moles of gas calculated using the tabulated compressibility of the gas.

The data of Olds et al. and Reamer et al. established some of the fundamental pressure and temperature relationships and provided some of the first accurate high pressure water content charts. Unfortunately, no form of useful model was developed at this time.

Wiebe and Gaddy\textsuperscript{10} measured the water content of pure carbon dioxide and the carbon dioxide content of water from 298 to 373 K at pressures from 0.1 to 65 MPa. Their apparatus used a quasi-static system, in which two stainless steel sample bombs were placed in a temperature controlled heat bath, with one serving as a pressure reservoir, and the other serving as the phase equilibration cell. The equilibration cell had the upper compartment packed with glass beads to prevent water spray. Three other cells, maintained at temperatures near 273 K, were employed to compress the gaseous carbon dioxide to the desired pressures and maintain cell pressure during an experiment. The effluent from the
sample cell was passed into a packed absorbent column "identical to that of Bartlett". Although this technique appears to have produced reasonable data, the phase equilibrium cell did not possess any sort of device for dispersing the entering carbon dioxide into the water. Not having a dispersion frit could create a non-equilibrium situation where the water content is slightly under that of the true equilibrium, because the gas would have had insufficient contact time to ensure complete saturation.

The investigations of Olds et al. and Reamer et al. used a liquid phase that had no dissolved ionic species. As any geochemist worth her salt will note, reservoirs with pure water are extremely rare. It is much more common for the reservoir to have an aqueous liquid phase with dissolved salts (known as a "brine"). Dodson and Standing carried out investigations of the solubility of natural gases in brines, where the aqueous phase contained up to 35,000 ppm of dissolved salts, and also the solubility of pure water in the natural gas phase from 0.1 to 34 MPa and from 310 to 394 K. They used an apparatus that was similar to that of Olds et al. in that a quantity of sample (either gas or aqueous liquid) was removed and the pressure in the cell kept constant using mercury from a pressure reservoir. Unlike the investigations of Olds et al. and Reamer et al. a chemical desiccant was used to remove the water from the expanded gas streams. The gas dissolved in the water or brine phase was measured by collecting the aqueous sample in a glass trap at ambient pressure. The quantity of water was determined by weighing the trap before and after ‘flashing’ the sample
to remove the gas. The gas was collected into a burette to determine the volume of flashed gas at a controlled temperature.

Reamer et al.\textsuperscript{12} investigated the phase behavior of the n-butane water system in the three phase region from 304 to 425 K, from 0.35 to 4.4 MPa. Reamer used a similar apparatus to that of Olds et al. except the measurement method was changed from the evacuated cold trap to a calcium chloride desiccant in order to avoid problems with condensing the butane along with the water. Gas phase samples were taken in the usual manner of using mercury to reduce the cell volume while the gas phase sample was throttled to ambient pressure and passed through the desiccant drying tube. In order to sample the lighter liquid phase, the gas phase had to be eliminated by increasing the pressure about 0.15 MPa above the 3 phase pressure. The assumption here is that the increased pressure did not appreciably change the composition of the lighter liquid phase. This sampling procedure is a bit suspect; without some form of visual observation, it is nearly impossible to determine if the entire ‘gas’ phase was condensed, and could lead to experimental errors. The lighter liquid sample was dehydrated in the same fashion as the gas phase samples. The composition of the water rich phase was not determined.

Skinner\textsuperscript{13} investigated the colder end of the water content spectrum, examining the water content of natural gas at temperatures below the hydrate formation temperatures. Skinner’s investigations used temperatures ranging from 222 to 294 K and pressures between 0.21 and 13.78 MPa. The apparatus
used a desiccant weight change method to determine the mass of water present in the natural gas stream. Gas volume was measured using a wet-test flow meter, a device normally used for calibrating other instruments. The natural gas used was taken directly from the Oklahoma Natural Gas Co. pipeline, with only a gas gravity (1.0 is the 'gravity' of air) of 0.7 listed for the composition. No detailed analysis of gas composition was made or attempted, which is unfortunate, as it does not facilitate comparison to the gas compositions of other researchers. The pressure was also not held constant, but slowly declined during Skinners investigations, which introduces more uncertainty into the measurements.

Deaton and Frost\textsuperscript{14} determined the water solubility of two different compositions of natural gas, at pressures ranging from 0.43 to 4.23 MPa, and at temperatures between 277 and 310 K. Instead of a cold trap or a desiccant, they chose a dynamic dew-point method for analysis. This type of measurement is completely independent of mass, and instead relies on visual observation of the temperature at which a condensed phase (liquid or solid) forms on the chilled mirror portion of a dew point testing apparatus. Unfortunately, detecting the presence of a condensed phase on the chilled mirror relied on operator experience so some error could be introduced into the measurements.

In Deaton and Frost's experiments, natural gas was saturated with water in a pressure cell immersed in a temperature-controlled bath. Saturated gas flowed out of the cell to a secondary pressure regulator, which reduced the
pressure to approximately atmospheric pressure, and then flowed into the
dew/frost point testing apparatus. Water content was determined by relating the
dew/frost point of the gas to the vapor pressure of liquid water or ice, depending
on which phase was present in the dew point tester. They found that gas
composition plays an important role in the equilibrium water content of natural
gases.

Expanding the species used in water content investigations, McKetta and
Katz\textsuperscript{15} investigated the equilibrium compositions of Methane + n-Butane + water
at temperatures between 310 and 411 K and pressures up to 20.68 MPa. Like
many other investigations, a static pressure cell was used to contain the system
and mercury was pumped into the static cell to maintain the pressure when
samples were withdrawn. Unlike previous investigations, three sampling ports
were provided so that the gas, lighter hydrocarbon rich liquid and heavier water
rich liquid could be sampled. A desiccant weight change method was used to
measure the water content in the hydrocarbon rich samples, and to measure the
volume of gas in the aqueous liquid sample. A visual observation window also
allowed investigators to see where the liquid-liquid and vapor liquid interfaces
were in the cell. McKetta and Katz investigated both the hydrocarbon rich liquid
and the water rich liquid to give a more complete picture of the phase behavior of
this ternary system.
Brooks et al.\textsuperscript{16} reported data for the n-butane-water system between 310 and 377 K and pressures up to 69 MPa. Again, the mass change of a desiccant packed tube was used to determine the water content of the vapor phase.

Kobayashi and Katz\textsuperscript{17} presented results for the propane-water system for pressures from 0.68 to 19.30 MPa and temperatures between 285 and 422 MPa. Measurements for both liquid phases were taken, and a thermodynamic analysis conducted for both the liquid and vapor phases. Kobayashi and Katz were the first to present a rigorous thermodynamic analysis to correlate the water content as a function of pressure and temperature for hydrocarbon + water mixtures.

Leland, McKetta and Kobe\textsuperscript{18} combined the results of Brooks et al. and filled in additional data points for the 1-butene-water system, covering pressures from 6.89 to 68.94 MPa and temperatures up to 427 K. However, Leland et al. did present some thermodynamic predictions of solubility based entirely on pure component properties and sound thermodynamics. The predictions performed well at lower pressures, but were in error at higher pressures, presumably because the theories were fit to lower density (and therefore lower pressure) data.

Bukacheck\textsuperscript{19} investigated the equilibrium moisture content of natural gas at 377 K and pressures between 6.89 and 68.9 MPa. The analytical method employed was a barium oxide desiccant to remove the water from the expanded gas using an apparatus that was similar to that of Olds et al. The results showed
that composition of the natural gas may be a factor in its equilibrium water content. A correlation was presented, but it did not explicitly take into account composition and was simply a Raoult's law type correlation with an additional parameter to correct for deviations from ideality due to composition. The correlation has been found to be in severe error at temperatures above 377 K.

Brooks, Haughn and McKetta\textsuperscript{20} reported equilibrium data for the 1-butene-water system at pressures up to 6.89 MPa and temperatures between 310 and 217 K. These investigations provided data on the solubility of 1-butene in the water rich phase, water in the 1-butene rich phase and vapor composition in equilibrium with the water rich phase.

Culberson et al.\textsuperscript{21-24} reported the solubility of methane and ethane in water at pressures up to 70 MPa using the standard technique of withdrawing a sample of the liquid phase into a large volume burette and measuring the volume of gas eluted from a given volume of water.

Selleck et al.\textsuperscript{25} measured the mutual solubilities of hydrogen sulfide and water from temperatures between 310 to 444 K and pressures from 0.1 to 34 MPa. The water content was measured by passing the saturated gas over calcium sulfate. Gas content of the aqueous liquid was measured by means of a variable glass piston-cylinder arrangement. Pressures were measured by means of a pressure diaphragm and temperatures were very precisely measured by a platinum resistance thermometer. The containment cell was made from alloy 310
stainless steel and was plated on the inside with chrome to a thickness of 0.003 inches.

McKetta and Wehe\textsuperscript{26} compiled most of the existing water content data, and produced a water content chart, which has been widely used in gas processing applications to predict the equilibrium water content of natural gas. On the chart, corrections for brine salinity and composition are included. Unfortunately, the chart has no sound theoretical basis, and is merely a group of best-fit lines drawn through approximately 30 years worth of experimental data. The chart also does not explicitly account for composition, and can be seriously in error when the gases contain more than 10\% of an acid gas, like carbon dioxide or hydrogen sulfide.

Todheide and Franck\textsuperscript{27} studied the mutual solubilities of water and carbon dioxide from 20 to 350 MPa at temperatures between 323 to 623 K. Their experimental method used a mechanically stirred cell with several sampling ports at various levels. Their 323 K results agree well with the results of Wiebe and Gaddy for the same system at pressures around 50 MPa. Their derived Henry's constants also agree well with those of Wiebe and Gaddy and Zawisza and Malesinska.

Takenouchi and Kennedy\textsuperscript{28} studied the mutual solubility of water and carbon dioxide from 383 to 773 K at pressures from 1.01 to 202 MPa. Their apparatus was originally constructed for measurements on the phase behavior of water + NaCl systems. It had no means of mechanical agitation or baffle
protection against entrainment. Their data differ widely from that of Todheide and Franck, and do not appear to match data of other investigators at lower pressures. Their Henry's constants for the water rich phase appear to diverge substantially from the values reported by Weibe and Gaddy or Zawisza and Malesinska. It appears from their data that substantial water was being entrained in the system at high pressures.

Danneil et al.\textsuperscript{29} measured the mutual solubilities of water and ethane from 473 to 673 K and from 2 to 110 MPa. They used the same apparatus that Todheide and Franck used for their carbon dioxide and water measurements, using magnesium perchlorate desiccant to measure the amount of water in the gaseous phase and used volumetric burettes to determine the amount of ethane in the liquid water phase.

Rigby and Prausnitz\textsuperscript{30} measured the solubilities of water in methane, nitrogen and argon over a shallow pressure range between 2.02 and 9.12 MPa, at temperatures between 298 and 377 K. Their analytical technique and procedure was much the same as Bartlett, and they also report second virial coefficients for the binaries measured. Unfortunately, the reported water contents appear to be considerably higher than the results reported by Olds et al. or those reported by Skinner.

Sharma\textsuperscript{31} measured the water content of various sweet gas mixtures using a desiccant method, covering the temperature range between 293 and 373 K and pressures between 0.34 and 20.68 MPa. At higher pressures, a manually
driven positive displacement pump was used to maintain pressure. Gas chromatography was used to analyze the gas compositions before and after each run.

O'Sullivan and Smith\textsuperscript{32} measured the solubility of methane and nitrogen in pure water and NaCl brines from 323 to 398 K over a pressure range from 10 to 61 MPa. Two different molar concentrations of brines were used, 1 and 4 molar.

Coan and King\textsuperscript{33} measured the solubility of water in carbon dioxide, nitrous oxide and ethane from 298 to 373 K up to pressures of 12.07 MPa. They used a flow system similar to that of Bartlett, except that they used a cold trap in addition to the desiccant. Pure component gas was saturated in a stainless steel equilibration cell that was inside of a thermostatically controlled bath. Effluent gas from the stainless steel cell was throttled down to ambient pressure and the water removed from the low pressure gas by use of a desiccant of a cold trap. They presented a correlation for predicting the solubility of water in the gas phase using a two term virial equation of state. A two term virial equation is valid up to pressures of approximately 10 MPa, but above this pressure the two term virial equation of state begins to break down, so this treatment is not useful for high pressures.

Malinin and Saveleva\textsuperscript{34} measured the solubility of CO\textsubscript{2} in NaCl and CaCl\textsubscript{2} brines, at ionic strengths of up to 5 at 298, 323 and 348 K at a constant pressure of 4.8 MPa.
Malinin\textsuperscript{35} reviewed all the available literature for the $\text{CO}_2 + \text{H}_2\text{O}$ systems, assembling an excellent analysis of the available literature data. He cross plotted most of the data, showing that there was a wide scatter in the data of Takenouchi and Kennedy.

Malinin\textsuperscript{36} also examined the solubility of $\text{CO}_2$ in mixed electrolyte solutions, using $\text{NaCl}$ and $\text{CaCl}_2$ mixtures to examine the amount of solubility reduction (the “salting out” effects) of the salts on the solubilities of the $\text{CO}_2$ in the aqueous brine phase.

Sloan et al.\textsuperscript{37} measured the water content of methane gas in equilibrium with hydrate at 10.34 and 6.89 MPa, over a temperature range spanning 249 to 280 K. Sloan et al. used a rotating ball-mill autoclave to form the hydrate. The autoclave was charged with water and methane gas, and cooled to form hydrate. Stainless steel balls inside the autoclave crushed the hydrate crystals that were formed, ensuring complete conversion to hydrate and complete saturation of the methane inside the autoclave. Methane gas entered the autoclave from a cylinder, equilibrated due to the rocking action of the cell, and the effluent water was absorbed in a glycol charged column. The sample was then analyzed using a gas chromatograph to determine how much water was present in the sample using a thermal conductivity detector. Using this type of method removes the inaccuracies associated with chilled mirror type dew point testers. Because the resolution of the chromatograph (i.e. the chromatograph has a sensitivity of about
$1 \times 10^{-7}$ moles, or about 1.8 micro grams) was better than the resolution of the scales available at the time, it was also more accurate than a desiccant method.

Aoyagi et al.\textsuperscript{38} used the same chromatographic analysis technique as the Sloan et al. to measure the water content of methane in equilibrium with hydrate, but the experimental set up was modified to include a circulating pump and a hand pump for more accurate pressure control. Aoyagi et al. extended the temperature range to about 243 K, and took new measurements at 2.06 and 3.44 MPa, while extending measurements at 6.89 and 10.34 MPa to lower temperatures.

Zawisza and Malesinska\textsuperscript{39} measured the mutual solubilities of CO$_2$ and water at pressures between 0.2 and 5 MPa, at temperatures up to 473 K. They employed a static saturation cell method. The reported water contents of carbon dioxide gas phase match well with the measurements of Weihe and Gaddy.

Gillespie and Wilson\textsuperscript{40} measured the mutual, binary solubilities of water and methane, carbon dioxide, hydrogen sulfide, n-pentane and the ternary solubility of water, methane and n-pentane from 293 to 533 K at pressures up to 20.68 MPa. The experimental apparatus consisted of a high pressure gas tank, a pressure regulator, a ballast tank to smooth out variations in pressure from the high pressure cylinder and a single saturation cell that was equipped was equipped with a steel dispersion frit and anti-entrainment baffles. A magnesium perchlorate desiccant was used to remove water from the liquid phase, while the liquid phase composition was determined by withdrawing a sample and flashing it
into a water phase and a gaseous phase. The volume of the gas phase was measured using a gas burette, while the water was weighed in a receiving bottle and desiccant charged tubes to determine the mass removed. For the ternary systems, a gas chromatograph was employed to determine the composition of the non aqueous components. The hydrocarbon rich liquid phase, if present, was analyzed using a gas chromatograph.

Crovetto et al.\textsuperscript{41} measured the solubility of methane in water at temperatures up to 600 K and pressures up to 90 MPa using a rocked stainless steel vessel. Her analytical technique was to withdraw a sample of the liquid phase and to flash the gases out of the water. The mass of the water was determined using gravimetric methods.

Song and Kobayashi\textsuperscript{42} measured the water content of a carbon dioxide mixture containing 5.31 mole percent methane from 6.2 to 13.7 MPa over a temperature range of 300 to 323 K. The equilibrium apparatus used a magnetically driven pump to withdraw a portion of the vapor and return it through the liquid phase, ensuring that the sample withdrawn is always at equilibrium. The analytical technique was identical to that used by Aoyagi, and was set up in much the same fashion.

Song and Kobayashi\textsuperscript{43} measured the water content of ethane and propane in equilibrium with liquid water or hydrates over a variety of conditions. For ethane, they measured the liquid and gas in equilibrium with hydrate for pressures of 2.483 MPa and 3.448 MPa, at temperatures from 240 to 283 K, as
well as in the three-phase coexistence non-hydrate regions at pressures ranging from 3.448 MPa to 4.828 MPa and temperatures from 288 to 304 K. For propane, they measured the water content of the propane-rich phase in equilibrium with hydrate covering temperatures from 235 to 276 K at a constant pressure of 1.097 MPa. Above the hydrate region the experimental conditions range from 282 to 300 K and pressures of 0.621 MPa to 0.897 MPa. They also measured isobaric water content data at 4.138 MPa for the liquid hydrocarbon-rich phase of four ethane-propane mixtures containing 30.5, 50.0, 75.0 and 89.5 mol% ethane with the remainder propane, in equilibrium with liquid water or hydrate at temperatures ranging from 271 to 298 K. The measurement setup was similar to that of their 1990 investigation for regions above the hydrate formation temperature, while investigations below the hydrate formation temperature used the blind cell used by Sloan and Kobayashi.

Dhima et al. measured the solubility of methane, ethane, n-butane, methane + ethane and carbon dioxide in water up from 2.5 to 100 MPa at 350 K using gas chromatography. The gas mixture under study was charged along with water into a 200 cm³ piston-cylinder cell. Equilibrium was ensured by means of a magnetic stirrer. The cell is pressurized by means of an oil displacement pump to the desired pressure. At the desired temperature and pressure, a sample of the water phase is withdrawn and flashed in a heated helium environment to liberate the gas dissolved in the water. The water is separated from the gas phase in a partial condenser operating at 273 K. The dried gas is
injected into a gas chromatograph for analysis. The total mass of water is
determined from the change in mass of the condenser. From the mass of the
water and the composition of the gas phase, the mole fractions of the aqueous
phase can be determined.

Al-Tolaihy and Jamieson\textsuperscript{45} investigated the water content in equilibrium
with sour natural gas (those natural gases having high levels of H\textsubscript{2}S and CO\textsubscript{2}).
The sour gas stream was bubbled through anhydrous methanol to scrub the
water vapor from the gas stream. A ratio of 25 liters of sour gas to 50 mL of
methanol was used. The methanol/water solution was fed to a thermal
conductivity detector (TCD) type gas chromatograph to determine the quantity of
water present. However, no studies of the vapor phase were made to determine
if this method was effective enough to remove all of the water from the gas
stream. A glycol solution, as those used by Kobayashi et al. would have more
effectively removed water from the gas stream than methanol alone.

Song et al.\textsuperscript{46} measured the water content of methane, liquid ethane and
liquid propane in equilibrium with hydrates at several pressures spanning a
temperature range of from 201 to 286 K. The experimental set up and
procedures were similar to that of Song and Kobayashi's 1994 work, but
additional cooling capacity was added by augmenting the cooling system with
liquid nitrogen. This enabled Song et al. to reach temperatures as low as 183 K.
Although the work does extend the temperature range over which the water
content of gases in equilibrium with water or hydrates have been studied, the
sampling procedure could have been improved; the flow scheme for hydrate studies would frequently result in blockage of the sample lines and would necessitate warming the apparatus up to dissociate the hydrate blockage.

**Review of Modeling Literature**

**Equations of state**

William Thomson (lord Kelvin) once said that “I am never content until I have constructed a mechanical model of the subject I am studying. If I succeed in making one, I understand; otherwise I do not.” The meaning of his words still ring true today; experimental data alone does not give you a complete understanding of any system. To do something useful (predict a water content, determine a solubility, etc), one must have a good mathematical model.

The first practical model (or, equation of state) for gases was developed by Clapeyron in 1834 based partially on Boyle’s experiments with air, where Boyle deduced that the volume of a gas was inversely proportional to pressure or $PV = \text{constant}$ and in part on the work of Charles and Gay-Lussac who found that the volume of a gas had a linear relationship with temperature or $V = V_0(1 + kT)$. Clapeyron put these together to form the very first equation of state for the ideal, or perfect gas:

$$PV = RT$$

(2.1)

where $P$ is the pressure, $V$ is the volume, $R$ is the universal gas constant and $T$ is the temperature in Kelvin.
The ideal gas law is useful so long as the molecules in the fluid are at a low enough density (either by high temperature or low pressure) such that the molecules do not interact with one another. As the molecules begin to interact, significant deviations from the ideal gas law are observed.

The ideal gas law assumes that molecules do not interact. J.D. van der Waals in his 1873 thesis was the first to recognize that this was unrealistic. Molecules experience both intermolecular attraction and repulsion. He showed that the liquid and gaseous states were merely parts of a continuum that could be described by a single equation of state. He proposed what became known as the van der Waals (vdW) equation of state:

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad (2.2)$$

Where $P$ is the pressure, $R$ the universal gas constant, $T$ the temperature, $V$ the volume and $a$ and $b$ are parameters derived from experimental $P,V,T$ data.

If the critical pressure and temperature for a pure species are known, one can use thermodynamic relationships to derive the values of the constants $a$ and $b$ for the van der Waals equation of state:

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}, \quad b = \frac{1}{8} \frac{RT_c}{P_c} \quad (2.3)$$

where $T_c$ and $P_c$ are the temperature and the pressure at the critical point, respectively. Although the (vdW) equation of state is a massive improvement over the perfect gas law, it is at best only moderately accurate. Around the critical
point and at high pressures where liquid like densities are encountered, the
equation of state is inadequate for technical and scientific use.

The vdW equation of state was originally published only for pure
components. Lorentz and Berthelot separately suggested the use of a few
'mixing rules' in order to extend the utility of the vdW equation of state to mixtures
of more than one component

\[ \sqrt{a} = \sum y_i \sqrt{a_i} \]
\[ b = \sum y_i b_i \]  
(2.4)

where \( y_i \) is the mole fraction of component \( i \), \( a_i \) and \( b_i \) are the parameters for
component \( i \). Although the exact form of the mixing rule suggested by Lorentz
and Berthelot may not have completely survived, their idea of combining
parameters based on the mole fractions still has great utility.

It has already been noted that the vdW equation of state does not predict
both liquid and gas volumes (and related properties) well. Soon after the vdW
equation of state was published, it was recognized that the 'a' parameter had a
rather strong dependence on temperature. However, it was not until Redlich and
Kwong 50 (RK) suggested a temperature dependence of \( \sqrt{T} \) that the next major
improvement in the cubic equation of state was born. According to Redlich 48,
there was no particular theoretical basis for the equation, so it is simply a case of
good scientific judgment in selecting the form of the equation:

\[ P = \frac{RT}{V - b} - \frac{a}{\sqrt{TV(V - b)}} \]  
(2.5)
where the a and b parameters are found by noting that at the critical point, the first and second derivatives of the pressure with respect to volume at fixed temperature should be zero, thus

\[
\left. \frac{\partial P}{\partial V} \right|_T = \left. \frac{\partial^2 P}{\partial V^2} \right|_T = 0
\]

(2.6)

and applying the derivatives, one arrives at:

\[
a = 0.427480 \frac{R^2 T_c^{2.5}}{P_c}
\]

(2.7)

\[
b = 0.086640 \frac{RT_c}{P_c}
\]

(2.8)

However, the constants appearing in (2.7) and (2.8) can be made adjustable and specific to a particular species in order to improve the ability of the equation to fit existing experimental data.

Modifying the Lorentz-Berthelot mixing rules, Redlich and Kwong suggested the following mixing rules:

\[
a = \sum \sum y_i y_j a_{ij}
\]

(2.9)

\[
a_{ij} = \sqrt{a_i a_j}
\]

(2.10)

\[
b = \sum y_i b_i
\]

(2.11)

where \(y_i\) is the mole fraction of species \(i\), and \(a_{ij}\) is the cross interaction energy between species \(i\) and species \(j\).

Despite being a substantial improvement over the vDW equation of state, the RK equation of state still has a few problems. As proposed, the mixing rules
contain no adjustable parameters so that the cross interaction energy can not be adjusted to better fit experimental data. The RK equation of state also tends to over predict the critical point of mixtures, but this problem is common to almost all cubic equations of state (including the vdW). The RK also suffers from the same defects that the vdW does for the liquid state, and can not be used by itself for calculating vapor-liquid equilibria.

About a decade after the RK equation of state was developed, a more complex theory of corresponding states was developed by Pitzer and Curl\textsuperscript{51}. When plotted on reduced coordinates, the log of the reduced pressure (P/P\textsubscript{o}) vs. the reciprocal of the reduced temperature (T/T\textsubscript{c}) of simple fluids like argon, krypton and xenon fall along the same straight line. Other fluids (e.g. methane, water) when plotted in the same fashion also fall on a straight line, but those lines have different slopes. Pitzer and Curl defined a third parameter, called the acentric factor to quantify the degree of deviation from the simple fluid slope:

\[ \omega = -1.0 - \log(P_{r}^{sat}) \bigg|_{T_{r}=0.7} \] \hspace{1cm} (2.12)

By adding this third parameter, it is possible to describe fluid behavior with greater accuracy.

The next evolution in the cubic equation of state came when the acentric factor was incorporated into the RK equation of state. Soave\textsuperscript{52} modified the RK equation of state (SRK), retaining the temperature dependence of the \( a(T) \) parameter, but modifying it to be a function of the acentric factor, \( a(T, \omega) \). Thus, the SRK equation of state is
\[ P = \frac{RT}{V - b} - \frac{a(T, \omega)}{V(V - b)} \]  
\tag{2.13}

where \( a(T, \omega) \) was fitted to reproduce the vapor pressures of hydrocarbons.

\[ a(T, \omega) = a^* \alpha = \frac{0.42748 \left( \frac{R^2 T_c^2}{P_c} \right)}{\alpha} \]  
\tag{2.14}

The function alpha is where the temperature and acentric factor are incorporated into the function

\[ \sqrt{\alpha} = 1 + \left(1 - \sqrt{T_c} \right) \left(0.480 + 1.574 \omega - 0.176 \omega^2 \right) \]  
\tag{2.15}

where \( \omega \) is the acentric factor. The addition of this third parameter greatly improved the ability of the equation of state to predict vapor and liquid densities, as well as phase equilibria.

Peng and Robinson\(^{53}\) proposed the next evolution of the cubic equation of state. Although the SRK improved predictions greatly, it was still not as good of a predictive tool in the region of the critical point for compressibility factor and liquid-like density calculations. Thus, Peng and Robinson proposed a new cubic equation (PR) that borrowed Soave's idea of incorporating the acentric factor, but performs better around the critical point. The equation is:

\[ P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \]  
\tag{2.16}

However, Peng and Robinson applied some alternate fitting criteria in order to improve the critical behavior. At the critical point
\[ a = 0.45724 \frac{R^2 T_c^2}{P_c} \]  
(2.17)

\[ b = \frac{0.07780 R T_c}{P_c} \]  
(2.18)

Like the SRK, the PR breaks the \( a(T) \) parameter into two parts:

\[ a(T) = a^* \alpha(T^*, \omega) \]
\[ \sqrt{\alpha} = 1 + \left(1 - \sqrt{T_c} \right) \left(0.37464 + 1.5422 \omega - 0.26992 \omega^2 \right) \]  
(2.19)

differing only from the SRK in the coefficients used to define \( a(T) \). Calculations made with the PR equation of state have generally better results for compressibility factor calculations at liquid-like densities than calculations made with the SRK.

The advantage of cubic equations of state is that they are simple, but despite this simplicity can do a very good job of calculating physical properties. The disadvantage of cubic equations of state are that they do not have any inherent ability to handle associating molecules like water or methanol, and they do not contain any molecular shape information. More complex equations of state do contain some of the needed molecular information, but they are more deeply rooted in statistical mechanics.

There are also hybrid cubic equations of state which explicitly incorporate association. Some of these hybrids use a 'chemical' theory of association to describe the association between molecules. This sort of theory requires some assumption to be made about the distribution of the number of monomer, dimer,
trimer and higher molecules present, and does not lend itself to predictive calculations. The other, far more successful type of hybrid uses a cubic with the association term from Statistical Associating Fluid Theory, and is generally termed Cubic plus association, or $CpA^{55}$. Because it is based on rigorous thermodynamics, this is much more amenable to making predictive calculations. The association term is discussed in more detail in chapter 3.

**Hard sphere equations of state**

In contrast to cubic equations of state, statistical thermodynamics gives an explicit method of accounting for molecular interactions beyond simply “attractive” or “repulsive”. Because atomic interactions such as hydrogen bonding, short range repulsion and long range attraction are quantified at the molecular level, equations of state based on more complex statistical thermodynamic treatments can give better phase equilibrium predictions than a cubic EoS. However, the problem with explicitly calculating the intermolecular interactions is that the calculations can become computationally intensive, (not to mention the equations themselves look a bit daunting on paper) which has to some extent discouraged their use.

Where as an ideal gas molecule has no attractive or repulsive interactions, a hard sphere type molecule has an infinite repulsion at the molecule’s radius, $\sigma$. However, practical use of the hard sphere model in scientific calculations did not happen until the work of Percus and Yevick$^{56}$ and was not suitably applied for
engineering use until Carnahan and Starling\textsuperscript{57} and Mansoori et al.\textsuperscript{58} developed a suitable equation based on the reduced density of the fluid:

\[ \eta = \frac{\pi N}{6} \rho d^3 \]  

(2.20)

where \( \rho \) is the molar density, \( N \) is Avogadro's number and \( d \) is the hard sphere diameter. Thus, the equation of state for the Helmholtz energy of a fluid of hard spheres is

\[ \frac{A}{NRT} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \]  

(2.21)

Although about 90\% of fluid structure is governed by these short range repulsive interactions, more information is still required to accurately predict the fluid structure of more complex molecules like long chain molecules (polymers) and hydrogen bonding molecules (alcohols, water). So while predictions for argon, xenon and other simple molecules worked well with the Carnahan-Starling-Mansoori-Leland equation over a wide variety of densities, more complex theories were needed to handle the differences in shape, intermolecular repulsion and hydrogen bonding effects encountered in more complex molecules.

The next step in the evolution of molecular based equations of state came with the Perturbed Hard Chain Theory (PHCT) of Beret and Prausnitz\textsuperscript{59}. This equation of state incorporates the repulsive contributions of the Mansoori et al. equation of state with the attractive terms of Alder et al.\textsuperscript{60} to more accurately predict how a fluid will behave. The PHCT equation of state is
\[ \frac{\tilde{P} \tilde{v}}{\tilde{T}} = \frac{1}{c} + \frac{4\eta - 2\eta^2}{(1-\eta)^3} + \frac{1}{\tilde{T} \tilde{v}} \sum_{n=1}^{4} \sum_{m=1}^{M} \left( \frac{mA_{mn}}{\tilde{v}^{m-1}} \right) \left( \frac{1}{\tilde{T}^{n-1}} \right) \] (2.22)

Where

\[ \tilde{P} = \frac{P(rv^*)}{\varepsilon q} \] (2.23)

\[ \tilde{T} = \frac{ckT}{\varepsilon q} \] (2.24)

\[ \tilde{v} = \frac{v}{rv^*} = \frac{v\sqrt{2}}{N_{A,v}r\sigma^3} \] (2.25)

The parameters \( \varepsilon \), \( rv^* \) and \( c \) are obtained from fitting to saturated vapor pressure and liquid density data for pure fluids.

PHCT is an improvement over previous equations of state because it allows one to deal with molecules that are on drastically different size scales, like ethylene (two carbon atoms long) and high molecular weight polyethylene (several thousand carbon atoms long). However, it still lacks the ability to accurately calculate physical properties of molecules with differing molecular structures (e.g. branched vs. linear polyethylene) and those with strong short range interactions like association\(^61\).

M.S. Wertheim provided the mathematics for the next large step forward in hard sphere equations of state. He worked out the mathematics necessary for determining the Helmholtz energy due to single hard spheres associating, or forming hydrogen bonds\(^62-65\).
Chapman et al.\textsuperscript{56–68} took the first order perturbation theory ideas of Wertheim and developed Helmholtz energy expressions that allowed Wertheim's ideas to be applied to the much more useful scientific and engineering problems of the thermodynamics of chains and of associating chains\textsuperscript{56–68}. The resulting simplifications are referred to as the Statistical Associating Fluid Theory, or SAFT equation of state, which revolutionized the prediction of behavior of polymer and associating systems. In general terms, the SAFT equation of state is an expression for the residual (residual meaning that the ideal gas contribution has been subtracted) Helmholtz energy. The general form of the equation is

$$A^{\text{res}} = A^{\text{Hard Sphere}} + A^{\text{Dispersion}} + A^{\text{Chain}} + A^{\text{Association}}$$ \hspace{1cm} (2.26)

Where $A$ is the Helmholtz energy.

The hard sphere term is calculated using Mansoori et al.\textsuperscript{58} expression for a hard sphere fluid:

$$A^{\text{Hard Sphere}} = mA^{\text{Carnhan-STARLING}} = m \frac{4\eta - 3\eta^2}{(1-\eta)^2}$$ \hspace{1cm} (2.27)

where $m$ is an adjustable parameter (generally referred to as the number of segments) that is determined for a pure fluid by fitting to saturated vapor pressure and liquid density data.

The chain formation term is

$$A^{\text{Chain}} = (1-m) \ln \left( \frac{1-0.5\eta}{(1-\eta)^{3/2}} \right)$$ \hspace{1cm} (2.28)
where $m$ has the same definition as in (2.27) and $\eta$ is defined in (2.20) The
dispersion and association terms of the SAFT equation of state are explained in
chapter 3.

**Complex equations of state**

When a large quantity of accurate PVT data is available, it is possible to
use a multiple parameter equation of state to get very accurate reproduction of
thermodynamic properties over a wide range. Due to the sheer volume of
physical property measurements for water, this type of treatment has been
applied with good results. Lester, Haar and Ghallager\textsuperscript{69} published one of the first
such equations of state. This equation of state is a multiple parameter equation
for the Helmholtz energy,

$$
\frac{A}{RT}(\rho, T) = \frac{A^{id}}{RT} + \frac{A^{res}}{RT} 
$$

(2.29)

Where $R$ is the universal gas constant, $T$ is the temperature and the $A^{id}$ and $A^{res}$
are multiple parameter expansions to calculate the ideal gas and residual
contributions for water. Lester, Haar and Ghallager's equation of state is good to
300 MPa and between 273.15 and 1273 K.

The next major improvement in such complex equations came from
Wagner and Pruss\textsuperscript{70}, when they applied a slightly different functional form to the
$A^{res}$ contribution, and incorporated new data to make the their equation of state
applicable to up to 1000 MPa and between 250 and 1273 K. This formulation
was adapted into the NIST/ASME standard equation for steam properties\textsuperscript{71}.
3. Modeling of Methanol + Alkane systems with CK-SAFT and PC-SAFT

Introduction

Mixtures of methanol + n-alkanes have significant industrial and scientific importance. Methanol is widely used in the petroleum processing industry to inhibit the formation of pipeline-blocking gas hydrates. However, the petroleum must have a low methanol concentration when delivered to the refiner in order to avoid steep penalties on the petroleum supplier. In order to properly design equipment or optimize the process, accurate vapor-liquid equilibrium (VLE) data or equations of state that can predict the phase behavior of mixtures containing methanol, particularly methanol at low concentrations, are needed. Conventional equations of state perform poorly for these systems.

From a scientific standpoint, mixtures containing both strongly associating (hydrogen bonding) and non-associating components are of interest because they are non-ideal systems that produce such interesting behavior as azeotropes and regions of vapor-liquid-liquid equilibria (VLLE). They are excellent systems to demonstrate the ability of theory to account for items such as hydrogen bonding, polarity and molecular shape. One such thermodynamic theory that is capable of accurately describing phase behavior for mixtures of associating species with non-associating species is the Statistical Associating Fluid Theory (SAFT) of Chapman et al., based on the thermodynamic perturbation theory of Wertheim. SAFT variants explicitly account for the formation of hydrogen bonds
between molecules and as such can represent, and in many cases predict, the liquid-liquid and vapor-liquid equilibria in alkanol-alkane mixtures.

In this study we use PC-SAFT and CK-SAFT to model vapor-liquid equilibria in 8 methanol + n-alkane systems and liquid-liquid equilibria in 7 methanol + n-alkane systems. In addition to the SAFT results, we present a few comparisons with Peng-Robinson Boston-Mathias (PR-BM) and predictive Soave, Redlich, Kwong (PSRK) cubic equations of state to show the phase equilibria one obtains using the parameter values provided in the ASPEN® process simulator. The PC-SAFT and CK-SAFT calculations use code developed at Rice University, while the results for the cubic equations of state use the ASPEN® process simulator.

Under the SAFT framework, fluids are modeled as collections of spherical chain segments. SAFT uses five parameters to describe a chemical species. Two of these parameters, \( m_i \) and \( \nu_i \), describe the number of segments and volume of segments used to model the species, one parameter \( \nu_i^0 \) describes the London dispersion energy between species and for associating species, two parameters describe the strength of the association bond \( (\epsilon_{AB}/k_B) \) and the volume of the association site \( (\kappa_{AB}) \). These parameters are typically determined by fitting to experimental vapor pressure and liquid density data. Once these parameters have been fit to pure component data, they are constant, regardless of thermodynamic state.
In order to reduce the number of parameters that require fitting to experimental data, Wolbach and Sandler fix values for the associating site strength ($\epsilon^{AB}/k_b$) and association site volume ($\kappa^{AB}$) using results from Molecular Orbital quantum mechanic calculations (MO) with a methanol model that has three association sites. They use two different MO methods to calculate values for $\epsilon^{AB}/k$ and $\kappa^{AB}$ of methanol: Hartree-Fock (HF) or Becke-3LYP (B3). Once $\epsilon^{AB}/k$ and $\kappa^{AB}$ are established using the MO calculation results, Wolbach and Sandler fit the remaining three parameters to experimental saturated vapor pressure and liquid density data for pure methanol. CK-SAFT parameters established using the Hartree-Fock method to calculate $\epsilon^{AB}/k$ and $\kappa^{AB}$ are designated CK-SAFT(HF) while those fit using the Becke-3LYP method are designated CK-SAFT(B3).

The Hartree-Fock (HF) and Becke-3LYP (B3) MO calculation models differ in the levels of rigor used in calculations, the B3 method is more rigorous than the HF method. The MO calculations are used to calculate the changes of enthalpy and entropy on association. At low density, $\epsilon^{AB}/k_b$ is related to the change in enthalpy on association, and $\kappa^{AB}$ is related to the change in entropy on association. Parameters for CK-SAFT(HF) and CK-SAFT(B3), as derived by Wolbach and Sandler are shown in table 1.
Equations of State Used in This Study

Both the CK-SAFT and PC-SAFT equations of state are given as the sum of Helmholtz energy contributions from different types of molecular interactions:

\[ A^{\text{res}} = A^{\text{ref}} + A^{\text{dispersion}} + A^{\text{assoc}} \] (3.1)

The only difference between CK-SAFT and PC-SAFT appears in the dispersion terms since the association and reference fluid contributions are identical between the two equations of state.

As the MO calculations are used to calculate \( \kappa^{AB} \) and \( \varepsilon^{AB}/k_B \) exclusively, it is useful to review how SAFT incorporates association. The association term, derived by Chapman et al. is based on the first order thermodynamic perturbation theory (TPT1) of Wertheim. Chapman et al. show that using Wertheim’s theory there is a relationship between the fraction of molecules NOT bonded at a particular association site and the Helmholtz energy contribution due to association. This relationship is

\[ \frac{A^{\text{assoc}}}{Nk_B T} = \sum_i x_i \left[ \sum_A \left[ \ln X_i^A - \frac{X_i^A}{2} \right] + \frac{1}{2} \bar{M}_i \right] \] (3.2)

For our case of a single associating component, the fraction of molecules of component i NOT bonded at site A is calculated as

\[ X_i^A = \left[ 1 + \rho \sum_j X_j \Delta^{AB} \right]^{-1} \] (3.3)

The association strength can be approximated as
\[ \Delta^{AB} = g(d_{ij})^{HS} \left[ \exp \left( \frac{E^{AB}}{k_B T} \right) - 1 \right] \left( \sigma_{ij}^{3} \kappa^{AB} \right) \] (3.4)

Although each association site can have its own value for \( \epsilon^{AB}/k_B \) and \( \kappa^{AB} \), a common simplification is to assume that all sites on a segment have the same volume \( \kappa^{AB} \) and interaction energy \( \epsilon^{AB}/k_B \). This leads to closed form solutions for \( \chi^{A} \).  

In CK-SAFT, the dispersion term is a power series in density and reduced temperature fit by Chen and Kreglewski to pressure, volume, temperature and physical property data for Argon. As such, this dispersion term does not explicitly account for differences in molecular shape.

For CK-SAFT, the dispersion term is\(^{74}\):

\[ A^{\text{Dispersion}} = \bar{m} \sum_{i}^{4} \sum_{j}^{8} D_{ij} \left[ \frac{u}{k_B T} \right]^{\zeta_{i,j}} \] (3.5)

An improved dispersion term was developed by Gross and Sadowski to account for the chain-like shape of the model fluid by applying Barker-Henderson theory to chains of square well spheres. This leads to a dispersion term of the form:

\[ \frac{A^{\text{Dispersion}}}{Nk_B T} = \frac{A_1 + A_2}{Nk_B T} \] (3.6)

where

\[ \frac{A_1}{Nk_B T} = -2\pi \rho \sum_{i=0}^{6} a_i \langle m \rangle \left( \zeta_3 \right)^i \sum_{i} \sum_{j} x_i x_j m_i m_j \left( \frac{u_{ij}}{k_B T} \right) \sigma_{ij}^{3} \] (3.7)
\[ \frac{A_k}{N k_B T} = -\pi \alpha \bar{m} k_B T \left( \frac{\partial \rho}{\partial P} \right) \sum_i \sum_j x_i x_j \bar{m}_i \bar{m}_j \left( \frac{u_i}{k_B T} \right)^2 \sigma_{ij} \sum_{i=0}^{\delta} b_i (\bar{m}) (\bar{\zeta}_3)^i \]  

(3.8)

Where the power series in equations (3.7) and (3.8) represent a fit to an integration over the hard chain pair correlation function. The parameters \( a_i \) and \( b_i \) are further represented by series expansions

\[ a_i (\bar{m}) = a_{0i} + \frac{\bar{m} - 1}{\bar{m}} a_{1i} + \frac{\bar{m} - 1}{\bar{m}} \frac{\bar{m} - 2}{\bar{m}} a_{2i} \]  

(3.9)

\[ b_i (\bar{m}) = b_{0i} + \frac{\bar{m} - 1}{\bar{m}} b_{1i} + \frac{\bar{m} - 1}{\bar{m}} \frac{\bar{m} - 2}{\bar{m}} b_{2i} \]  

(3.10)

The parameters \( a_{0i} - b_{2i} \) are adjustable constants for the model. Each of the 42 adjustable parameters in equations (3.9) and (3.10) are fit to vapor pressure and saturated liquid density data for pure alkanes, and are fixed for all fluids. For the CK-SAFT, CK-SAFT(HF), CK-SAFT(B3) and PC-SAFT equations of state, once the dispersion constants (\( D_i \) or \( a_{0i} - b_{2i} \)) are fit, they are treated as constants for all fluids.

For CK-SAFT(HF) and CK-SAFT(B3), Wolbach and Sandler establish \( \varepsilon^{AB}/k_B \) and \( \kappa^{AB} \) by relating these parameters to the change in energy and entropy on hydrogen bonding from the MO output generated by the HF or B3 calculation methods. They fit the remaining three SAFT parameters to pure component saturated vapor pressure and liquid density data.

When dealing with mixtures of two or more distinct chemical species, a mixing rule must be employed to determine the effective square well depth (\( u_i \)) for the mixture dispersion interactions between different chemical species of type
i and type j. In this study, conformal van der Waals one fluid theory (VDW1) is used to define a hypothetical pure fluid that has the same residual properties as the mixture of interest. By VDW1, the mixing rule for CK-SAFT is

$$\frac{u}{k_b T} = \frac{\sum_i \sum_j \lambda_{ij} \lambda_{jj} \left[ \frac{u_{ij}}{k_b T} \right](v_{ij}^*)}{\sum_i \sum_j \lambda_{ij} \lambda_{jj} (v_{ij}^*)}$$

(3.11)

$$u_{ij} = u_{ij}^0 \left[ 1 + \frac{e_{ij}}{k_b T} \right]$$

(3.12)

PC-SAFT does not use the temperature dependence in equation 12 and instead the dispersion energies are invariant with temperature. For PC-SAFT the VDW1 mixing rules are incorporated into equations 7 and 8.

Within the SAFT framework, it is possible to model alcohols with different numbers of association sites depending on how one views the electron pairs on the oxygen molecule. If each oxygen electron is treated as being able to accept one proton hydrogen from another hydrogen bonding molecule, then the alcohol will have three association sites: two acceptor sites from the oxygen and one donor site from the hydrogen. Alternatively, one can treat the oxygen electrons as one acceptor site, in which case the alcohol has two association sites: one acceptor site on the oxygen and one donor site on the hydrogen.

To avoid confusion between different association models, a nomenclature of $N_a(i,j)$ is adopted, where $N_a$ is the total number of sites on associating species.
a, i is the number of proton acceptors and j is the number of proton donors. This presents a clearer picture of how each hydrogen bonding species is modeled. Wolbach and Sandler treat methanol using the more rigorous 3(2,1) model for both CK-SAFT(HF) and CK-SAFT(B3). In contrast, PC-SAFT and CK-SAFT parameters fit entirely to saturated vapor pressure and liquid density data use the simpler 2(1,1) model for methanol. Differences between association site size or strength are noted by a prime or a star, respectively (e.g. if the donor site had a different association energy than the acceptor site, it is a 2(1,1*) model). Economou et al. show that rigorous models and approximate models for

<table>
<thead>
<tr>
<th>Table 1. Schematics of commonly used association models.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Based on the number of proton donors and acceptors a molecule has, it will form a different number of association bonds. Filled circles represent proton donors, open circles represent proton acceptors. For more details, please see Huang and Radosz</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Schematic</th>
<th>Type</th>
<th>Shorthand Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Schematic 1" /></td>
<td>Two sites; one proton acceptor and one proton donor. E.g. alkanols</td>
<td>2(1,1)</td>
</tr>
<tr>
<td><img src="image" alt="Schematic 2" /></td>
<td>Three sites; two proton acceptors, one electron proton. E.g. alkanols (rigorous)</td>
<td>3(2,1)</td>
</tr>
<tr>
<td><img src="image" alt="Schematic 3" /></td>
<td>Four sites; three proton donors and one proton acceptor. E.g. Ammonia (rigorous)</td>
<td>4(1,3)</td>
</tr>
<tr>
<td><img src="image" alt="Schematic 4" /></td>
<td>Four sites; two proton acceptors and two proton donors. E.g. Water (rigorous)</td>
<td>4(2,2)</td>
</tr>
</tbody>
</table>

SAFT give very similar phase behavior predictions, so the differences between the approximate 2(1,1) and the more rigorous 3(2,1) models for methanol are expected to be small.

The possible association models are shown in table 1. Allowed types of
intermolecular associations and a schematic of what the SAFT parameters represent are shown in figure 1

The allowed hydrogen bonding interactions in this study are shown in 'a', where an acceptor (shaded) site on molecule 1 can only form an association with a donor site (clear) on molecule 2. Interactions where an acceptor site on molecule 1 can bond with another acceptor site on molecule 2, as shown in 'b' and where an acceptor site bonds with multiple donor sites, as shown in 'c' are prohibited.

The lower panel shows the model parameters. All fluids require the parameters on the left, \( v_{cc}^0 \), \( m \), and \( u_r^0 \) that describe the model sphere size, number of spheres per model molecule and dispersion interactions between the model molecules, respectively. Associating molecules require two additional parameters to describe the association strength (\( \varepsilon^{AB}/k_B \)) and volume of site-site overlap (\( \kappa^{AB} \)).

**Figure 1**

Acceptor or donor sites bonding to more than one donor or acceptor site are prohibited within the SAFT framework. Association sites are modeled as small regions on the surface of a hard sphere segment. When two molecules are correctly oriented so the sites overlap, the molecules interact (associate) with
one another via a square-well potential with a depth of \(e_{i,j}/k_B\). The volume that these sites overlap is the bonding volume \(\kappa_{i,j}\). Further details are given by Chapman et al.\(^\text{66}\) and Jackson et al.\(^\text{75}\).

Methods

<table>
<thead>
<tr>
<th>SAFT Model</th>
<th>(\nu^0)</th>
<th>(m_i)</th>
<th>(\mu_{ii}/k_B)</th>
<th>(e_{i,j}/k_B)</th>
<th>(\kappa_{i,j})</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK SAFT</td>
<td>12.00</td>
<td>1.776</td>
<td>216.13</td>
<td>2714</td>
<td>0.04856</td>
<td>76</td>
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<td>8.10</td>
<td>2.679</td>
<td>222.57</td>
<td>1930</td>
<td>0.04472</td>
<td>77, 78</td>
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<td>CK-SAFT(B3)</td>
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<td>1470.0</td>
<td>0.01641</td>
<td>77, 78</td>
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<tr>
<td>PC SAFT</td>
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<td>1.5255</td>
<td>188.90</td>
<td>2899.5</td>
<td>0.03518</td>
<td>79</td>
</tr>
</tbody>
</table>

Pure component parameters used in this study, as taken from the literature, are listed in tables 2 and 3. In addition to the pure component parameters, binary mixtures use an additional temperature-dependent binary interaction parameter, \(k_{ij}\), to fit the calculated results to the experimental data taken from the literature.
Two possible ways of comparing results from VLE and LLE calculations made with various equations of state are setting the $k_{ij}$ to 0.0 (a predictive calculation), or optimizing the $k_{ij}$ value so the calculations are fitted to experimental data. We present calculations using both fitted and predictive values. With $k_{ij} = 0$, SAFT gives qualitatively correct phase behavior. This shows

<table>
<thead>
<tr>
<th>Chemical</th>
<th>SAFT dispersion type</th>
<th>$v_{ii}^{oo}$</th>
<th>$m_i$</th>
<th>$u_{ii}^{0}/k_b$</th>
<th>Ref.</th>
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<td>2.0020</td>
<td>208.11</td>
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<td>CK</td>
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<td>76</td>
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<tr>
<td></td>
<td>PC</td>
<td>21.722</td>
<td>2.3316</td>
<td>222.88</td>
<td>79</td>
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<tr>
<td>Pentane</td>
<td>CK</td>
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<td>4.091</td>
<td>200.02</td>
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<td></td>
<td>PC</td>
<td>22.871</td>
<td>2.6896</td>
<td>231.2</td>
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<td></td>
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<td>23.458</td>
<td>3.4831</td>
<td>238.4</td>
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<td>CK</td>
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<td>206.03</td>
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<td></td>
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<td>3.8176</td>
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<tr>
<td>Nonane</td>
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<td>6.883</td>
<td>203.56</td>
<td>76</td>
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<tr>
<td></td>
<td>PC</td>
<td>24.204</td>
<td>4.2079</td>
<td>244.51</td>
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<tr>
<td>Decane</td>
<td>CK</td>
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<td>7.527</td>
<td>205.46</td>
<td>76</td>
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<td>PC</td>
<td>24.083</td>
<td>4.6627</td>
<td>243.87</td>
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</table>
SAFT can predict non-ideal solution behavior (e.g. azeotropic) from only pure component data.

Conventional cubic equations of state typically require fitting $k_{ij}$ to mixture data before showing qualitatively correct phase behavior. As shown in figure 2 for the methanol + propane system, the Peng-Robinson Boston-Mathias (PR-BM)\textsuperscript{53, 80, 81} equation of state (EOS), using the default ASPEN\textsuperscript{®} $k_{ij}$ values does not predict an azeotrope\textsuperscript{82}. The predictive Soave-Redlich-Kwong (PSRK)\textsuperscript{83-85} exhibits

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{VLE with the methanol + propane system at 313 K. Dashed lines are the ASPEN suggested $k_{ij}$ parameters for the Peng-Robinson-Boston-Mathias (PR-BM) equation of state. PC-SAFT correctly shows the presence of an azeotrope, while the PR-BM predicts only ideal solution behavior. The predictive Soave-Redlich-Kwong equation of state also poorly correlates the experimental data, and produces liquid-liquid phase splitting. PSRK uses UNIFAC to determine the mixing energy change for unlike molecules.}
\end{figure}
splitting. PSRK\textsuperscript{64} uses UNIFAC to determine the mixing energy change and does not require binary interaction parameters ($k_{ij}$).

As shown in figure 3, the PR-BM EOS using $k_{ij}$ parameters supplied by ASPEN\textsuperscript{®} does predict an azeotrope, but does not quantitatively reproduce the data. Changing the $k_{ij}$ in attempt to better fit the data results in liquid-liquid phase splitting, which is typical for cubic equations of state. PC-SAFT, with a $k_{ij}$ of 0, represents the data more accurately than the fitted PR-BM EOS, and PC-SAFT can quantitatively reproduce the experimental to within the experimental precision of the data with a fitted $k_{ij}$ value.

For VLE calculations the $k_{ij}$ value is optimized so that the difference between experimentally determined azeotrope pressure and calculated azeotrope pressure is minimized. Alternate methods, such as adjusting the $k_{ij}$ value to reproduce experimentally determined vapor to liquid mole fraction (y/x) ratios or ‘k values’ produce similar $k_{ij}$ values.
These $k_{ij}$ values are correlated, and that correlation is applied to predict the LLE phase behavior, showing adequate agreement between the LLE experimental data and the calculations for the alkanes C5 through C7. Improved reproduction of the data for all LLE systems is possible using a $k_{ij}$ value that is fit directly to the LLE experimental data.
Turning now to the MO based calculations, it is insightful to examine the pure component behavior. CK-SAFT(HF) calculations yield pure methanol vapor pressures similar to those calculated by CK-SAFT and PC-SAFT using parameters fit entirely to saturated vapor pressure and liquid density data, with similar trends in vapor pressure deviation, as shown in table 4. All three reproduce the NIST recommended \(^{86,87}\) vapor pressures within a few percent. In contrast, CK-SAFT(B3) calculations predict methanol vapor pressures above those observed experimentally at temperatures below 400 K, while predicting vapor pressures below those observed experimentally above 400 K. At 490 K the pure methanol vapor pressure calculated with CK-SAFT(B3) parameters is almost 20% below the NIST\(^{86,87}\) recommended vapor pressure value. This fact helps to explain some of the mixture calculation results discussed below.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>NIST</th>
<th>CK-SAFT</th>
<th>% dev</th>
<th>PC-SAFT</th>
<th>% dev</th>
<th>CK-SAFT(\text{HF})</th>
<th>% dev</th>
<th>CK-SAFT(\text{B3})</th>
<th>% dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>16.94</td>
<td>16.88</td>
<td>-0.3</td>
<td>16.41</td>
<td>-3.1</td>
<td>16.56</td>
<td>-2.2</td>
<td>17.04</td>
<td>0.6</td>
</tr>
<tr>
<td>313.10</td>
<td>35.35</td>
<td>35.19</td>
<td>-0.5</td>
<td>35.08</td>
<td>-0.8</td>
<td>35.01</td>
<td>-0.9</td>
<td>36.32</td>
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<td>343.1</td>
<td>124.85</td>
<td>123.77</td>
<td>-0.9</td>
<td>121.17</td>
<td>-2.9</td>
<td>125.96</td>
<td>0.9</td>
<td>128.79</td>
<td>3.2</td>
</tr>
<tr>
<td>373.1</td>
<td>329.76</td>
<td>350.48</td>
<td>6.3</td>
<td>346.41</td>
<td>5.1</td>
<td>358.39</td>
<td>8.7</td>
<td>351.83</td>
<td>6.7</td>
</tr>
<tr>
<td>430.0</td>
<td>1535.9</td>
<td>1629.75</td>
<td>6.1</td>
<td>1643.08</td>
<td>7.0</td>
<td>1644.11</td>
<td>7.0</td>
<td>1452.82</td>
<td>-5.4</td>
</tr>
<tr>
<td>470.0</td>
<td>3560.4</td>
<td>3753.49</td>
<td>5.4</td>
<td>3828.78</td>
<td>7.5</td>
<td>3719.52</td>
<td>4.5</td>
<td>3049.52</td>
<td>-14.3</td>
</tr>
<tr>
<td>490.0</td>
<td>5128.5</td>
<td>5383.29</td>
<td>5.0</td>
<td>5515.49</td>
<td>7.5</td>
<td>5281.69</td>
<td>3.0</td>
<td>4181.89</td>
<td>-18.5</td>
</tr>
</tbody>
</table>

CK-SAFT(HF) and CK-SAFT(B3) VLE calculations are shown for the methanol + butane\(^{88,89}\) system in figures 4 and 5. A temperature dependent \(k_{ij}\) is used in all calculations to fit the experimental data. As shown in figure 4, CK-SAFT(HF) and CK-SAFT(B3) calculations predict similar phase behavior at 273
K; CK-SAFT(HF) has an average absolute deviation (AAD) of 14.7% while CK-SAFT(B3) has an AAD of 14.4%. As temperature increases, CK-SAFT(B3) does not reproduce the experimental data as well as CK-SAFT(HF). At 323 K, CK-SAFT(B3) has an AAD of 11.8%, almost twice that of CK-SAFT(HF)'s AAD of 6%, while at 373 K, CK-SAFT(B3) has an AAD of 12%, almost three times that of CK-SAFT(HF)'s AAD of 4.3%. Clearly, the CK-SAFT(B3) parameter set is not capable of reproducing phase behavior over as broad of a temperature range as CK-SAFT(HF). It is interesting to note that CK-SAFT(B3) does not predict an azeotrope at 373 K.
In figure 5, the same data is modeled using CK-SAFT with all parameters fit to saturated vapor pressures and liquid densities, and CK-SAFT(HF). The CK-SAFT calculations shown in figure 5 have an AAD of 11.9% at 273 K, 2.5% at 323 K and 1.4% at 373 K. This would tend to indicate that it is preferable to fit the association parameters to experimental data rather than calculate them from quantum mechanics.

The calculations presented in figures 4 and 5 have a $k_{ij}$ value that is optimized to reproduce the experimentally determined azeotrope pressure. Typically, the calculation fit can be improved by increasing the $k_{ij}$ value, but for

![Image](image_url)

Methanol + Butane VLE generated with CK-SAFT(HF) (solid line) and CK-SAFT(B3) (dashed line) parameters for 273, 323 and 373 K. Both parameter sets are able to correlate the low temperature VLE with AAD% of ~12%. At higher temperatures above 323 K, increasing the $k_{ij}$ value leads to liquid-liquid phase splitting, which is not indicated by the experimental data (points).

**Figure 5.**
the MO based parameters at temperatures above 323 K, increasing the $k_{ij}$ value causes phase splitting.

VLE calculations made with PC-SAFT and CK-SAFT using parameter sets fit to pure component vapor pressure and saturated liquid density data are shown in figures 6 through 10 for various systems of methanol + (n-alkane). As shown in figure 6 for the methanol + propane system, both PC-SAFT and CK-SAFT have approximately the same ability to model the phase behavior of these systems. While the calculated liquid phase compositions agreed with the

![Graph showing VLE calculations](image)

VLE calculations fitted to the experimental data set are presented for the methanol + propane system. Both PC-SAFT (solid line) and CK-SAFT (dashed line) show an excellent ability to correlate the experimental data (points) for 313 K (CK $k_{ij}=0.032$ PC $k_{ij}=0.041$) and 343 K (CK $k_{ij}=0.037$ PC $k_{ij}=0.042$)

**Figure 6**
experimental data, the vapor phase calculations slightly underestimate the amount of methanol in the alkane rich phase. As shown in figure 7, both PC-SAFT and CK-SAFT qualitatively predict VLE data for the methanol + hexane system with \( k_{ij} = 0 \).

As temperature increases, quantitative reproduction of the data is not possible unless \( k_{ij} \) is non-zero, as shown in figures 7\textsuperscript{90, 91} and 8. Once the \( k_{ij} \) value is established, both CK-SAFT and PC-SAFT have about the same ability to correlate experimental data. PC-SAFT more accurately reproduces the shape of the bubble point curve at high alkane concentration, while CK-SAFT is more accurate at low alkane concentration as shown in figure 8\textsuperscript{90, 91}. PC-SAFT gives a better estimate of the vapor phase compositions.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{VLE calculations for methanol + hexane with a \( k_{ij} \) of 0.0, showing that PC-SAFT and CK-SAFT, from only pure component parameters, will predict the presence of azeotropic behavior in systems. CK-SAFT (dashed line) correlate the data slightly better when \( k_{ij} = 0.0 \) than PC-SAFT (solid line).}
\end{figure}
Plot of VLE for the methanol + hexane system with fitted $k_i$ values. Both PC-SAFT (solid line) and CK-SAFT (dashed line) are able to correlate the data accurately. PC-SAFT tends to more accurately correlate the data in the alkane rich region once the $k_i$ value is fitted, while CK-SAFT tends to slightly better represent the behavior in the methanol rich region. 

Figure 8.
Table 5. VLE $k_{ij}$ values for PC-SAFT and CK-SAFT
This table lists the fitted binary interaction parameters ($k_{ij}$) values used in this study. PC-SAFT values are listed first, followed by CK-SAFT values after the slash mark.

<table>
<thead>
<tr>
<th>Methanol</th>
<th>Propane</th>
<th>Butane</th>
<th>Pentane</th>
<th>Hexane</th>
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<td>0.074</td>
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</tr>
</tbody>
</table>
VLE for the methanol + heptane system at 313 K. Both CK-SAFT and PC-SAFT accurately correlate the data, with $k_{ij}$ values of 0.042 for CK-SAFT and 0.045 for PC-SAFT.

**Figure 9.**

For all the VLE systems studied here, the $k_{ij}$ parameter is between 0.0 and 0.08, and is a linear function of temperature for all methanol + alkane systems. VLE $k_{ij}$ values determined by fitting to the azeotrope point are presented for all the systems modeled here in table 5. In a previous study, Enders and Kahl\textsuperscript{92} show that CK-SAFT could correlate data over a 45 K temperature range with a constant $k_{ij}$ value. In this investigation, we find linear temperature dependence is necessary to correlate date over a temperature range of 190 K, as shown in figures 9\textsuperscript{93} and 10\textsuperscript{94}.

When the $k_{ij}$ values are plotted against temperature for each system, the slope of the line for PC-SAFT is less than that of CK-SAFT, showing that the temperature dependence of PC-SAFT is less than that of CK-SAFT. A general
correlation for $k_{ij}$ based on the molecular weight of the alkane molecule and the temperature, was obtained by fitting to data from propane (C3) to decane (C10).

$$k_{ij} = A*T + B$$  \hspace{1cm} (3.13)

where, for CK-SAFT

$$A = -2.6459*10^{-6}*\text{MW} + 4.6380*10^{-04}$$  \hspace{1cm} (3.14)

$$B = 1.1399*10^{-03}*\text{MW} - 0.13473$$  \hspace{1cm} (3.15)

and for PC-SAFT

$$A = -3.7681*10^{-6}*\text{MW} + 6.0760*10^{-4}$$  \hspace{1cm} (3.16)
Comparison of fitted $k_{ij}$s for pentane and heptane are shown with the general

\[ B = 1.3832 \times 10^{-3} \times MW - 0.16606 \]  
(3.17)

High temperature VLE for the methanol-heptane system is also well reproduced by PC-SAFT and CK-SAFT. It is interesting to note that over ~190K temperature range that the $k_{ij}$ values for both CK-SAFT and PC-SAFT are linear functions of temperature.

**Figure 10.**

correlations in figure 11 for CK-SAFT and figure 12 for PC-SAFT. As shown in
the preceding figures, CK-SAFT(HF) tends to predict the phase equilibria better
than CK-SAFT(B3), but neither reproduce the data as well as PC-SAFT or CK-
SAFT. Turning from the VLE calculations to the Liquid-liquid equilibria (LLE)
calculations, LLE calculations using the MO parameter sets are in poor
agreement with experimental data. In general, LLE calculations made with the
MO derived parameter sets have three things in common: they predict an upper
Plot of correlation $k_{ij}$ vs. fitted $k_{ij}$ values for CK-SAFT. The $k_{ij}$ values determined from the correlation adequately reproduce the $k_{ij}$ values determined from data fitting. The correlation is based on the best fit $k_{ij}$ values determined for C3 through C10.

**Figure 11**

critical solution temperature (UCST) up to 50% higher than the experimentally

Plot of correlated $k_{ij}$ values vs. fitted $k_{ij}$ values for PC-SAFT. Note that the slope of the $k_{ij}$ correlation for PC-SAFT is less than the $k_{ij}$ correlation slope for CK-SAFT, indicating that PC-SAFT $k_{ij}$ have a lesser temperature dependence.

**Figure 12**
determined UCST temperature, they predict that the solubility of methanol is
greater in the alkane-rich phase than experimental data suggest and they predict
the solubility of alkane in the methanol rich phase is less than the experimentally
determined solubility. It is not possible to fit LLE calculations to the experimental
data by adjusting the $k_{ij}$ value for either the CK-SAFT(HF) or CK-SAFT(B3)
parameter sets.

The results for PC-SAFT and CK-SAFT LLE calculations are shown for
butane-decane in figures 13 through 18, for several isobars, ranging between .1
and 150 MPa. As with the VLE calculations, a $k_{ij}$ parameter is required to
reproduce the experimental data. Table 6 shows $k_{ij}$ values determined by fitting
to experimental LLE data in order to minimize the average absolute

<table>
<thead>
<tr>
<th>Methanol +</th>
<th>Butane</th>
<th>Pentane</th>
<th>Hexane</th>
<th>Heptane</th>
<th>Octane</th>
<th>Nonane</th>
<th>Decane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, Bar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.039</td>
<td>0.039</td>
<td>0.031</td>
<td>0.0331</td>
<td>0.034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.0323</td>
<td>0.0345</td>
<td>0.038</td>
<td>0.032</td>
<td>0.033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.038</td>
<td>0.039</td>
<td>0.038</td>
<td>0.032</td>
<td>0.033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.033</td>
<td>0.035</td>
<td>0.038</td>
<td>0.032</td>
<td>0.033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.037</td>
<td>0.038</td>
<td>0.037</td>
<td>0.033</td>
<td>0.033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>0.034</td>
<td>0.035</td>
<td>0.033</td>
<td>0.033</td>
<td>0.033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.033</td>
<td>0.034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1400</td>
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<td>0.035</td>
<td>0.033</td>
<td>0.034</td>
<td>0.034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.036</td>
<td>0.035</td>
<td>0.033</td>
<td>0.034</td>
<td>0.034</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6. LLE $k_{ij}$ values for PC-SAFT and CK-SAFT. PC-SAFT values are
presented first, followed by CK-SAFT values in italics. $k_{ij}$ values were held constant for each
isobar to minimize the amount of data fitting required to reproduce these systems.
Liquid-liquid equilibria for the methanol + butane system as predicted by PC-SAFT and CK-SAFT. Calculations made by fitting the $k_{ij}$ value to the experimental data. Note that, for these shorter alkanes, CK-SAFT performs substantially better than PC-SAFT, but both equations of state predict relatively good results for the alkane rich phase. The methanol rich phase is somewhat poorly represented at lower pressures, where the amount of methanol is under predicted.

**Figure 13**

deviation. This $k_{ij}$ value is held constant for each isobar. An alternate method of determining the $k_{ij}$ values is to use the values predicted from the correlation based on VLE data. Using the general $k_{ij}$ correlation based on VLE calculations, we are able to predict LLE behavior for the systems methanol + pentane through methanol + heptane. Calculations for other systems were fitted to experimental data.

Figure 13 shows the methanol + butane$^{95}$ system. As shown in the figure, the predictions made with CK-SAFT for the alkane rich phase agree quite well with the experimental data, while PC-SAFT tends to under-predict the amount of methanol present in the alkane rich phase. Both PC and CK SAFT predict a
methanol rich phase that is slightly lean in methanol, but which improves with increasing pressures.

Figure 14 depicts the methanol + pentane\(^{95}\) system in which both variants of the equation of state show adequate agreement with the experimental data. As shown in figure 14 CK-SAFT more accurately reproduces the solubility of methanol in both phases at temperatures below 97% of the UCST, but over predicts the UCST, whereas PC-SAFT more accurately captures the UCST but tends to underestimate the amount of methanol in the alkane rich phase while overestimating the amount of methanol in the methanol rich phase at temperatures below about 97% of the experimentally observed UCST. The

![Figure 14](image)

Liquid-liquid equilibria for the methanol + pentane system. CK-SAFT tends to predict better phase equilibria in the alkane rich phase. In the methanol rich phase, PC-SAFT tends to predict better equilibria closer to the UCST, while CK-SAFT tends to predict better equilibria far away from the UCST, and tends to over predict the UCST.

**Figure 14**
differences in phase behavior are solely attributable to the dispersion term.

For the methanol + hexane\textsuperscript{96, 97} system in figure 15, PC-SAFT is in better agreement with the experimental solubilities overall, giving semi quantitative results at lower pressures and quantitative results at higher pressures. PC-SAFT even comes very close to predicting the UCST, which CK-SAFT predicts is both at a higher temperature and at a higher mole fraction of methanol than the experimentally determined UCST. In the methanol + heptane\textsuperscript{97-99} system shown in Figure 16, PC-SAFT comes very close to describing the data in a quantitative

![Graph showing liquid-liquid equilibria for the methanol + hexane system. Both PC-SAFT and CK-SAFT have similar abilities to reproduce the experimental data in the alkane rich phase, with both equations of state slightly under estimating the methanol present in the alkane rich phase. In the alcohol rich phase, however, CK-SAFT tends to overestimate the amount of methanol present from up to 34 mole %, where as PC-SAFT tends to be considerably closer to the experimental data with a maximum error of 15 mole %, while being considerably closer to the experimental UCST. Figure 15.]
fashion, reproducing both the UCST and the solubilities far from the UCST very accurately over all pressures. CK-SAFT, on the other hand shows good agreement only at lower pressures far removed from the UCST. For all pressures, CK-SAFT predicts a UCST that is 10-16 K higher than the experimentally determined UCST, and 5-13% too rich in methanol. CK-SAFT also predicts a methanol rich phase that is richer in methanol than experimentally

![Graph showing liquid-liquid equilibria](image)

Liquid-liquid equilibria in the methanol + heptane system for PC-SAFT (solid line) and CK-SAFT (dashed) lines. PC SAFT is capable of nearly quantitative description of the experimental data, while CK-SAFT over estimates the upper consolute solution temperature (UCST) and the amount of methanol present in the methanol rich phase.

**Figure 16**

determined compositions. Methanol + octane and methanol + decane are shown in figures 17 and 18.
As shown in figure 17 for the methanol + octane\textsuperscript{97, 98, 100} system, PC-SAFT is still able to reproduce the experimental data more faithfully than CK-SAFT, however, both equations of state are beginning to show the same deviations from the experimental data; they both do a adequate job of predicting the composition of the alkane rich phase, but they both predict a UCST that occurs at a higher temperature and higher methanol fraction than the experimentally determined UCST point.

Figure 17

Liquid-liquid equilibria for the system methanol + octane from 1 MPa to 150 MPa. Filled circles are from Kiser et al., filled triangles are from Kurihara et al. and hollow points are from Ott et al. As with the other alkanes longer than C6, PC SAFT tends to more closely predict the UCST. Both SAFT variants tend to predict up to 12% more methanol in the methanol rich phase.
For the methanol + decane\textsuperscript{96} system, the deviation continues to increase. PC-SAFT still predicts values that are closer to the experimentally determined values, but the deviation is of a similar order of magnitude as CK-SAFT.

Both PC and CK-SAFT are capable of reproducing both VLE and LLE behavior for the highly non-ideal methanol-alkane systems. The SAFT parameters fit to liquid density and saturated vapor pressure data perform significantly better than those derived by Wolbach and Sandler from molecular orbital calculations. However, this does not completely discount the use of MO calculations to determine SAFT parameters when experimental data is non

![Graph showing liquid-liquid equilibrium](Image)

Liquid-Liquid equilibria in the methanol + decane system. Neither CK SAFT of PC SAFT do an acceptable job of predicting the liquid-liquid equilibria in this system. It is interesting to note that, unlike the lower weight alkanes, PC SAFT is closer to the experimental data.

Figure 18.
existent.

The MO values are calculated using isolated pairs of molecules\textsuperscript{76}. One might expect that multibody polarizability effects are important for hydrogen bonding and polar molecules, and that explicitly incorporating these dipolar effects will improve the ability of the MO based parameters to predict data. Quadrupolar contributions are not expected to be as important in these sorts of systems because the dipole strength of methanol is so great. The HF parameters probably performed better because the Hartree-Fock calculation method is less rigorous\textsuperscript{101} than the Becke-3LYP calculation method, and as such has more cancellation of error.

Both PC and CK-SAFT required a temperature dependent $k_{ij}$ parameter for fitting VLE and LLE data. For specific methanol-n-alkane systems used in this paper, the correlations presented will give a $k_{ij}$ value that can be used to predict VLE phase behavior within 3-8% of experimental values. For LLE behavior in systems where the alkane is shorter than octane, PC SAFT generally gives adequate results for all the systems, but in general the $k_{ij}$ values had to be established for the heptane through decane systems by fitting the $k_{ij}$ value to experimental data rather than using the VLE correlation. The general correlations given can be used to give estimates of the $k_{ij}$ required to model the phase behavior for higher molecular weight alkanes for VLE, and can be used as a starting point for LLE calculations.
CK-SAFT and PC-SAFT give reasonable estimates of the LLE for methanol + alkane systems using a $k_{ij}$ based solely on VLE data for pentane through heptane. For octane and heavier alkanes, CK-SAFT predicts a UCST that is at a greater temperature than the experimentally determined critical temperature, and at a greater mole fraction of methanol than the experimentally determined composition. PC-SAFT performs well for heptane and gives reasonable estimates for octane. For the systems with nonane and decane in them, PC-SAFT deviates in the same fashion as CK-SAFT, predicting a methanol rich phase too rich in methanol and a UCST that is too high in temperature, but to a lesser extent.
4. Experimental Design and Apparatus Construction

Introduction

In order to measure the water content of methane, ethane, methane + carbon dioxide and ethane + carbon dioxide gas mixtures at high pressures, a new apparatus had to be constructed. The new equipment had to fulfill the following criteria:

- Operational within 10 months of signing contract
- Metallurgy capable of withstanding 120 MPa (18,500 pisa) at 477 K (~400 F), pH levels as acidic as 3.5 without corrosion
- Capable of measuring with uncertainties of only 2-5%
- Maximize operator safety without incurring unreasonable costs

The general experimental method used in this study is a steady state flow method. Flow methods use a source of gas to maintain pressure in a sample cell while the gas phase is removed at a constant rate for analysis. Flow methods eliminate problems of water absorption on tubing that can be encountered in static type measurements. Flow methods rely on having sufficient mixing so that the gas entering the cell is at equilibrium, and require some form of static mixer (steel dispersion frit, glass dispersion frit or nozzles) to disperse the entering gas into tiny bubbles, and sufficient testing to ensure that the flow rates are not so high as to cause under-saturation of the gas.

Before detailed design and construction work could begin, several experimental techniques were screened for measuring water content in a flowing
gas stream in order to determine which ones would work best with the flow system. The techniques that we examined were cold trapping, desiccants, gas chromatography and electrical resistance measurements.

The first technique screened was a reaction chromatography technique used by Adeeva et al.\textsuperscript{102} and Borisova et al.\textsuperscript{103} where they measured the amount of water present in samples of coal and in ethylene, respectively by reacting the water with calcium carbide in order to form acetylene:

\[ H_2O + CaC_2 \rightarrow \frac{1}{2} C_2H_2 + CaO \]  \hspace{1cm} (4.1)

This is desirable from the chromatography standpoint, as acetylene can be detected using the more sensitive Flame Ionization Detector (FID). Unfortunately, the stoichiometry shows that the reaction produces only half as much gas as water initially present. This presents a bit of a problem, as this decreases the sensitivity. Despite this limitation, the method was screened. Tests were run using an Antek gas chromatograph at 110 C with a blank, 3 meter stainless steel column, and integration was performed using a HP model 3390A integrator. 1 uL of liquid water was injected into a 6" by 3/8 O.D. stainless steel tube packed with CaC2 and sealed at both ends by septa. The tube was connected into the injection port and helium swept the gas phase contents into the column. The experimental repeatability was poor, as shown in table 7 below. This is not to say that the method is invalid, but more to say that it was more difficult to set up than desired. It is believed that the water was not completely reacting with the CaC2 to form acetylene, causing the wide variation in error.
Table 7. Integration area for gas chromatography

<table>
<thead>
<tr>
<th>Water Volume µL</th>
<th>Integrator area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 ± 0.02</td>
<td>545477</td>
</tr>
<tr>
<td>1.0 ± 0.02</td>
<td>474747</td>
</tr>
<tr>
<td>1.0 ± 0.02</td>
<td>237845</td>
</tr>
</tbody>
</table>

The second method screened was the physical ‘freezing out’ of water in a u-tube, as practiced by Olds et al\textsuperscript{104}. The advantages to this method are its relative simplicity as one merely immerses the trap into a dewar filled with acetone and dry ice. One of the disadvantages is that evacuating the trap before and after the experimental run is time consuming. The other major disadvantage is that the trap can clog, blocking the flow of gas into the trap. These disadvantages were deemed to be small enough and a small volume cold trap, complete with magnetically coupled ball valves, was fabricated.

Figure 19. Cold Trap
The 34 cm\textsuperscript{3} internal volume cold trap has one inlet, one outlet valve with perforated downcorner. A silicone rubber o-ring was used to seal the body to the head, and Teflon packings were used to seal the valve stems. Connections were made using 1/16 Swagelok tubing. Penny in center shown for scale.

Figure 20. Head detail of cold trap.
Shown at right is the head of the light weight cold trap, with the inlet valve disassembled. The valve stem and packing assembly is shown in the right half of the photo. A rare earth magnet in the stem held the ball bearing for movement, and allowed the ball to seat easily.
Photos of the unit are shown in figures 19 and 20. This method was used for a short while before the desiccant absorption method was adopted.

Because of repeated problems with the cold traps either becoming obstructed with ice or with valves failing to seal, the cold trapping was only used for a few weeks before it became apparent that this method was going to be excruciatingly slow.

The next method screened was the chemical reaction of water with a desiccant, magnesium perchlorate. The water rapidly and irreversibly bonds to the magnesium perchlorate, according to the reaction

\[ 10H_2O + Mg(ClO_4)_2 \rightarrow MgClO_4 * 10(H_2O) \]  

(4.2)

Where the right hand side of the reaction represents the hydrated form. Although the reaction is irreversible at temperatures below about 423 K, the water can be driven off at temperatures above 463 K. The equilibrium mass of water vapor with magnesium perchlorate is \(1 \times 10^{-6}\) grams of water per liter of gas\(^{30}\), which means that effectively all water is removed from the samples.

However, there was an open question as to physical absorption of heavier gases (C\(2^+\) and CO\(_2\)) in the desiccant. This was tested as a preliminary measure prior to desiccant use, and the results are shown below in table 8.

<table>
<thead>
<tr>
<th></th>
<th>Volume of gas</th>
<th>Apparent mass change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>1.0</td>
<td>+0.01 mg</td>
</tr>
<tr>
<td>Methane</td>
<td>0.9</td>
<td>-0.01 mg</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.9</td>
<td>+0.00 mg</td>
</tr>
</tbody>
</table>
Tubes were filled with desiccant, flushed with dry nitrogen and the weight of the tube recorded. Dried sample gas was then passed through the tube, and the weight of the tube after the run was recorded. The tube was flushed again with dry nitrogen and the weight recorded. The nitrogen charging is used to ensure that any mass changes observed were the result of hydrocarbon absorption and not gas buoyancy. As one can see, the desiccant does not appear to retain carbon dioxide, methane or ethane. The results indicate the maximum error involved in making the measurements is at the very edge of the last digit (0.01 mg) of the scale's readability. The nitrogen charge was abandoned later in favor of charging with the gas mixture being measured as this saved time.

Lastly, a GE-Panametrics electrical resistance sensor was screened for measuring the low-temperature isotherms (~310 K). The GE-Panametrics sensor is an aluminum oxide/gold sensor that measures the change in the resistance across the sensor as water is absorbed/desorbed on the sensor. As the water content changes, so does the resistance across the sensor. The sensors are calibrated by GE using NIST traceable equipment. The units perform satisfactorily under most conditions, but are limited to a maximum practical operating temperature of approximately 320 K, which means that they are unsuitable for higher temperature measurements. However, they are superior to the desiccant measurements at low temperatures and high pressures because
they do not require large sample volumes in order to obtain good measurement results. The sensor was used for the low temperature measurement of methane and ethane systems.

Having screened the available measurement techniques, a combination of cold trapping, desiccants and electrical resistance measurements were used in the experimental work. The measurements were in generally in good agreement with each other, differing by approximately 5%.

**Calibration of Equipment**

The major pieces of equipment requiring calibration were the four pressure transducers, the wet test flow meter and the thermocouples used to measure temperatures. All thermocouples were checked against a NIST traceable Leeds and Northrup Platinum resistance thermometer, accurate to within 0.001 C. The thermocouples read to within 0.2 K of the PRT indicated temperature from 273 to 423 K. A National Instruments PCI 4153 data acquisition board with a CBT-68 terminal block was used to provide cold junction compensation for the thermocouples and ground referencing for the pressure transducers, as well as communication with the logging computer.

Pressure transducers were calibrated using a Ruska dead weight tester and a hydraulic gauge tester. Pressure was generated using the dead weight tester or hydraulic pump and pressures were read using Heise gauges, accurate to 0.5% of full scale, with full scales of 500, 5,000 and 10,000 psia, as appropriate to the full scale of the transducer. The transducers were connected
to the tester and the pressure read from the gauges. A linear calibration was laid into the LabVIEW control computer for each transducer. The system was depressurized and re-pressurized to check each transducer for hysteresis. An offset of 0.1 psi was observed for the 0-1,500 psi transducer, 50 psi for the 0-10,000 psi transducer and 75 psi for the 0-20,000 psi transducer. For pressures exceeding 500 psi, a hydraulic gauge tester was used instead of the Ruska dead weight tester as a gauges were not available to fit the Ruska dead weight tester. The pressure transducers were spot checked yearly using nitrogen gas and the 0-5,000 psi Heise gauge. The 1-1500 psi transducer had an uncertainty of 0.1% of full scale, the 0-10,000 had an uncertainty of 0.5% of full scale, and the 0-20,000 had an uncertainty of 0.3% of full scale.

The Precision Scientific wet test flow meter calibration was checked using a Ruska 1000 cm$^3$ positive displacement pump. The pump was evacuated and carbon dioxide or methane gas was charged into the pump to atmospheric pressure. The pump was vented to ensure that the contents were at atmospheric pressure, and then connected to the wet test flow meter, and the desired volume pumped through. For volumes in excess of 1000 cm$^3$, the pump was cycled again, with a vent step to ensure the contents of the pump started at atmospheric

<table>
<thead>
<tr>
<th>Volume in cm$^3$</th>
<th>Meter reading, ft$^3$</th>
<th>Volume in, ft$^3$</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999 CH$_4$</td>
<td>0.0694</td>
<td>0.06941</td>
<td>-0.01</td>
</tr>
<tr>
<td>1999 CO$_2$</td>
<td>0.0694</td>
<td>0.06941</td>
<td>-0.01</td>
</tr>
<tr>
<td>997 CH$_4$</td>
<td>0.0346</td>
<td>0.03462</td>
<td>-0.05</td>
</tr>
<tr>
<td>997 CO$_2$</td>
<td>0.0346</td>
<td>0.03462</td>
<td>-0.05</td>
</tr>
</tbody>
</table>
pressure. The readings are summarized in table 9 below, indicating that within the volumetric uncertainty of the tubing used to connect the pump to the meter, the factory calibration of the flow meter is accurate, and suitable for our purposes. Generally, the smallest sample size is 6 L (0.2 ft³), and the smallest water deposition is 0.015 grams, which would lead to a relative error of 0.2% in the mole fraction of water reported. There was no discernable difference between the volumes for each of the gases as far as the flow meter was concerned.

The independence of flow rate was also verified. Five flow rates ranging from 0.001 ft³/sec to 0.05 ft³/sec were used to establish the flow rates at which the mass of water removed did not change, indicating sufficient residence time for complete saturation. As shown in table 9b, the mass of water recovered from the three u-tubes is constant until 0.015 ft³/sec, and at 0.05 ft³/sec the flow of gas is too fast to ensure complete saturation. Thus, the experimental flow rates were run between 0.0005 ft³/sec and 0.005 ft³/sec. This also enabled tighter pressure control as the slower flow rate allowed for lower pump speeds to be used and more time to adjust flow rates.

<table>
<thead>
<tr>
<th>Run</th>
<th>Mass of water removed, mg</th>
<th>Flow rate ft³/sec</th>
<th>Volume ft³ φ 15 C and 1.013 MPa</th>
<th>% mass in first u-tube</th>
<th>% mass in second u-tube</th>
<th>% mass in third u-tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>236.75</td>
<td>0.0001</td>
<td>1.840</td>
<td>99</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>237.18</td>
<td>0.0005</td>
<td>1.844</td>
<td>99</td>
<td>1</td>
<td>0</td>
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<tr>
<td>3</td>
<td>235.9</td>
<td>0.001</td>
<td>1.829</td>
<td>98</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>238.8</td>
<td>0.0015</td>
<td>1.817</td>
<td>97</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>150.23</td>
<td>0.005</td>
<td>1.818</td>
<td>80</td>
<td>19.9</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>152.5</td>
<td>0.005</td>
<td>1.860</td>
<td>80</td>
<td>19.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Experimental Set Up

The solubility of water in these supercritical hydrocarbon gases is measured using a flow scheme similar to that of Benson\textsuperscript{105} or Rigby and Prausnitz\textsuperscript{106}. Figure 21 shows the important components of the experimental apparatus, which consists of a gas cylinder (S), a 1000 cm\textsuperscript{3} Ruska boost
pump(P1), a 500 cm³ Ruska main pump(P2), a 24 foot temperature equilibration coil(EC), the saturation cell(SC), on-off and throttling valves (TV1 and TV2), analysis train and a flow meter(F). Both EC and SC are contained in a thermostatically controlled air bath, which is controlled to within 0.3 K using a 1.8 KW heater coupled to an OMEGA CN9000A PID temperature controller. The controller parameters were determined using the Cohen-Coontz tuning method.

The 1000 cm³ Ruska pump is equipped with a direct current (DC) drive motor and a rapid traverse alternating current (AC) motor. When operated from the drive motor, the pump is capable of flow rates from 0.001 cm³/hr to 4000 cm³/hr. The traverse motor is capable of moving the piston from full displacement back to zero in about 2 minutes. Each full revolution of the pump drive shaft displaces 5.0 cm³ of volume, and is accurate to ±0.01 cm³. Although the DC motor of the pump was originally designed to be run from a computer controller, problems with the computer led to its replacement with a variable transformer (variac). The variac's output voltage could be adjusted to vary the DC motor RPM and produce the desired flow rate, but the modification defeated the forward position safety interlock which prevented bottoming the piston against the cylinder. This was deemed unacceptable, and an additional relay was added to prevent inadvertent bottoming out of the piston. This pump is capable of generating pressures up to 86 MPa. Teflon chevron packings provide the mechanical seal between the piston and the cylinder. These packings were tightened at periodic intervals to prevent leaks.
The 500 cm³ Ruska piston cylinder pump is capable of generating pressures up to 172 MPa. Power for the piston is provided by a rapid traverse motor or a reducing gear box transmission, capable of delivering the flow rates shown below in table 10. Like the 1000 cm³ pump, this pump is also equipped with an electrical resistance heater to keep the gas at the desired temperature. Also like the 1000 cm³ pump, Teflon chevron packings are used to form the mechanical seal, and were tightened periodically to ensure that no leaks were occurring.

<table>
<thead>
<tr>
<th>Transmission lever</th>
<th>Drive lever</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>A</td>
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<tr>
<td>C</td>
<td>80</td>
</tr>
<tr>
<td>D</td>
<td>320</td>
</tr>
</tbody>
</table>

Gas enters the system from the cylinder and is compressed to the desired pressure using positive displacement pumps P1 and P2. For high temperature runs, a 500 cm³ sample cylinder is installed between P1 and P2 and it resides in the heat bath. This cylinder is filled with 250 cm³ of degassed water, and acts as an additional saturator for the low pressure runs when the experiment is being run from cylinder pressure. From pump P2, the gas enters the equilibration coil where it is heated up to bath temperature. All pressure and temperature data from the pumps, heat bath and saturation cell are recorded using a data logger written in LabVIEW.
A detailed drawing of the saturation cell is given in figure 22. The cell has a nominal internal volume of 1,300 cm³, with an internal diameter of approximately 7.5 cm. Gas enters the cell and flows through a glass dispersion frit (PF) which disperses the gas into the liquid water as bubbles of a nominal diameter of 0.01 mm. A stainless steel retaining ring (RR) holds the frit in place at the bottom of the cell. The bubbles travel through the liquid water phase and into the head space of the saturation cell. A stainless steel baffle and an anti-entrainment section (shown in grey) prevent any water spray from leaving the saturation cell. Gas exits the saturation cell through two throttle valves; (TV1) is a standard vee stem valve, while TV2 is a precision needle valve for precise flow control, which reduces the outlet pressure to approximately 1 bar before passing to the analytical train. Three different pressure transducers (PT) monitor cell pressure; pressures below 70 bar use a Heise transducer, pressures from 70 to 700 bar use a Data Instruments transducer, and pressures from 700 to 1400 bar use a Sensometrics transducer. A J-type thermocouple (TC) located in a thermowell (TW, shown by cross hatching) monitors cell temperature. The J-type thermocouple was calibrated by OMEGA engineering against the ice and boiling points of water, and the melting points of tin and zinc, and was checked against a NIST traceable PRT to confirm the accuracy. An Autoclave Engineers rupture disc (RD) mounted in the anti-entrainment section provides over pressure protection. The dashed line indicates the approximate water level in the cell.
Figure 22. Saturation cell schematic.
This figure shows the internal details of the high-pressure saturation cell. The porous frit and retaining ring disperse the incoming gas into 1-2 micron bubbles, facilitating mass transfer. Cell temperature is recorded using a thermowell with a j-type thermocouple inside. Over pressure protection is provided by a 19,500 psia rupture disc, and internal pressure is measured by two pressure transducers, one 0-10,000 and one 0-20,000 depending on the pressure under investigation. The anti-entrainment baffle section is made from 304 stainless and Teflon. The O-rings were either Viton for the hydrocarbon rich mixtures, or Teflon for the carbon dioxide rich mixtures.
Analytical train A consists of the General Electric(GE)-Panametrics moisture analyzer (PMA), three desiccant charged stainless steel u-tubes (U) and gas flow meter (F). The PMA measures the water content by measuring the resistance across an aluminum oxide sensor; as the water present in the gas stream changes, so does the resistance across the sensor, which is converted by the PMA into a mole fraction and a mass of water per volume reading. The unit is calibrated by GE using NIST traceable standards, and is recalibrated by GE yearly. Both PMA and the desiccant charged tubes are used at temperatures below 333 K but temperature limitations of the PMA prevent its use above this temperature. All tubing between the throttle valve (TV1) and analytical train is maintained 10-20 K above air bath temperature using electrical heating tape to prevent condensation. The expansion pressure inside the detector was maintained constant during a run, and generally varied between 20 and 25 psia.

When using the desiccant charged u-tubes, the density of the sample gas inside the u-tubes will generally be slightly different from the density of the air inside the tubes when charging with desiccant. This buoyancy difference can lead to minor measurement errors if not taken into account. After several experimental tests, we found that purging the u-tubes with nitrogen (dried using a combination of Dehydrite®, magnesium perchlorate and molecular sieve 4a) before and after the experimental run is sufficient to eliminate buoyancy effects without introducing or removing detectable quantities water from the u-tubes. This procedure, although accurate and dependable, proved to be inconvenient as
it introduced an additional step into the process. Later, when the u-tubes were re-charged with desiccant, the same gas as the one under investigation was used to flush the air out of the u-tubes. This eliminated an extra weighing and flushing step.

In addition to the u-tubes for the 500 and 1000 psia runs at 300 and 400 F for all species, a receiving bottle of 355 cm³ internal volume was used before the desiccant charged u-tubes to capture the liquid water. This prevented complete saturation of the desiccant in the first u-tube. The receiving bottle was also flushed with the gas under investigation prior to weighing to eliminate buoyancy errors. The receiving bottle was constructed from thin wall aluminum and standard 3/8 stainless steel tubing, and the aluminum-stainless steel connections were further reinforced using high tensile strength epoxy resin.

A Sartorius CP-250D series scale, with an accuracy of 0.01 mg and a maximum capacity of 300 g is used to weigh the u-tubes. The scale had an internal calibration and temperature correction features. Calibration entailed ensuring the scale was level using the provided leveling gauge and pressing the calibrate button on the scale. The calibration is checked periodically against a set of standard grade Ohaus weights.

Materials

The methane and ethane used are ultra high purity grade (99.995% pure) from the Matheson gas company. The 90% methane, 10% carbon dioxide mixture was prepared by the Aeriform company, and has a stated molar
uncertainty of 0.01 moles. The 5% ethane, 95% carbon dioxide mixture is also
from Aeriform gas company, and has an uncertainty in the composition of 0.05
mole. Standard laboratory grade deionized, UV sterilized water with a maximum
conductance of 0.25 micro siemens ($\mu$S) is used without further distillation. The
anhydrous ACS grade magnesium perchlorate used is from VWR.

Experimental Procedure

2 L of deionized water is boiled under a slight vacuum (approximately 76
Torr pressure) at room temperature in a 4 L sample cylinder to remove dissolved
oxygen and nitrogen present in the water. Methane, ethane or gas mixture
(hereafter referred to as simply ‘gas’) is bubbled slowly into the cylinder until the
pressure in the sample cylinder reaches approximately 0.2 MPa. After a one hour
equilibration period, the gas is vented and the process repeated twice more to
ensure that no unwanted oxygen or nitrogen remain dissolved in the water. After
degassing, the water is used to completely fill the 1.3 L saturation cell, as shown
in figure 23. Gas is connected to the outlet of the analysis train and is used to
displace 250 to 400 cm$^3$ of water in order to create a gas cap in the saturation
cell. Sufficient gas is added to pressurize the cell and equilibration coil to
approximately 2 MPa. The heat bath is set to the desired temperature T and
allowed to equilibrate for approximately 12 hours until the cell internal
temperature has stabilized.
Because of the differences in the behavior of methane, ethane and carbon dioxide as they were compressed, the experimental procedure varied slightly depending on the composition of the gas and the pressure of interest. For pressures below the source cylinder pressure (13.78 for methane, 4.83 MPa for ethane, 10.34 MPa for the 10% CO₂ + methane mixture and 3.79 MPa for the 5% ethane + CO₂ mixture) for all gases, pump P2 was put in its maximum forward position, valves V1- V3 were opened and pump P1 used to control the flow rate and pressure as the variac/DC motor was able to control the pressure more precisely than the tank pressure regulator. For temperatures below 422 K, valve V6-V9 were opened, while valves V4, V5 and V10 were shut. For temperatures above 423 K but below pressures of 6.89 MPa, valve V6 was shut and valves V4 and V5 opened so that flow went...
through the pre-saturation column, ensuring that the gas was completely saturated.

For pressures above the cylinder pressure for the methane rich mixtures, pumps P1 and P2 are completely filled at cylinder pressure, and then valves V1 and V2 are closed, while valves V3, V6-V9 remain open. Pump P1 is used to maintain pressure up to 20.68 MPa. At pressures above 20.68 MPa, pump P1 is used to charge P2 up to 31.02 MPa, at which point valves V1-V7 are closed, while V8 and V9 remain open. Pump P2 is used to then charge and maintain the cell pressure.

For pure ethane cylinder pressure, a sample cylinder of 500 cm³ was added between gas source S and pump P1. This cylinder was evacuated using the lab vacuum pump for 24 hours. Valves V1 and V1' were opened allowing gas to charge the cylinder, while valve V2' was shut. The cylinder was then immersed in an ice bath. After the cylinder came to bath temperature, valves V1 and V1' were shut, V2' opened and the sample cylinder removed from the ice bath and heated to 373 K, boosting pressure in pump P1. Then, valve V2' was closed and the cylinder immersed in the ice bath. Once the cylinder had cooled to bath temperature, V1 and V1' were opened and the cycle repeated until the pressure in P1 was boosted to the desired pressure. Then the procedures outlined for methane above were followed to compress the gas.

For the ethane + CO₂ mixture, generating higher pressures by first cooling the mixture was not possible as it would cause one component to potentially
“dew” out, resulting in a change in the composition of the gas. The only answer in this case was consistent, tedious cycling of pump P1 coupled with heating pump P2 to 316 K for the 316 K isotherm experiments or 338 K for all other temperatures. For 1.72 and 3.45 MPa experiments, pump P1 was charged directly from the gas cylinder without the need for additional compressions. For pressures above 3.45 MPa pump P1 was charged from the cylinder by opening V1 and V2, and then V2 was closed. Pump P1 was then engaged and V3, V6 and V7 opened to pressurize pump P2. Once P1 had reached maximum travel position, V3, V6 and V7 were closed. This process could be repeated to build the pressure in pump P2 to 12.78 MPa. Building these pressures in excess of 15 MPa in pump P2 and the saturation cell could take on the order of days. Also vexing was the fact that there was usually only enough carbon dioxide rich gas available for two experimental runs at pressures above 40 MPa.

Since pressurization tends to raise the cell temperature approximately 0.5 K, the cell is allowed to come to thermal equilibrium with the bath before an experiment starts. For all mixtures, the cell was allowed to equilibrate for at least 12 hours when transitioning between pressures (i.e. from 1.72 to 3.44 MPa) and for at least 1 hour between experiments at the same pressure.
Once the cell is at the same temperature as the bath, the throttle valves are opened so that gas flows out of the cell and into the analysis train at a rate of 0.014 to 0.028 L-s\(^{-1}\) of expanded gas at ambient temperature and pressure. Cell pressure is maintained through a continuous flow of gas from either the cylinder, pump P1, or pump P2. Approximately 6-15 L of gas is used to equilibrate the analysis train so it is at steady state. This volume was determined by repeated experiments, taking the same sized sample at various purge volumes until the measurements yielded consistent results. The results of this experiment showed that about 6 L of gas flow were necessary for the analysis train to reach a steady

\textbf{Figure 24. Valve layout diagram}

All valves and auxiliary connections (vacuum pump, vents) are shown in this figure. The dashed cylinder shown between source S and Pump P1 could be added or removed as needed to provide a low temperature reservoir to facilitate compression of ethane.
state. Upon reaching steady state, if the desiccant traps are used valve V15 is switched from the vent to the chemical absorption tubes. If the PMA is in use, valves V12 and V14 are opened, while V15 is switched to the blocked position on the valve. The pressure from the transducer mounted in the expansion line is entered into the PMA.

An experiment will use between 15 and 56 L of expanded gas and a typical experiment will deposit in excess of 10 mg of water in the u-tube traps. Cell and pump pressures are constantly monitored and the pump flow rate is manually adjusted to maintain constant cell pressure throughout the experiment. The desired cell pressure is maintained by adjusting the variac on P1 or shifting the transmission on P2 to maintain the desired flow rate. Should this not be sufficient to maintain the pressure in the cell as constant, needle valve TV2 is adjusted so that the pressure is constant. Once a sufficiently large sample volume of gas passes through the analysis train, TV1 and V15 are closed, and a hemostat closes the Tygon tubing line from the last u-tube to the flow meter. The traps (and receiving bottle, if used) are removed, sealed and weighed. Gas volume is recorded using the flow meter, and this volume is corrected from ambient temperature and pressure to 0.1013 MPa and 288.65 K. Each (pressure, temperature) point is repeated a minimum of three times to ensure repeatability and accuracy. If any result differs by more than 3% from the mean of the three results, another data point is taken. At the beginning of each experiment, the tubes are packed with fresh desiccant and flushed with dried
gas, sealed using Suba-Seal® stoppers and weighed. Experiments have shown that the sealed tubes do not pick up more than 0.01 mg of mass over a 24 hour period and that traps do not pick up more than 0.01 mg of mass when the traps are connected and disconnected to/from the expansion train. These results indicate that the measurement technique is adequate. Once enough gas has flowed through the expansion train so that it is at steady state, the tubes are connected to the expansion train and the wet-test flow meter using Tygon® tubing and clamps. After the experiment, the tubes are disconnected, sealed, and weighed. The tubes are then flushed with dry nitrogen and re-weighed.

The volume of gas injected is used in conjunction with the model calculated compressibility factor and the volume of gas purged and sampled to double check for leaks in the system. Should the amount of gas input exceed the amount of gas withdrawn through conditioning and sampling, the purge and vacuum valves are checked to ensure they are closed, and a 2 hour pressure monitoring test is run. Should the cell pressure decrease during this time period, the system is taken off line and checked using Snoop and a Gow-Mac hydrocarbon detector for leaks.
5. Experimental Results and Discussion

The systems methane + water and ethane + water will be presented first. Shown in figures 25-27 for methane, 28-30 for ethane, 31-32 for the 90% methane+10% carbon dioxide and 33-34 for the 5% ethane+95% carbon dioxide system. In figure 25, the available data for methane + water literature investigations are plotted for the low temperature (298-344 K) data, while figure

![Graph showing mole fraction of water in methane phase vs. pressure.](image)

**Figure 25.** Water Content of Gaseous Methane from 298 to 344 K. Note that even at very high pressures, the methane gas shows no sign of an increasing solubility of water.
26 shows the mid range temperature (348-422 K) and figure 27 shows the high temperature (444-520 K) data.

In figure 25, the low temperature results from all investigations show that the general trend is to have increasing water content with increasing temperature, and decreasing water content with pressure, with the water content leveling out to a nearly constant value at pressures above 80 MPa. Note that the data of this investigation agree well with those of Olds et al. but those Rigby and Prausintz seem to contain slightly too little water.
Figure 26. Water Content of Gaseous Methane From 348 K to 422 K.
Data from Olds et al., Rigby and Prausnitz and this work. The same trends observed for the lower temperatures are repeated for the higher temperatures.

The water contents of the mid range temperature methane gas are shown in figure 26, showing that the trends first observed at the lower temperatures are observed for the higher temperatures. The water content begins to level out at approximately 85 MPa, instead of approximately 80 MPa. Finally, the high temperature data are shown in figure 27. The water content of the gaseous phase can be in excess of 50 mole % at the lower pressures for these systems. However, the same trends of water content with respect to pressure and temperature hold, and the water content becomes nearly constant at pressures exceeding 90 MPa.
Figure 27. Water Content of Gaseous Methane From 444 K to 510 K. Note that the water content of the methane gas is nearly constant at pressures above 90 MPa, and that the results of Olds et al. agree quite reasonably with the results of this work.
<table>
<thead>
<tr>
<th>Pressure, MPa</th>
<th>310.93</th>
<th>313.87</th>
<th>366.48</th>
<th>422.04</th>
<th>466.48</th>
<th>477.59</th>
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<td>3.45</td>
<td>2.21E-03 ±5%</td>
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<td>1.25E-01 ±4%</td>
<td>4.16E-01 ±5%</td>
<td>5.47E-01 ±6%</td>
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<tr>
<td>6.89</td>
<td>1.25E-03 ±5%</td>
<td>1.33E-02 ±5%</td>
<td>7.47E-02 ±4%</td>
<td>2.24E-01 ±5%</td>
<td>2.95E-01 ±5%</td>
<td></td>
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<tr>
<td>20.68</td>
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<td>6.00E-03 ±5%</td>
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<td>41.37</td>
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<td>3.97E-03 ±5%</td>
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<td>89.63</td>
<td>4.67E-04 ±5%</td>
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<tr>
<td>96.53</td>
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<tr>
<td>110.32</td>
<td>3.34E-02 ±3%</td>
<td>4.55E-02 ±3%</td>
<td>4.92E-02 ±4%</td>
<td>4.92E-02 ±4%</td>
<td>4.92E-02 ±4%</td>
<td></td>
</tr>
</tbody>
</table>

The water content for all the pure methane isotherms studied in this investigation is shown in table 11. The change in temperature from 310.9 to 313.9 K was to keep outside of the hydrate stability region, which at above 80 MPa was approximately 312.15 K. The reported points are the average of the three experimental runs made at the indicated temperature and pressure. At 311 and 314 K, the resistance sensor was used. Resistance measurements are assigned a weight of 0.25 and the average of the gravimetric measurements is assigned a weight of 0.75.

The ethane + water system is also broken down into low, medium and high temperature figures, shown in figures 28-30. Low temperature (310-366 K) results for the ethane + water are shown in figure 28, while the intermediate temperature results (377-444 K) are shown in figure 29, and the high
temperature results (444-510 K) are shown in figure 30. The same trends are observed for the ethane + water system as were seen in the methane + water system: the water content increases with increasing temperature and decreases to a nearly constant value at high pressures. For the low temperature ethane + water system, no solubility increase was observed near the gas critical point. For the low temperature measurements, our measurements are in good agreement at approximately 310 K those of Reamer et al. At high temperatures, our measurements agree quite favorably (within the experimental error) with those of
Reamer, and are very close to those of Danneil et al.\textsuperscript{29} near 477 K, but show a slightly lower water content than that of Danneil et al. at pressures above 110 MPa. However, this discrepancy is slight, and is close to the experimental error (0.01 mole/mole) reported by Danneil et al. Our results agree well with the trends of Danneil et al, and Reamer et al. namely that the water content of ethane becomes nearly constant at pressures above 120 MPa.

The experimental results are shown in table 12, where each state point was determined by taking a weighted average of the three gravimetric
experiments. Resistance based measurements are included at 315 K and the value reported is a weighted average, with the average of the three gravimetric points assigned a weight of 0.75 and the resistance measurement assigned a weight of 0.25.

![Graph showing mole fraction of water in ethane phase vs. pressure (MPa)].

**Figure 30. Water Content of Gaseous Ethane from 466 to 510 K**

Data from Danneil et al., Reamer et al. and this work.
<table>
<thead>
<tr>
<th>Pressure, MPa</th>
<th>314.82</th>
<th>366.48</th>
<th>422.04</th>
<th>466.48</th>
<th>477.9</th>
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<td>1.21E-01 ±3%</td>
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<td></td>
<td>3.72E-02 ±3%</td>
<td>4.78E-02 ±3%</td>
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Figure 31. Water content of 90% CH₄ + 10% CO₂, mixture from 421 to 463.5 K.

Data for the low temperature (314-366 K) 10% CO₂, 90% Methane mixture is shown in figure 31. Note that although this system has a slightly higher water content, it behaves in much the same manner as the pure methane+water or pure ethane + water systems, except that the amount of water present is slightly higher. The same trends are shown in the high temperature system.

Experimental results are shown in table 13. Each reported point is the average of three experiments at the given pressure and temperature. The panametrics sensor was not used during the course of the carbon dioxide investigations. Experiments were only run to a temperature of 463.5 K due to
Concerns about the CO₂ plasticizing

Figure 32. Water content of a 90% CH₄ + 10% CO₂ mixture from 314 to 366 K

Note that the system behaves much like the methane+ water or ethane+ water systems, but with a slightly increased water content.

The o-ring seal and causing the saturation cell to rapidly depressurize, generally leading to a large mess.
<table>
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<th>Pressure, MPa</th>
<th>Temperature, K</th>
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<tr>
<td>103.47</td>
<td>5.43E-04 ±7%</td>
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</table>
Figure 33. Water content of a 5% ethane, 95% CO₂ gas at 316 K
The behavior of this system is markedly different than either the pure carbon dioxide or pure ethane systems. Like carbon dioxide, the system shows a solubility minimum, but unlike carbon dioxide, the solubility of water in the gas phase at pressures above 20 MPa is markedly lower than pure carbon dioxide. The error bars on the highest pressures have been doubled over their calculated values because these points consist of only two experimental runs, instead of the usual three. This represents a possible error of 14% by mole.

High carbon dioxide (95%) mixture results are shown in figures 33-35 for the 5% ethane, 95% carbon dioxide mixture. The experimental points taken are in a slightly different fashion from the previous systems, as the phase behavior of this system exhibits a solubility minimum; as such many points were taken around the suspected area of the minimum, while fewer were taken at higher pressures. Results are shown in figure 33 for the low temperature (316 K), figure 34 for the intermediate temperature (364 K) and in figure 35 for high temperature (421 K).
Figure 34. Water content of a 5% ethane, 95% CO₂ gas at 364.15 K
At 364 K, solubility minimum becomes less pronounced than at lower temperatures, and the pressure at which the minimum occurs increases.

The low temperature results shown in figure 33 show a dramatic solubility increase (relative to the behavior seen in pure ethane) much like that shown with pure carbon dioxide. However, unlike carbon dioxide, the solubility of water at high pressures in the 5% ethane, 95% carbon dioxide mixture is markedly less than that of pure carbon dioxide at this temperature. It appears that the effect of even a slight amount of ethane in the carbon dioxide is to depress the water content at high pressures, while having a minimal effect on the water content at pressures below the solubility minimum. In figure 33, the high pressure points had the error bars increased to reflect the fact that only two experiments were performed to determine the water content, instead of the usual three.
Figure 35. Water content of a 5% ethane, 95% carbon dioxide gas at 421.15 K

At this temperature, the solubility minimum is very small, but still present. Again, the error bars were doubled for the 41 and 89 MPa points because only two experiments were run for these points.

At 364 K, the solubility minimum is less dramatic than that observed at 314 K, but never the less is still present. Again, the effect of the ethane is to depress the solubility of water at high pressure relative to pure carbon dioxide, while essentially not changing the water content at pressures below the solubility minimum.

At 421.15 K, the solubility minimum is extremely small to the point of being negligible, but the high pressure behavior remains the same, attaining its limiting value at a much lower pressure relative to carbon dioxide or ethane. For the isotherms studied for the 5% ethane, 95% carbon dioxide mixture, it appears that
Table 14. Water content of a 5% ethane + 95% CO₂ (mole basis) gas as mole fraction

<table>
<thead>
<tr>
<th>Pressure, MPa</th>
<th>Temperature, K</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>316.5</td>
<td>364.15</td>
<td>421.15</td>
</tr>
<tr>
<td>1.72</td>
<td>0.00569 ±5%</td>
<td>0.04296 ±5%</td>
<td>-</td>
</tr>
<tr>
<td>2.87</td>
<td>0.2126 ±5%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.45</td>
<td>0.00351 ±5%</td>
<td>0.02667 ±5%</td>
<td>-</td>
</tr>
<tr>
<td>6.90</td>
<td>0.00270 ±5%</td>
<td>0.01632 ±5%</td>
<td>0.094 ±5%</td>
</tr>
<tr>
<td>8.62</td>
<td>-</td>
<td>0.01421 ±5%</td>
<td>-</td>
</tr>
<tr>
<td>9.22</td>
<td>0.00274 ±6%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13.45</td>
<td>-</td>
<td>0.01340 ±5%</td>
<td>-</td>
</tr>
<tr>
<td>13.79</td>
<td>-</td>
<td>-</td>
<td>0.052 ±6%</td>
</tr>
<tr>
<td>14.36</td>
<td>0.0031 ±5%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20.69</td>
<td>-</td>
<td>-</td>
<td>0.0515 ±6%</td>
</tr>
<tr>
<td>24.14</td>
<td>-</td>
<td>-</td>
<td>0.0529 ±5%</td>
</tr>
<tr>
<td>41.35</td>
<td>0.00350 ±14%</td>
<td>0.0143 ±14%</td>
<td>0.052 ±14%</td>
</tr>
<tr>
<td>89.61</td>
<td>0.00340 ±14%</td>
<td>0.0144 ±14%</td>
<td>0.052 ±14%</td>
</tr>
</tbody>
</table>

The water content essentially becomes constant at fixed temperature with increasing pressures at pressures above 40 MPa.
6. Vapor and Liquid Modeling of Light Hydrocarbon Systems With and Without, Carbon Dioxide, Hydrogen Sulfide or Brines

Modeling wet gas systems is of special interest to the oil and gas industries, as these systems are encountered in drilling, processing, transport and storage of hydrocarbon products. The proposed model follows an approach outlined by Cox and Moore\textsuperscript{107}.

General Phase Equilibrium Relationships

For the hydrocarbon + water system under consideration, the general phase equilibrium relationships are:

\[ f_{i}^{\text{liq}} = f_{i}^{\text{vap}} \]  \hspace{1cm} (6.1)

where is \( f_{i}^{\text{liq}} \) the fugacity of component \( i \) in the aqueous phase and \( f_{i}^{\text{vap}} \) is the fugacity of component in the hydrocarbon rich vapor phase. For the vapor phase, the fugacity can be written as:

\[ f_{i}^{\text{vap}} = y_{i} \hat{\phi}_{i}^{\text{vap}} (P, T, y) P \]  \hspace{1cm} (6.2)

where \( y_{i} \) is the mole fraction of component \( i \) in the vapor phase, \( \hat{\phi}_{i} (P, T, y) \) is the fugacity coefficient of the component in the gas phase, and \( P \) is the system pressure. For the purposes of this study, the fugacity coefficient in the vapor phase is calculated using the Peng-Robinson equation of state.

The liquid phase (in this case aqueous) fugacity can be calculated using an activity coefficient model or an equation of state model. For the equation of state model, the fugacity can be written as
\[ f_i^{liq} = x_i \hat{\phi}_i^{liq}(P, T, x) P \] (6.3)

where \( x_i \) is the mole fraction of species \( i \) in the liquid phase, \( \hat{\phi}_i^{liq} \) is the fugacity coefficient in the aqueous phase and \( P \) is the system pressure.

For the aqueous liquid, the liquid phase fugacity is written as

\[
\ln \left( f_{H_2O}^{liq}(P, T) \right) = \ln \left( \phi_{H_2O}^{sat}(T) P_{H_2O}^{sat}(T) \right) + \int_{P_0}^{P} \left( \frac{\nu_{H_2O}^{liq}(P, T)}{RT} \right) dP 
\] (6.4)

Where is \( \nu_{H_2O}^{liq} \) the volume of liquid water at \((T, P)\), \( P \) is the system pressure, \( P_{H_2O}^{sat} \) is the vapor pressure of water, \( \phi_{H_2O}^{sat} \) is the fugacity coefficient of water at saturation pressure and \( f_{H_2O}^{liq} \) is the fugacity of water.

Since cubic equations of state do not calculate the fugacity coefficients of water accurately, the aqueous phase fugacity is calculated using an accurate correlation for liquid phase fugacities\(^{108}\), or an equation of state explicit for water\(^{71}\). Although we are not investigating conditions were a second, hydrocarbon rich liquid phase could form, the presence of a hydrocarbon rich liquid phase can be accounted for explicitly using the Peng-Robinson equation of state to calculate \( \hat{\phi}_i^{liq} \).

**Gas Phase Calculation Methods**

The Peng-Robinson equation of state is written in the form:

\[
P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}
\] (6.5)
Where $P$ is the pressure, $R$ the universal gas constant, $T$ the absolute temperature, $v$ the volume, and $a(T)$ and $b$ are parameters for each chemical species. However, solving pressure explicit (or volume explicit) forms of any equation of state can be difficult to do numerically, as the pressures and volumes have large ranges in their possible values, which makes solving for these a difficult, unbounded optimization problem. However, the compressibility factor $Z = \frac{P_v}{RT}$ is generally bounded between 0 (liquid like densities) and 1 (gas like densities), which is amenable to a Newton-Raphson or Rachford-Rice type solution scheme. The equation can be re-arranged and written explicitly in terms of the compressibility factor:

$$Z = \frac{1}{\left(1 - \frac{B_{\text{Mix}}}{Z}\right)} \frac{A_{\text{Mix}}}{B_{\text{Mix}}^2} \left( \frac{B_{\text{Mix}}}{Z} \left( \frac{B_{\text{Mix}}}{Z} \right) ^2 \right)$$

(6.6)

$$b_i \rho \equiv \frac{B}{Z} \quad Z \equiv \frac{P}{\rho RT} \quad A_{\text{Mix}} \equiv \frac{\alpha_i P}{RT^2}$$

(6.7)

where $P$ is the system pressure, $R$ is the universal gas constant and $T$ is the system temperature, in Kelvin.

$$a_i \equiv \zeta_i \alpha_i; \quad \zeta_i \equiv 0.45723553 \frac{R^2 T_{\text{c.d.}}^2}{P_{\text{c.d.}}} \quad b_i \equiv 0.0779607 R \frac{T_{\text{c.d.}}}{P_{\text{c.d.}}}$$

(6.8)

$$\alpha_i \equiv \left[1 + \kappa_i \left(1 - \sqrt{T_{\text{r.d.}}} \right) \right] \quad \kappa_i \equiv 0.37464 + 1.54226 \omega_i - 0.26993 \omega_i^2 \quad T_r = \frac{T}{T_{\text{c.d.}}}$$

(6.9)

$$A_{\text{Mix}} = \sum_i \sum_j \gamma_i \gamma_j A_{ij} \quad B_{\text{Mix}} = \sum_i \gamma_i B_i$$

(6.10)
where \( P_{c_i} \), \( T_{c_i} \), and \( \omega_i \) are the critical pressure\(^{109}\), critical temperature and acentric factors for species \( i \) and \( y_i \) is the mole fraction of species \( i \) in the gas phase.

For more than one component in the gas phase, some mixing rules must be employed in order to determine what the interactions are between different chemical species. For our purposes, we use a simple geometric rule as suggested by Peng and Robinson

\[
A_{ij} = (1 - k_{ij}) \sqrt{A_{ii} A_{jj}}
\]

(6.11)

where \( A_{ii} \) and \( A_{jj} \) refer to the pure component values as calculated in equation (6.7), and \( k_{ij} \) is a binary interaction parameter.

**Aqueous Phase Calculations**

As stated earlier, two methods were investigated in order to determine the aqueous phase fugacity. The first is a correlation by Saul and Wagner\(^{108}\) for liquid water from freezing to the critical point. As shown in equation (6.4), we need the saturation pressure, saturation fugacity coefficient and liquid volume at the pressure and temperature of interest.
\[
\ln\left( f_{H,O}(P,T) \right)_{\text{pure}} = \ln\left( \phi_{H,O}^\text{sat}(T) P_{H,O}^\text{sat}(T) \right) + \int_{\rho_{\text{sat}}}^{P} \left( \frac{V_{H,O}(P,T)}{RT} \right) dP 
\]

(6.12)

The fugacity coefficient at saturation is calculated using a correlation fit to the 1995 ASME/NIST steam tables.

\[
274 < T < 647 \text{ K}
\]

\[
\phi_{H_2O}^\text{sat} = 1 - 0.00134092747753865 \times \exp\left( 9.7 \times \left( 1 - \frac{274}{T} \right) \right) + 0.00195670
\]

(6.13)

As correlated by Saul and Wagner, the saturation vapor pressure and liquid density of liquid water can be written as

\[
\ln\left( \frac{P_{H_2O}^\text{sat}}{P_c} \right) = \frac{T_c}{T} \left( -7.85823\tau + 1.83991\tau^{1.5} - 11.7811\tau^{2} + 22.67075\tau^{3.5} - 15.9393\tau^{4} + 1.77516\tau^{5.5} \right)
\]

(6.14)

\[
\frac{\rho^\text{sat}(T)}{\rho_c} = 1 + 1.99206\tau^{1/3} + 1.10123\tau^{2/3} - 0.512506\tau^{5/3} - 1.75263\tau^{10/3} - 45.4485\tau^{8/3} - 6756.15\tau^{10/3}
\]

(6.15)

\[
\tau = 1 - \frac{T}{T_c}
\]

(6.16)

Equations (6.13) to (6.15) are sufficient to perform calculations at pressures close to the saturation pressure, but at pressures far above saturation pressures, the density of the liquid phase can be considerably larger than that at saturation. In order to improve the density (and the liquid volume) at pressures far removed from saturation pressure, the following correlation was fit to the density data of the 1995 steam tables:

\[
\rho(P,T) = \rho^\text{sat}(T) + P \left( 200000.0 \left( \frac{1}{T} \right)^2 - 464.022 \left( \frac{1}{T} \right) + 3.947 \times \exp\left( \frac{T - 0.819T_c}{T_c} \right) - 2.924 \right)
\]

(6.17)
\[ V^L = \frac{1}{\rho(P,T)} \]  

(6.18)

as changes in the liquid volume have a dramatic effect on the fugacity at higher pressures, it is important to have this behave properly at high pressures. Equation (6.17) is a modification of Saul and Wagner's correlation in order to improve the density predictions. Unmodified, the Saul and Wagner correlation only predicts saturation densities, which can be substantially lower than the high pressure densities. This has been tested up to 200 MPa and shows reasonably good agreement with the data of the steam tables.

However convenient a correlation is, it is generally preferred to have an equation of state approach for calculating aqueous fugacities. Wagner and Pruss\textsuperscript{110} developed such an equation of state for the properties of water that has been adopted as the standard reference equation of state for water and steam by the American Society of Mechanical Engineers (ASME) and the National Institute for Science and Technology (NIST). The NIST/ASME\textsuperscript{71} formulation is a Helmholtz explicit equation of state valid from temperatures between \( \sim 250 \) to \( 1273 \) K and pressures from \( 0 \) to \( 1000 \) MPa. The basic formulation of the equation of state is:

\[
\frac{A(\rho,T)}{RT} = \frac{A^\text{ig}}{RT} + \frac{A^\text{res}}{RT}
\]  

(6.19)

where \( A \) is the total Helmholtz energy, \( A^\text{ig} \) is the ideal gas Helmholtz energy, and \( A^\text{res} \) is the residual contribution to the Helmholtz energy. The full details of this formulation can be found in Wagner and Pruss\textsuperscript{110} paper. Properties such as the
saturation pressure, fugacity and entropy among others, can be found by taking the appropriate derivatives, which Wagner and Pruss worked out in their paper. Thus, the fugacity is calculated from manipulations of equation (6.19).

**Fugacity of hydrocarbons in the aqueous liquid phase**

For calculations involving the solubility of the non-water components in the aqueous liquid phase, we can write the fugacity of each of the non-water, non-electrolyte components using an activity model as:

\[
f_i^L = x_i \gamma_{i,h}(I) H_i(T, P)
\]  

(6.20)

Where \(x_i\) is the mole fraction of species \(i\) in the aqueous liquid phase, \(\gamma_i(I)\) is the Henry’s law activity coefficient to correct for the presence of dissolved salts in the water, \(H_i(T,P)\) is the Henry’s constant between species \(i\) and water at temperature \(T\) and pressure \(P\). For the purposes of modeling methane, ethane, propane, carbon dioxide and hydrogen sulfide, we have used a correlation by Harvey\(^{111}\) for the Henry’s constant at saturation pressure. The correlation is:

\[
\ln H(T) = \ln \left( \frac{P_{\text{Sat}}}{P_{\text{solute}}} \right) + \frac{A}{\tau} + B(1 - \tau)^{0.355} + C \exp(1 - \tau) \tau^{-0.41}
\]

(6.21)

\[\tau = \frac{T}{T_{c,solute}}\]

where the vapor pressure of our solvent, water, is calculated using the NIST/ASME water equation of state or the Saul and Wagner correlation, depending on which is used for the fugacity calculations. However, as the
experimental work deals with high pressure phase equilibria, the Henry’s constant will vary with pressure.

For the hydrocarbons, carbon dioxide and hydrogen sulfide, the Kirchevsky-Kasarnovsky (KK) equation was found to describe the variation in Henry’s constant adequately from 0-150 MPa and from 274 to 510 K.

\[ \ln(H_i(T,P)) = \ln H_i^0(T) + \frac{V_i^\infty}{RT} \left( P - P_{\text{sat}} \right) \]  
(6.22)

In order for (6.22) to be a valid description of the phase behavior, a plot of \( \ln \left( \frac{f}{x_i} \right) \) versus \( P - P_{\text{sat}} \) must be a straight line. Shown in figures 36 to 38a are plots of \( \ln \left( \frac{f}{x_i} \right) \) versus \( P - P_{\text{sat}} \) for methane, ethane and carbon dioxide, which show that this holds up to 60 MPa for methane, 150 MPa for ethane and 150 MPa for carbon dioxide. Showing this relationship for methane at higher pressures was impeded by a lack of quality liquid phase data. In generating these plots, the fugacity was calculated as \( f = y_i \phi P \), where the fugacity coefficient is calculated using the Peng-Robinson equation of state, and experimental mole fractions were used for the concentrations in the liquid and vapor phases. For each species, the available experimental data\(^8\text{-}10, 27, 32, 39\) at temperatures around 313 K and 477 K was used to construct the plots to ensure linearity of the components for the entire temperature range studied in this investigation. As shown in figure 36 for methane, figure 37 for ethane and 38a for
carbon dioxide, the slopes are linear over quite a large pressure range, indicating that the KK equation is valid for these conditions.

In order to use the KK equation in phase equilibria calculations, we need to calculate the value of the partial molar volume at infinite dilution. Some correlation or theory is needed. A simple, effective corresponding states type correlation was proposed by Lyckman et al\textsuperscript{112}:

\[
\frac{P_{\text{ext}} v_{\text{ext}}^T}{RT_{\text{ext}}} = 0.95 + 2.35 \left( \frac{TP_{\text{ext}}}{cT_{\text{ext}}} \right) \quad (6.23)
\]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{Plot of ln(f/x) vs. P-P_{\text{sat}}w for methane}
\end{figure}

Note that the plots for both temperatures are linear, suggesting that the Kirchevsky-Kasarnovsky-Dodge-Wood equation is an adequate description of what is happening in the aqueous phase.
Where $P_{c,i}$, $T_{c,i}$ and $v^\prime_i$ are the critical pressure, critical temperature and partial molar volume at infinite dilution. $C$ is the cohesive energy density of water, which is defined as:

$$c = \frac{\Delta H_w - RT}{v^\prime_{H_2O}} = \frac{h^0 - h^l - RT}{v^l_{H_2O}}$$  \hspace{1cm} (6.24)$$

Where $\Delta H_w$ is the enthalpy of vaporization, $h^0$ is the enthalpy at temperature $T$ and zero pressure, $h^l$ is the enthalpy of the liquid at temperature $T$ and saturation pressure and $v^l$ is the molar volume of the liquid water at saturation. All of these

![Figure 37. Plot of ln(f/x) vs P-P_{sat} for ethane. Data from Danneil et al (square) and this work (diamond)](image-url)
quantities can be calculated using the NIST/ASME equation of state or \( \nu_{H_2O}^i \).

can be calculated with the Saul and Wagner correlation, and \( c \) can be calculated using the following correlation that was fit to NIST/ASME steam table data:

\[
c = a(T)^2 + b(T) + d
\]

(6.25)
Figure 38a. Plot of ln(f/x) vs P-P_{satw} for carbon dioxide.
Data from Zawisza and Malesinska, Weibe and Gaddy and Todheide and Franck

Where T is the temperature in K, and the coefficients are shown in table 16. Although equation (6.23) is quite satisfactory for predicting the partial molar volume at infinite dilution of the n-alkanes and carbon dioxide, it does not accurately predict the partial molar volume for hydrogen sulfide (H₂S). H₂S is similar in chemical make up to H₂O, as both have a electronegative species, the S and the O, respectively. Given these similar structures, we should expect an attraction between the molecules, which would lead to a negative partial molar volume. When plots of experimental data are constructed for the H₂S + water
system like those plotted in figures 36-38a, we see that the trends are linear (but with scatter), but have a negative slope, as

![Graph showing ln(f/x) vs Psatw for hydrogen sulfide](image)

**Figure 38b. Plot of ln(f/x) vs P-Psatw for hydrogen sulfide**

Data from Gillespie and Wilson

shown in figure 38b. As equation (6.22) shows, the slope of such a plot is the partial molar volume at infinite dilution divided by RT, while the intercept is the Henry’s constant at zero pressure. The partial molar volume at infinite dilution was correlated using the same reducing function as Lyckman et al. to correlate the partial molar volume of hydrogen sulfide in water as:

\[
\frac{P_{c,H_2S}V_{H_2S}^\infty}{RT_{c,H_2S}} = -0.2992 + 12.464 \left( \frac{TP_{c,H_2S}}{CT_{c,H_2S}} \right) 
\]

(6.26)

The values of the partial molar volume at infinite dilution as derived from plotting versus the partial molar volumes as calculated from the correlation are shown in table 17.
Effects of salts on phase equilibria

Water and natural gas systems are very rarely found without the presence of some dissolved salts in the aqueous phase. This salt can have a major effect on the solubility of water in the gaseous phase and the solubility of the gases in the aqueous phase. The change in solubility of water in the gas phase due to the presence of salts is calculated using the highly accurate model for geothermal brines developed by Pitzer et al.\textsuperscript{113, 114}

Salt effects on vapor phase

The presence of salts in the aqueous phase serves to reduce the fugacity of the liquid water, thus reducing the amount of water present in the gaseous phase. Pitzer developed a highly accurate model for geothermal brines based on the properties of sodium chloride (NaCl), in which properties for the activity coefficient and osmotic coefficient were correlated to the ionic strength of the solution. The ionic strength of the solution is defined as

\[ I (mol/kg) = \frac{1}{2} \sum \left( Z_m^2 M_m + Z_x^2 M_x \right) \] (6.27)

The correlation developed by Pitzer\textsuperscript{113} for the osmotic coefficient and activity

<p>| Table 17. Partial molar volume at infinite dilution of Hydrogen Sulfide. |
|---------------------------------|------------------|-------------------|</p>
<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>( V^\ast, ) experimental cc/mol</th>
<th>( V^\ast, ) correlation cc/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>-90.01</td>
<td>-89.78</td>
</tr>
<tr>
<td>366</td>
<td>-84.61</td>
<td>-84.92</td>
</tr>
<tr>
<td>477</td>
<td>-72.12</td>
<td>-72.03</td>
</tr>
</tbody>
</table>
\[ \phi - 1 = |Z_m^i Z_x^j| f^\phi + m \frac{2v_m v_x}{v} B_{MX}^\phi + m^2 \frac{2(v_m v_x)^{1.5}}{v} C_{MX}^\phi \]  

(6.28)

\[ \ln \gamma_z = |Z_m^i Z_x^j| f^\gamma + m \frac{2v_m v_x}{v} B_{MX}^\gamma + m^2 \frac{2(v_m v_x)^{1.5}}{v} C_{MX}^\gamma \]  

(6.29)

The osmotic coefficient can be used to calculate the change in the aqueous activity due to the presence of the salts

\[ \phi = \frac{-1000 \ln \left( a_{H_2O} \right)}{m_i \sum \nu_i m_k} \]  

(6.30).

By re-arranging equation (6.30), we can solve for the activity of water, and correct the fugacity as calculated by equations (6.12) or (6.19) for the presence of the ionic species:

\[ f_{H_2O}^{Sali} = a_{H_2O} f_{H_2O}^{Pure} \]  

(6.31)

Salt effects on aqueous liquid phase

However, the presence of the salts will also change the amount of gases that are soluble in the aqueous phase (the so called salting out/in effects). For the n-alkanes, carbon dioxide and nitrogen, correlations were fit to experimental data\textsuperscript{32, 34, 36, 41} of the form\textsuperscript{36, 107}

\[ \log_{10} \gamma_{i,n} (I) = a_i (I^2) + b_i \]  

(6.32)

In this correlation, we have assumed that the behavior for alkanes of greater molecular weight than propane behave in the same fashion as methane and ethane.
<table>
<thead>
<tr>
<th>Species</th>
<th>$a_i$</th>
<th>$b_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, ethane, propane</td>
<td>3.729750E-03</td>
<td>1.255522E-01</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>6.101777E-03</td>
<td>1.003281E-01</td>
</tr>
</tbody>
</table>

### Effects of geothermal pressures and temperatures on solubility

As pressures exceed 150 MPa, and temperatures exceed ~550 K, water behaves much differently than at lower pressures and temperatures, becoming increasingly acidic and an increasingly good solvent for silica and other components which at ambient conditions are generally insoluble. As experiments at these conditions are exceedingly difficult to perform, we must have some way of estimating the solubility of salts and silica, and of determining their effect on the water fugacity.

Fortunately, such a method was developed by Lindsay\textsuperscript{115}, and is generally referred to as a ‘model substance approach’. The basis of the model substance approach is to use well characterized substances (in this case, water and sodium chloride) to approximate the needed quantities. Lindsay also suggested the use of writing the equilibria in a certain format to make extrapolation more independent of changes in heat capacity and volume. These concepts can be traced back to the ideas of Gurney, who (it turns out, quite correctly) posited that if the ionic structure of the fluid before and after the reaction were about the same, changes in volume and heat capacity could be neglected. These are referred to as ‘isocoulombic’ reactions, and are generally of the form
\[
AB_{aq} + C^+_{aq} \rightleftharpoons A^+_{aq} + CB_{aq} \tag{6.33}
\]

\[
AB_{aq} + D^-_{aq} \rightleftharpoons B^-_{aq} + AD_{aq} \tag{6.34}
\]

When written in this form, the large contribution of the ion-solvent interactions to the change in heat capacity and volume is minimized. Minimizing these effects makes it possible to extrapolate data taken at room temperature and pressure to conditions far removed with a good degree of accuracy, by using water and sodium chloride as 'model substances' to stand in for the properties of the actual ions in solution.

The thermodynamic equilibrium constant $K$ for the arbitrary reaction $A+B \rightarrow C+D$ is defined as:

\[
K = \frac{a_a a_d}{a_b a_c} = \frac{m_a m_d}{m_b m_c} \frac{\gamma_c \gamma_d}{\gamma_a \gamma_b} \tag{6.35}
\]

where $a_i$ is the activity of chemical species $i$, $m_i$ is the molality of species $i$ and $\gamma_i$ is the activity coefficient. We can rearrange this to be in a slightly more convenient (after all, we are interested in the molalities!) form

\[
\frac{m_c m_a}{m_b m_d} = Q = \frac{K}{\Gamma} = K \frac{\gamma_a \gamma_b}{\gamma_c \gamma_d} \tag{6.36}
\]

We can directly relate $K$ to the change in the Gibbs energy by

\[
\Delta G^0 = -RT \ln K \tag{6.37}
\]

where $\Delta G^0$ is the change in standard (usually at 298 K and 1 atm) Gibbs energy, $R$ is the universal gas constant, and $T$ is the absolute temperature. The reason
for an isocoulombic formulation will become readily apparent when one considers the effects of changing temperature upon K. For K the change with temperature can be written as

$$\ln K = C + \frac{\Delta h^0}{RT} + \frac{\Delta c_p^0}{R} \ln T$$  \hspace{1cm} (6.38)

Where $\Delta h^0$ is the change in the standard partial molar enthalpy and $\Delta c_p^0$ is the change in the partial molar heat capacity, and C is an integration constant.

Although the change in enthalpy has been tabulated for many reactions near ambient conditions, the change in heat capacity is not widely tabulated, making calculations difficult. Therefore, in order to obtain an estimate of K at the temperature of interest, we must write the reaction in an isocoulombic form in order to neglect the change in the partial molar heat capacity.

For an example, the reaction of Carbon Dioxide to Carbonic acid can be written as:

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq) \leftrightarrow H^+ + HCO_3^-$$  \hspace{1cm} (6.39)

but (6.39) can be written in isocoulombic form as

$$CO_2(aq) + OH^- \leftrightarrow HCO_3^-$$  \hspace{1cm} (6.40)

We can now write the isocoulombic thermodynamic equilibrium value \textsuperscript{115} Kq as

$$\log K_q = \log K - \log K_w$$  \hspace{1cm} (6.41)

Where $K_w$ is the self ionization constant for water. This can be calculated from Marshall and Franck's\textsuperscript{116} correlation for log $K_w$, where the solvent density can be calculated using the Saul and Wagner treatment or the NIST equation of state for
steam with comparable results. We can now calculate the isocoulombic thermodynamic equilibrium constant at T2 (K_{a,T2}) as

$$\log K_{a,T2} = \log K_{a,T1} + \frac{\Delta h^0}{2.303R} \left( \frac{1}{T1} - \frac{1}{T2} \right)$$  \hspace{1cm} (6.42)

However, in order to make useful calculations at geothermal conditions, we must also consider changes in the activity coefficient ratio for the water, \( \Gamma_w \) as indicated in equation (6.36). For water, \( \Gamma_w \) is

$$\frac{\gamma_{H^+} \gamma_{OH^-}}{a_{H^+} a_{OH^-}} = \Gamma_w \left( \frac{\gamma_{\pm NaCl}^2}{a_{\pm NaCl}} \right)$$  \hspace{1cm} (6.43)

Lindsay\(^{115} \) showed that the mean molal activity coefficient for sodium chloride as calculated using the Pitzer correlations could be used as an acceptable stand in for the activity coefficients in equation (6.43), and the activity of water can be calculated from the Pitzer correlations, so that all of the quantities in equation (6.36) are reasonably estimated. For higher ionic charged species, (more than Z=1) Lindsay proposed to estimate the activities as:

$$\gamma_{|z|} \sim \gamma_{\pm NaCl}^2$$  \hspace{1cm} (6.44)

where Z is the ion charge.

**Binary interaction parameter fitting procedure**

For the purposes of this study, we have fit the binary interaction parameters to binary data for methane + water, ethane + water, propane + water, carbon dioxide + water and hydrogen sulfide + water, based on this investigation and the investigations of others. A screening of experimental data was performed
to remove poor data. First, the gas phase water contents of the various non-water species were plotted as the log(mole fraction of water) versus 1/ (absolute temperatures), as suggested by Kobayashi\textsuperscript{117}, for each isobaric series at various temperatures to check for substantial scatter. Consistent data should fall along a straight line. Data sets that had a correlation coefficient (r-squared value) of less than 0.995 were rejected as containing too much scatter.

The phase equilibrium values were then calculated using a fixed $k_{ij}$ value for each isotherm. The average absolute deviation from each data point in the set

$$\text{AAD\%} = \frac{\sum_{i=1}^{N} |y_{exp} - y_{eoi}|}{y_{exp}} \times 100$$

was calculated and $k_{ij}$ was adjusted, and the calculation repeated until the deviation from experimental data was minimized.

It was determined that the binary interaction value was not completely independent of temperature for hydrocarbon + water species. This is not surprising, as the strength of the hydrogen bonding interaction between water molecules decreases with increasing temperature. As such, the interaction parameters for water and the other components are expected to vary slightly with temperature. The determined binary interaction parameters for methane + water, ethane + water, carbon dioxide + water and hydrogen sulfide + water are shown in table 18. These have been correlated as functions of temperature. For methane, ethane and carbon dioxide, the recommended correlation is

$$eT^2 + fT + g$$ (6.46)
Table 19a. Binary interaction parameters between water and species listed as fitted to experimental binary data

<table>
<thead>
<tr>
<th></th>
<th>Methane$^{8,30}$</th>
<th>Ethane$^{29}$</th>
<th>Carbon Dioxide$^{27,33,39}$</th>
<th>Hydrogen Sulfide$^{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp, K</strong></td>
<td><strong>k_{ij}</strong></td>
<td><strong>Temp, K</strong></td>
<td><strong>k_{ij}</strong></td>
<td><strong>Temp, K</strong></td>
</tr>
<tr>
<td>511</td>
<td>0.35</td>
<td>511</td>
<td>0.37</td>
<td>477.15</td>
</tr>
<tr>
<td>477</td>
<td>0.37</td>
<td>477</td>
<td>0.42</td>
<td>423.15</td>
</tr>
<tr>
<td>466</td>
<td>0.405</td>
<td>466</td>
<td>0.425</td>
<td>373.15</td>
</tr>
<tr>
<td>444</td>
<td>0.44</td>
<td>444</td>
<td>0.46</td>
<td>348.15</td>
</tr>
<tr>
<td>422</td>
<td>0.445</td>
<td>422</td>
<td>0.46</td>
<td>323.15</td>
</tr>
<tr>
<td>410</td>
<td>0.445</td>
<td>410</td>
<td>0.475</td>
<td>298.15</td>
</tr>
<tr>
<td>337</td>
<td>0.45</td>
<td>377</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>366</td>
<td>0.47</td>
<td>366</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>344</td>
<td>0.47</td>
<td>344</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.48</td>
<td>315</td>
<td>0.488</td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>0.485</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 19b. Coefficients used in correlating temperature dependence in table 19a.

<table>
<thead>
<tr>
<th>Species</th>
<th>e</th>
<th>f</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>-3.5867E-06</td>
<td>2.3165E-03</td>
<td>1.0073E-01</td>
</tr>
<tr>
<td>Ethane</td>
<td>-5.57292E-06</td>
<td>3.99740E-03</td>
<td>-2.20684E-01</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>-8.34368E-07</td>
<td>-1.08072E-04</td>
<td>3.51499E-01</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0</td>
<td>0</td>
<td>0.10</td>
</tr>
</tbody>
</table>
7. Model Results

![Graph showing solubility of water in methane + water, ethane + water, and carbon dioxide + water systems](image)

**Figure 39. Model results for Methane + Water system**
Square points are from Rigby and Prausnitz, diamonds from Olds et al. and circles are this investigation. Binary interaction parameters (kij) calculated using eq. 6.34

First, the model results will be presented for the binary species of methane + water, ethane + water and carbon dioxide + water. Next the results for the ternary methane + carbon dioxide + water and ethane + carbon dioxide systems will be presented, followed by the hydrogen sulfide + water system. Finally the results for brine systems will be presented. In figure 39, the methane+water system is shown for the results of this investigation, that of Olds et al. and the work of Rigby and Prausnitz for the solubility of water in the vapor phase. Equation was used to correlate the binary interaction parameters. Please note
that the y-axis is $-\log(Y_{H_2O})$, in order to get everything to fit on one graph.

The model reproduces the experimental data quite satisfactorily up to pressures of 110 MPa and over the temperature range from 310 to 510 K. The results of Rigby and Prausnitz at 373 and 348 K, however, appear to have some systematic deviation from the data of this investigation and Olds et al., and from the Rigby and Prausnitz data sets at 298 and 323 K.

**Figure 40. Results for the ethane + water system**

Lines calculated with the $k_{ii}$ value predicted by equation 6.34. Diamonds this work.

Shown in figure 40 are the results for the ethane + water system plotted in the same fashion. Again, the model does a very good job of reproducing the experimental data for all investigators.

Next, we present the CO$_2$+ water results of Weibe and Gaddy and Todheide and Franck, up to 150 MPa. Note that because of the smaller
temperature range covered in each figure, the y-axis is listed as mole fraction of water in the gaseous phase, and not as the -log(mole fraction of water). In figure 41, we show the low temperature results (298 and 323 K) for Weibe and Gaddy's work. The astute observer will notice that the calculated values are slightly below the experimental values, but are still within the experimental uncertainty. This was a compromise between the binary data and the ternary data, as fitting the ternary data with CO$_2$+water interaction parameters fit to minimized binary data at 298 and 323 K produced ternary results that contained, on average, 15% too much water. It was found that by fitting the binary data to the lower limit of the experimental uncertainty that it was possible to model both the both the binary systems and the ternary systems within the

![Figure 41. Model Results for Low temperature CO$_2$+ Water](image-url)
limits of experimental uncertainty.

Shown in figure 42 for the higher temperatures (348-473 K), the model captures the phase behavior of the system rather nicely, and is able to capture the solubility increase at increasing pressures at 348 K, while showing that this effect is largely absent at higher temperatures. Unfortunately, the data of Todheide and Franck has an experimental uncertainty of 0.01 mole fraction, making it difficult to completely characterize the extent of the solubility minimum at higher temperatures.

![Graph showing model results for high temperature CO₂ + Water](image)

**Figure 42. Model Results for High Temperature CO₂ + Water**

The 90% CH₄ + 10% CO₂ + water results are presented next in figures 43 and 44. The binary interaction values used are those that have been correlated
to binary data as a function of temperature, equation (6.46). It should be noted that the y-axis is presented as the mole fraction of water in the vapor phase and NOT the negative log of the mole fraction, as these data sets span a smaller temperature range.

![Graph](image)

**Figure 43. Model Results for 90% CH₄+10% CO₂ at 314 and 366 K.** Interaction parameters are calculated using 6.34, showing the model's ability to give relatively good prediction of ternary data with interaction parameters derived from binary parameters. CO₂-CH₄ parameters set to 0.18 for all temperatures per Reid et al.

As shown for the low temperature results in figure 43, the model accurately predicts all of the experimental values over a wide pressure range, and is within the experimental uncertainty to up to pressures of 110 MPa. The higher temperature results are shown in figure 44, and with the exception of the 21 MPa
Figure 44. Model Results for 90% CH₄ + 10% CO₂ at 421 and 463 K.

Points this investigation, lines this model. Model does adequate job of reproducing ternary data to pressures of 110 MPa.

point at 463 K, fall within the experimental uncertainties for all data points.

Shown next are the 5% ethane + 95% CO₂ results. Again, the interaction parameters between CO₂ and water are the parameters that were fit to the low-side of the experimental uncertainty of the binary CO₂ + water data, while the ethane + water interaction parameters were those that were fit to the binary ethane + water data. The ethane + CO₂ interaction parameter was set to 0.2, as suggested by Reid. As shown in figure 45, the mixture has some decidedly interesting behavior. At pressures below the solubility minimum, there is not a great deal of change in the water content due to the presence of the ethane. The
slope of the water content curve to the solubility minimum is shallower, compared with pure carbon dioxide. However, above the solubility minimum, the effect of the 5% ethane is to depress the water content 30-40% from what would be expected from pure carbon dioxide. Points from Weibe and Gaddy are shown in figure 45 to reveal the magnitude of the solubility decrease. As an example, the water content of the 5% ethane+95% carbon dioxide mixture at 316 K is about the same as the water content of pure carbon dioxide at 298 K, or about a 30% decrease in the solubility of water over what would be expected for pure carbon dioxide at 316 K.

![Figure 45. Model Results for 5% C₂H₆+95% CO₂ at 316, 366 K](image)

Square points this work, diamond and triangles are 100% CO₂ Weibe and Gaddy
Higher temperature (423K) results are shown for the 5% ethane+95% CO₂ system in figure 46, which shows that, again, the water contents of the gas mixture at pressures below the solubility minimum are similar to those expected from pure carbon dioxide, but at pressures above the solubility minimum, we

![Graph showing mole fraction of water in gas phase against pressure in MPa.]

**Figure 46. Model results for 5% C₂H₆, 95% CO₂ at 423 K**

again see about a 30% decrease in the water content compared to the pure carbon dioxide behavior as measured by Todheide and Franck. At this temperature, there appears to be only a very slight solubility minimum, which again is similar to the trends observed with pure carbon dioxide, that the magnitude of the solubility minimum decreases with increasing temperature.
Presented in figure 47 is the phase behavior of the water+ H₂S system from 310 K to 444 K. The model was slightly disappointing at temperatures within 50 K of the critical temperature, predicting a solubility increase that was far too rapid in the H₂S gas phase while predicting reasonable H₂S solubilities in the aqueous liquid phase. However, at temperatures below the critical temperature or temperatures greater than 50 K above the critical temperature, excellent results are obtained. No new data was taken\(^{25, 40}\) for systems involving H₂S in the course of this investigation. In figure 47 the solid line represents the model.
predictions for the water solubility in the gas phase and the dashed lines are the predictions for the solubility of H₂S in the aqueous liquid phase.

![Graph showing solubility](image)

**Figure 48. Model Results for CH₄+H₂O+NaCl Brine**

Shown on the left axis is the solubility of methane in pure water (open squares) and in a NaCl brine of ionic strength 1 (filled squares) and ionic strength 4 (filled diamonds). On the right axis is the solubility of water in the methane.

Lastly, the effects of salts are shown with the methane + water and carbon dioxide + water systems. Figure 48 shows the data of O'Sullivan and Smith at 324 K for two brines (l=1 and l=4) and pure water. The results show that the Pitzer model and equation (6.32) are adequate to describe the effects of salts on the phase behavior of the hydrocarbon + water systems. The excellent results at high pressures confirm that the system is still obeying the KK equation and that the partial molar volumes at infinite dilution are adequately predicted.
Figure 49. Model Results for CO₂ + Water+NaCl brine
The solubility of CO₂ in varying strengths of NaCl brine (Circle I=0, square I=1.73, diamond I=5.03) at 298 K. As observed for the methane + water system, the effect of the salt is to lower the solubility of CO₂ in the brine (so called salting out effect) and to lower the water content in the CO₂ gas phase(dashed lines).

In figure 49, the CO₂+Water system is shown for the isobaric data of Malinin. The effect of the added salt is to depress the amount of water present in the gaseous carbon dioxide, and to reduce the amount of gas present in the aqueous liquid (brine). Even for a relatively strong brine (I=5), the results are within a few percent. However, due to the lack of higher pressure data, it is difficult to tell whether the KK equation is obeyed, and if the partial molar volume of carbon dioxide is behaving differently due to the presence of the salts.
8. Conclusions

This investigation has provided some new results for the high pressure, moderate temperature phase behavior of binary methane+water and ethane+water, and the ternary methane+carbon dioxide+water and ethane+carbon dioxide+water systems. We have shown that for the methane+water and ethane+water binaries from 310-477 K from 3 to 110 MPa that there is no supercritical solubility increase, and that the water content in the vapor phase is decreasing, and appears to be trending a to a constant, temperature dependent value at high pressures. This is consistent with the lower pressure, lower temperature work of Olds et al., Reamer et al. and Danneil et al.. We have also provided improved lower pressure (between 3 and 7 MPa) results, that show the same trends as those reported by Rigby and Prausnitz, but show that these results are not consistent with those of Olds et al. and this investigation, showing slightly too little water in the hydrocarbon phase.

For the ternary systems, we have shown that the water content of 10% carbon dioxide+90% methane system shows the same trends as the pure methane+water system, but has a slightly higher water content due to the presence of the carbon dioxide. The 5% ethane,+95% carbon dioxide system, on the other hand, has a much different phase behavior than the pure ethane+water system, but shows a super critical solubility increase like the pure carbon dioxide system. Unlike the pure carbon dioxide system, the magnitude of the solubility increase is not as great, and it does not show as rapid of a change
around the pressure of the solubility minimum, but instead shows a more gradual increase. Like the pure carbon dioxide + water system, the water content becomes nearly constant with pressure at pressures above \( \sim 40 \) MPa, but this water content is substantially lower than the pure carbon dioxide + water system, but substantially higher than the pure ethane + water system. The water solubility minimum begins to disappear with increasing temperature, and is negligible at 463 K, showing that the solubility minimum is definitely an effect due to the compressibility of the carbon dioxide at lower temperatures and higher pressures.

We have also developed a relatively simple, but accurate engineering model to describe the phase behavior of this system. The model uses a Peng-Robinson equation of state in conjunction with either an accurate correlation for the saturation density and pressures of liquid water or with a highly precise equation of state to calculate the fugacity of the water phase. A Henry's law approach is used to model the fucacities of the gases dissolved in the liquid phase, and Pitzer's highly accurate model for geothermal brines is used in conjunction with an empirical correlation to model the "salting out" effects of the brine on the dissolved gases.

The model uses a single binary interaction parameter for each species, which was found to be a function of temperature. The binary interaction parameter was established by fitting to experimental data such that the error between the calculated mole fractions and the experimental mole fractions is
minimized. Ternary results for the 90% methane+10% carbon dioxide system and the 5% ethane+95% carbon dioxide system were in good agreement with the experimental data using parameters fit to the binary systems of methane+water, ethane+water and carbon dioxide+water. The results were not as good for hydrogen sulfide+water at temperatures near the critical temperature, which showed a solubility minimum that was not quite at the proper pressure, and which showed that the water content increased more rapidly with pressure than was experimentally determined.

The model showed good agreement with brine data for the methane+NaCl+water system and the carbon dioxide+NaCl+water systems over a variety of temperatures and pressures.
9. Future Work

The work detailed here does a fairly comprehensive job of examining the high pressure phase behavior of methane, ethane and mixtures of those two gasses with varying concentrations of carbon dioxide. One open question that could be relatively easily answered with the existing equipment is how the water content varies with carbon dioxide concentration in the carbon dioxide concentration range between 10 % and 95%. A percentage of carbon dioxide around 60% to 70% by mole should be used to investigate the behavior, as the model indicates that this should be in the transitional region between pure-hydrocarbon like behavior and carbon dioxide like behavior.

There is an absolute dearth of vapor phase water content data for any hydrocarbon gas at any pressure in equilibrium with brines. The data would not have to cover a very high pressure (1 to 30 MPa), would only need a few isotherms (say 298 K, 398 K and 500 K), but would need to have a variety of saline concentrations (5 to 20 ionic strength). The salt could be NaCl, but CaCl₂ would also be useful. This would serve as a good check on the model, and would be of great benefit to industry.

The trouble with such an experimental set up would be the changing saline concentration as water is removed during the course of an experiment. One possible solution is to use a computer controlled pump to inject water into the saturation cell at the rate at which it is being removed by the hydrocarbon
gas. Out of a typical run, not more than 1 to 5 cm$^3$ would be required, which could easily be introduced into the system by a piston-cylinder pump. A magnetically driven agitator would also be necessary to ensure that the brine phase stayed at a constant concentration and did not develop concentration gradients.

Standard stainless steels such as 304 and 316 would suffer from chloride attack of the metals, and as such would be a poor choice. Hastelloy-C would be an appropriate, but expensive choice for the wetted parts. A properly constructed Pyrex liner might, or some form of inert coating, like Teflon, might also enable less expensive 304 or 316 to be used.

Another open question, and one for which there is scant data available, is how a mixed gas will behave in the presence of a mixed brine. This would be especially interesting in the case of acid gases like carbon dioxide and hydrogen sulfide.
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