Accurate phase equilibrium measurements of CO₂ mixtures

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Abstract

A new setup for accurate measurement of phase behavior of CO₂-rich mixtures relevant for CCS has been designed, covering a range between -60 and 150 °C in temperature and 0.4 and 20 MPa in pressure. In order to design safe and efficient infrastructure for CCS, the exact properties of these mixtures are required, and currently there are large knowledge gaps that need to be closed regarding the phase behavior. This paper reports a description of the experimental setup, how uncertainties will be verified and contained, and the very first test measurements performed using the setup.

1. Introduction

In order to realize large-scale carbon capture and storage (CCS), it is necessary to describe and predict the behavior of the fluids along the value chain from capture to storage. Currently, there are still large knowledge gaps regarding the thermo-physical properties of many CO₂ mixtures and conditions relevant for CCS [1, 2]. SINTEF Energy Research, Ruhr-Universität Bochum, and NTNU are collaborating on a project called CO₂Mix designed to address this gap by experimentally determine selected thermo-physical properties of CO₂-mixtures relevant for CCS transport and conditioning [3].

One of the key properties that is investigated in the CO₂Mix project is the phase state at equilibrium, using a dedicated experimental setup that has been constructed in the labs of SINTEF Energy Research in Trondheim [4]. Knowing the exact phase state as a function of mixture composition, temperature, and pressure is important in order to design process equipment and systems for conditioning and transport, and to specify the maximum allowed concentration of different impurities. For instance, in order to avoid corrosion, it is important to be aware of the conditions under which free water will be present. In addition, accurate phase behavior knowledge is important in order to make robust routines for start-up and shut-down of the systems, as well as for the understanding of an uncontrolled depressurization. Finally, phase equilibrium (PVTx) data are prerequisites for the development of accurate equations of state from which other important thermodynamic properties can be derived.

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The primary objective for the measurements to be conducted on the phase equilibrium rig will be to provide vapor-liquid equilibrium data for binary mixtures. However, the rig will also be suitable for testing multicomponent mixtures and to study other types of phase equilibria, for instance with two liquid phases present (VLLE). In addition, we plan to equip the rig with instrumentation that can detect and possibly determine the composition of solid and hydrate phases.

The rig is using an analytical approach where the phases that exist inside the equilibrium cell are sampled and analyzed [5]. Hence, no exact knowledge of the total composition is required. One of the main objectives when designing the rig was to obtain a capability to deliver data of high quality, aiming for absolute accuracies better than 10 mK in temperature and 0.1 % in pressure. Particular care has been taken in the design of the sampling system and in the selection of a gas chromatograph (GC) with detectors and columns suitable for the mixtures to be studied. In addition to careful design and operation of the setup, accurate measurement requires accurate means and adherence to systematic routines for the calibration of the different sensor systems. This includes a system for preparation of calibration gas mixtures for the GC, since the composition of commercially available mixtures of the components under study often is not certified to high enough accuracy.

In this work, the measurements obtained so far will be summarized. The focus will be on how uncertainties are contained and verified through control measurements, careful design, calibration system and routines, as well as quality check of the final measurements including comparison with existing models and measurement data. Further, it will be discussed and quantified how uncertainties in measurements of pressure, temperature, and composition add up to a combined uncertainty that ultimately will define the reliability of fluid behavior prediction in CCS systems. Following the guidelines from Fluid Phase Equilibria and IUPAC [6], standard rather than expanded uncertainties [7] should be used for the reporting of phase equilibria data.

### Nomenclature

- \( x_{eq} \): Mole fraction of gas or liquid phase at equilibrium
- \( \Delta x_{eq} \): Deviation of measured mole fraction \( x \) from real equilibrium value
- \( p \): Pressure
- \( s_{sample} \): Estimated sample standard deviation of composition measurements
- \( T \): Temperature
- \( u_p \): Estimated standard uncertainty in pressure
- \( u_T \): Estimated standard uncertainty in temperature
- \( u_{x,cal} \): Estimated absolute standard uncertainty of GC
- \( u_{x,analysis} \): Estimated standard uncertainty in composition measurements
- \( u_{x,eq} \): Estimated total standard uncertainty in equilibrium composition measurements

### Abbreviations:

- CCS: Carbon capture and storage
- GC: Gas chromatograph
- SPRT: Standard platinum resistance thermometer
- SRK: Soave-Redlich-Kwong
- VLE: Vapor-liquid equilibrium
- VLLE: Vapor-liquid-liquid equilibrium

## 2. Experimental infrastructure

The experimental setup is described in a previous publication [8], and only a brief overview will be provided here.

### 2.1. Phase equilibrium rig

A photograph and a schematic piping and instrumentation diagram of the installed phase equilibrium setup is shown in Figs. 1-2. The phase equilibrium test cell has an internal volume of 100 ml and consists of a hollow sapphire cylinder sealed by two titanium flanges. \( \text{CO}_2 \), impurity components / mixtures, and liquids can be injected separately into the cell using syringe pumps, enabling dynamic control of both the cell pressure and total composition. The injection pipes are connected to valves embedded in the titanium flanges, minimizing the dead volume of the cell. The temperature of the cell is controlled by placing the cell in a thermostatic bath.

In order to monitor the temperature and thermal uniformity as close to the cell content as possible, 25 \( \Omega \) standard platinum resistance thermometers (SPRTs) are placed in each flange. Gas phase pressure inside the cell is measured accurately by isolating a pressure sensor array from the fluid under test at various temperatures and level of aggressiveness using a differential pressure sensor setup [9].

For composition measurements, small samples can be extracted from the cell using two capillaries. One capillary is meant for the vapor sampling and has its inlet close to the top of the cell. The other capillary can be adjusted vertically to accommodate
changes in liquid levels. The inner diameter of the capillaries is 150 μm, with a length of approximately 40 cm for the liquid phase sampler and 30 cm for the gas phase sampler. The sample amount is controlled by electromagnetic valves at the top of the capillaries, which can open for a specified period of time. The extracted sample is sent to a gas chromatograph (GC) for analysis. The GC is equipped with three different detectors suitable for different components. The sample valve and the tubing leading to the GC are heated, which ensures that any liquid sample from the cell quickly evaporates before being sent to the GC.

To compensate for the cell pressure drop caused by sampling, a bellows inside the cell can be expanded to decrease the cell volume. In order to reduce the time needed to reach equilibrium, the cell is equipped with a magnetic stirrer.

Fig. 1. Phase equilibrium cell lifted out of thermostatic bath (left) and the full experimental rig (right)

Fig. 2. Principle drawing of phase equilibrium cell.
2.2. Calibration gas preparation

Gas mixtures with components relevant for CCS and with an accuracy desired for this project are not commercially available. Currently, the GC has been calibrated using a commercial CO₂-N₂ gas mixtures with nominal CO₂ mole fractions of 0.10, 0.30 and 0.50 specified with a relative uncertainty in CO₂ content of ± 0.5 %. For this project purpose, this uncertainty is unacceptably high. Hence, an in-house setup has been designed and constructed in order to prepare calibration gas mixtures gravimetrically.

The setup is shown in Fig. 3. An ABBA-methodology [10, 11] is used, where the mass of the gas is determined by comparing the mass of the gas cylinder with another mass with known and certified mass. Environmental factors like draft, atmospheric pressure, temperature, humidity, and vibrations are all sources to weighing errors. To control these parameters, the weighing setup is located in a small closed compartment placed on top of a concrete block for minimizing vibration. Two identical gas cylinders of 10 liter, one empty tare cylinder and the other to be filled with gas, are lying horizontally on a frame which can be slid back and forth. Two electric motors are used for lowering or lifting the cylinders. In this way, the gas cylinder can be exchanged by the tare cylinder, and vice versa, in a controlled manner without having to open the compartment and with minimum disturbance of the environmental conditions inside. On top of both cylinders certified OIML weights [12] can be placed to minimize the weight difference between the two cylinders. The purpose of the tare cylinder is to minimize the buoyancy differences. Initial verification of the setup shows a repeatability of better than 3 mg in the weighing of the cylinders. Hence, if the calibration gas cylinder is reasonably filled, accuracy around 1 ppm should be in reach, far better than other sources of error in the composition measurements.

The gas mixtures which will be prepared using this setup typically need to be homogenized before being used for calibration of the GC. The homogenization will be ensured using a mechanical roller with optionally heated encapsulation, shown in Fig. 4. For mixtures with a condensation temperature below room temperature heating is needed in order to ensure that the mixtures are single phase, depending on the composition.

![Fig. 3. Picture and schematic drawing of the comparator mounted on a concrete block for minimized vibration, placed inside a compartment with a lid that can be opened. Under operation, it is not necessary to open the lid.](image-url)
2.3. Other calibration infrastructure

The lab is equipped with fix point cells for temperature calibration to be discussed further in Section 3. A recently calibrated dead-weight tester will be used for pressure sensor calibration.

3. Uncertainty in temperature measurements

The SPRTs will be calibrated at five fix points of the International Temperature Scale of 1990 (ITS-90) [13]. To cover the temperature range of interest between -60 and 150 °C, the fix points utilized are the triple point of mercury, the triple point of water, the melting point of gallium, the freezing point of indium and the freezing point of tin. At temperatures between -60 °C and the triple point of mercury, -38.8344 °C, we will have to extrapolate beyond the calibration range.

So far, calibration of the SPRTs has been carried out in-house using fix point cell for the triple point of mercury, water and the melting point of gallium. Two calibration measurements have been carried out at the melting point of gallium four months apart. The results from the second calibration of the upper flange SPRT is shown in Fig. 5. The resistance measurement points during the melting plateau all fall within a corresponding temperature variation of 2 mK, with the estimated uncertainty of the calibration being less than 0.1 mK. Comparing with the previous calibration, the results indicate a drift in the resistance of this SPRT corresponding to approximately + 0.1 mK/month.

![Graph showing resistance ratio drift](image)

**Fig. 5.** Measured ratio between the resistance of the upper flange SPRT and a calibrated reference resistor during the melting plateau of gallium.

A measurement of the temperature in the thermostatic bath at 12 different points around the cell has been carried out using an additional 100 Ω SPRT, indicating a uniformity of approximately ± 10 mK at a bath temperature of -60 °C. The temperature variations inside the smaller dimensions of the cell interior are expected to be smaller, which is confirmed by the measured
temperature difference in the range of ± 3.5 mK shown in Fig. 6. The measured uniformity of the bath is somewhat worse than its specifications of ± 7 mK at -80 K, probably due to the obstruction of the bath fluid flow caused by the cell. A modification of the bath to improve the uniformity is currently being tested.

In Fig. 6, the stability of the temperature measured in the cell flanges is plotted. The temperature is within ± 5 mK of the mean at all times, with a standard deviation of 2.3 mK, and the temperature variation of the upper and lower flange is strongly correlated. Again, the temperature stability is somewhat inferior to the bath specifications. Based on the testing results obtained so far, it is believed that the aim of a combined accuracy, stability and uniformity of less than 10 mK is achievable.

4. GC Calibration

The GC needs to be calibrated for each mixture to be analyzed. This is done by analyzing gas mixtures of accurately known composition to create calibration curves. These are typically made from analyzing 3 to 5 different sample compositions and using the relative detector response area of one component compared to the other. Comparing the relative area of an unknown sample to the calibration curve then gives the composition of the sample. It is also important to know the detector's response factor to varying sample volumes, as the sample volume will vary for liquid and gas samples under different pressures. To analyze this, calibration sample loops of different volumes are used, in the range from 5 μl to 1 ml. Analysis of the detector's response to varying sample volumes has yet not been fully performed, hence a linear response has been assumed for the initial VLE experiments.
Significant drift in the detector response has been experienced when analyzing known samples on a day to day basis. To quantify the drift and minimize the uncertainty caused by this, calibration of the GC will be performed both in advance and after each VLE experiment. If needed, such calibration can in fact take place between individual samples as well.

Finally, the sampling system can be verified by injecting calibration gas mixture into the phase equilibrium cell, while ensuring that this mixture is single phase both in the gas cylinder, injection system, and cell, such that the composition is not distorted.

5. Initial vapor-liquid equilibrium experiments

The phase equilibrium set-up has recently been put into test-operation just before the conference, investigating the binary system CO₂ and N₂. Significant amounts of experimental data exist for this system [1], making it suitable for verification of the set-up. Yorizane et al. [14] reported measurements on this binary system at a temperature of 273.2 ± 0.1 K, for 12 different pressures in the range between 4.5 and 11.45 MPa, with a relative uncertainty of ± 0.5 % in the pressure measurements. It appears as if, and will be assumed in the following, that the composition data of the liquid and gas phase at 273.2 K has been switched in reference [14]. It was decided to aim for a state within this data series, with a pressure approximately halfway between the vapor pressure of pure CO₂ and the pressure of the critical locus of the N₂/CO₂ binary system at this temperature.

The cell temperature was 272.9 K and the pressure stabilized at 8.14 MPa. The target temperature of 273.15 K was not reached because it was discovered after the pressure was stabilized that the measurements provided by the SPRTs were not consistent, and required recalibration. Hence, the calibrated temperature sensor of the bath with a repeatability of ± 0.1 K was used. After recalibration of the SPRTs, the uncertainty in the temperature measurements is expected to decrease by more than a decade as discussed in Section 3.

After evacuation, the cell was first loaded with CO₂ and then with N₂. Most of the internal volume of the sampling capillaries will consist of CO₂ after the cell has been loaded, since mass transfer between the contents of the capillaries and the rest of the cell will be restricted by the small inner diameter of the capillaries. Hence, the capillaries should be purged prior to sampling in order to achieve accurate phase equilibrium composition measurements.

After stabilizing the cell pressure, the sampling capillaries were purged by opening the sampling valves several times. These purge samples were analyzed by the GC, and it was determined that the capillaries were properly purged when the measured composition had stabilized. That the capillaries were properly purged was later confirmed through volume measurement estimations. After purging, 5 samples were extracted from each phase, in alternating order.

The average CO₂ mole fraction of the liquid and gas phase measured by the GC was 0.897 and 0.632, respectively, with an estimated standard deviation of 0.0054 and 0.0026.

The high standard deviation can be explained by several factors:

- Short-term fluctuations in GC response: During earlier calibration runs with fixed injection volume, the estimated standard deviation of GC measurements series has been much lower, but may be affected by changes in sample mass. As discussed in Section 3, ways of improving and characterizing the GC performance is underway, and determination of the GC response factor between each sample is a possible option.

- Stirring: Since this was a first initial test of the setup, the magnetic stirrer was operated during the measurements. This could have prevented the two phases from settle properly.

- Boil-off in liquid sampling capillary: Due to the gravitational pressure fall through the capillary and the heating from the ambient and sampling valve, the local composition in the upper part of the liquid capillary will change with time. In this first trial, the time between each liquid sample could be up to 25 minutes, and it is estimated that the volume of each liquid sample was only 5 % of the capillary volume.

- Pressure compensation: The bellows was not in operation in order to compensate for the volume extracted from the cell. This resulted in a pressure drop of about 3 kPa from the start of the purging to the end of the experiment.

6. Uncertainty analysis and comparison with previous work

The samples were taken at a temperature of 272.9 K with an estimated uncertainty of \( u_T \approx 0.1 \) K. The measured pressure was declining from 8.1381 to 8.1364 MPa, giving an estimated average pressure of 8.1374 MPa. The estimated uncertainty in this pressure value, \( u_p \approx 1.4 \) kPa, includes the decline in the measured pressure and the uncertainty provided by the pressure measurement system specifications, which is higher than the calibrated uncertainty. As the uncertainties of the bath and pressure measurement system by convention are given as expanded uncertainties by the suppliers, these are probably conservative estimates, but both systems should be recalibrated before regular measurements start. For the composition measurements, there are too few samples to say something about the interdependence between the different sampling points, and the standard deviation of the measurement points seems like a reasonable estimate for the overall uncertainty of the GC area count.

In addition, the uncertainty of GC calibration should be added. Based on 12 different calibration runs with 5 samples in each, the absolute standard uncertainty of the GC is estimated to be \( u_{x,\text{cal}}=1.6 \times 10^{-3} \) around a CO₂ mole fraction of 0.6, and \( u_{x,\text{cal}}=0.6 \times 10^{-3} \)
around a CO₂ mole fraction of 0.90, assuming a linear GC response and including significant uncertainties in calibration gas composition. As discussed in Section 3, we expect this uncertainty to be brought significantly down.

In order to know the total uncertainty in the measurement, the sensitivity of the equilibrium mole fractions to temperature \( \partial x_{eq}/\partial T \) and pressure \( \partial x_{eq}/\partial p \) in the gas and liquid phase should be estimated. The deviation between the true and measured composition, \( \Delta x_{eq} \), and the estimate of the total uncertainty in the phase equilibrium measurement, \( u_{x,eq} \), is then given by:

\[
\Delta x_{eq} = \Delta x_{\text{analysis}} + \frac{\partial x_{eq}}{\partial T} \Delta T + \frac{\partial x_{eq}}{\partial p} \Delta p \Rightarrow u_{x,eq} \approx \sqrt{u_{x,\text{analysis}}^2 + \left(\frac{\partial x_{eq}}{\partial T}\right)^2 u_{T}^2 + \left(\frac{\partial x_{eq}}{\partial p}\right)^2 u_{p}^2}
\]  

(1)

Here, \( \Delta x_{\text{analysis}} \) is the deviation between the cell composition of the liquid or gas phase and its measured value, whereas \( u_{x,\text{analysis}} \) is the estimated standard uncertainty of the composition measurement. \( u_{x,\text{analysis}} \) is estimated from:

\[
u_{x,\text{analysis}} \approx \sqrt{u_{x,\text{cal}}^2 + s_{x,\text{sample}}^2}
\]  

(2)

\( s_{x,\text{sample}} \) is here the estimated sample standard deviation.

The sensitivities of the mole fractions with respect to temperature and pressure were estimated using a standard SRK model [15], and are tabulated with the uncertainties in the measurement of mole fractions, temperature and pressure, and the total standard uncertainty in terms of mole fractions for the measurement point in Table 1.

| Phase    | Sensitivities at 273.15 K, 8.1 MPa | Uncertainties |
|----------|-----------------------------------|---------------|
|          | \( \frac{\partial x_{eq}}{\partial T} \) (1/K) | \( \frac{\partial x_{eq}}{\partial p} \) (1/MPa) | \( u_{x,\text{analysis}} \) (K) | \( u_{T} \) (K) | \( u_{p} \) (MPa) | \( u_{x,eq} \) |
| Liquid   | 0.0013                             | -0.027        | 0.005 | 0.1 | 0.0014 | 0.0054 |
| Vapor    | 0.012                              | -0.025        | 0.003 | 0.0032 | 0.0032 |

For this mixture at this particular temperature and pressure, it can be seen that the measurement of the composition \( u_{x,\text{cal}} \) is the dominant source of uncertainty in our test measurement. Even if the temperature uncertainty is much higher than demonstrated earlier, and both the temperature and pressure uncertainty are conservatively estimated, the total uncertainty is not significantly affected. At this pressure and temperature, the specified uncertainty of the rig of 10 mK in temperature is equivalent to uncertainties in the composition measurements of \( 13 \times 10^{-6} \) in the liquid phase and \( 0.00011 \times 10^{-3} \) in the gas phase, whereas the specified uncertainty of 0.1 % in pressure is equivalent to an uncertainties of 0.0002 in both the gas and liquid phase. However, the relative importance of the different uncertainties will of course be very different at state points, for instance close to the critical point and for mixtures with more similar phase properties like CO₂ and SO₂.
An isotherm at 273.15 K based on the SRK model, the data of Yorizane et al. [14] and the data obtained in this work are plotted in Fig. 8a, and an isobar at 8.1 MPa made using SRK are displayed in Fig. 8b. With the given standard uncertainties and known deviation from the $T=273.16$ K and $p=8.1$ MPa, both the measured gas and liquid compositions are in correspondence with both the model and the data of [14].

7. Conclusion

A new facility designed for measurements of phase equilibria of CO$_2$-rich mixtures relevant for CCS conditioning and transport has just been installed. The setup aims for high accuracy in pressure, temperature, and composition measurements for pressures between 4 and 200 bar and temperatures between -60 and 150 °C. The setup is using an analytical method, where the fluid phases present are analyzed and knowledge of the total composition inside the cell is not necessary. On the other hand, a prerequisite is that the GC used for chemical analyses has to be calibrated using mixtures with composition known to great accuracy.

In this paper, the infrastructure and routines that has been established in order to minimize and quantify the uncertainties for the setup have been described. Sophisticated calibration equipment to constrain the measurement uncertainties in pressure, temperature, and composition has been installed and is in service. Further, the very first test measurement with the setup has been reported. The uncertainties in pressure, temperature, and composition of this first experiment has been analyzed and compared.

For the test measurement of the N$_2$ / CO$_2$ system at 8.1 MPa and 273 K, the composition measurement was the dominant source of uncertainty. However, we see the potential for greatly improved composition measurements, and the aim is to deliver reference data for multiple systems useful for the CCS community in years to come.

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