Vapor-liquid equilibrium of the nitrogen-argon system at 100 K

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Abstract. Mixed-refrigerant cycles (MRC) are state-of-the-art for efficient LNG production. The development of cryogenic mixed-refrigerant cycles (CMRC) at temperatures below 100 K relies on physical property data of cryogenic mixtures such as vapor-liquid equilibria and enthalpies. This data is insufficient for some binary mixtures and unavailable for most multi-component systems. The cryogenic phase equilibria test stand CryoPHAEQTS provides precise physical property data of cryogenic fluid mixtures at temperatures from 15 K to 300 K and at pressures up to 150 bar. Contrary to previous apparatus in the literature, CryoPHAEQTS uses cooling of the equilibrium cell by a pulse-tube cryocooler. Temperature is measured by two CERNOX® sensors directly immersed in the liquid/vapor phase. Pressure is measured through a capillary and a differential pressure sensor connected to a secondary system containing three high precision sensors. Up to three occurring phases can be sampled directly from the cell and analyzed by gas chromatography. Measurement uncertainties are ±13 mK in temperature, ±1 mbar in pressure, and ±1% in composition. Prior to publishing new phase equilibrium data, the test stand is benchmarked against available vapor-liquid equilibrium data of the widely investigated nitrogen-argon system. In this paper, we report on the first measurement results of cryogenic mixtures in CryoPHAEQTS and compare them against the literature data.

1. Introduction
Precise physical property data of cryogenic fluids is crucial to both the physical understanding of molecular interactions and process design. Particularly, cryogenic mixed-refrigerant processes rely on thermal properties, i.e. vapor-liquid equilibria (VLE), and caloric properties, i.e. heat capacities. At cryogenic temperatures, this data is insufficient for some binary mixtures and unavailable for most multi-component systems. To provide this fundamental data, the cryogenic phase equilibria test stand CryoPHAEQTS has been built at KIT. CryoPHAEQTS provides precise phase equilibria data for multi-component systems including flammable or oxidising components in a temperature range from 15 K to 300 K and at pressures up to 150 bar. To validate the accuracy of the test stand, the widely investigated nitrogen-argon system is used as a benchmark.

First, the apparatus is described in section 2, followed by a description of the methods and materials being used in section 3. The results are presented and compared against literature data in section 4 and final conclusions are drawn in section 5.
2. Description of the apparatus

Design details of the CryoPHAEQTS test stand and first commissioning results have been published previously [1, 2]. It uses an isothermal analytical method with sampling and vapor phase circulation. This method is versatile since it can be applied to different multi-component systems, requiring no modifications besides the calibration of the gas chromatograph (GC). The equilibrium cell with a volume of 100 mL is surrounded by two aluminum shields inside in a high-vacuum cryostat. The first shield is connected to the first stage of a pulse-tube cryocooler, while the second shield and the equilibrium cell are thermally anchored to the second cryocooler stage. The cryocooler temperature is controlled by a counter-heater. Top and bottom cell temperatures are measured with two CERNOX® sensors installed in the cell wall. These temperatures are controlled individually with heaters in order to account for vertical inhomogeneities introduced by different thermal conductivities and heat capacities of the vapor and the liquid phases. Another two CERNOX® sensors are directly immersed into the fluid phases inside the cell.

The cell has four capillary outlets: one is used for pressure measurement, while the other three are placed at different heights for vapor-liquid-liquid sampling. Since a small heat flux is directed from the middle of the cell to the top and bottom, condensation is not considered to happen spontaneously in the bulk phase, but rather on the cell wall. To avoid liquid carry over, the pressure sensing and the vapor phase sampling capillaries are extended into the vapor bulk phase. The pressure sensing capillary is connected to a differential pressure sensor with a range of \(-50\text{ mbar}; +50\text{ mbar}\). Three pressure sensors with respective ranges from 0 bar to 10 bar, 10 bar to 70 bar and 70 bar to 150 bar are installed on the secondary side.

The vapor phase can be recirculated to achieve faster equilibration, using a room-temperature gas circulator installed outside the cryostat after a counter-flow heat exchanger. The circulating mass flow is measured by a warm Coriolis mass flow meter. Combined with a thermal mass flow sensor at cryogenic temperature [3, 4] that is currently being installed, the measurement of the heat capacities of vapor phases in equilibrium and of supercritical fluids is possible. The circulating gas is led back to the counter-flow heat exchanger and pre-cooled to about 100 mK above the equilibrium cell temperature to avoid premature condensation. When the gas circulation is turned off, a siphon keeps the liquid phase inside the equilibrium cell.

3. Methods and materials

3.1. Gas chromatography

All gases have been supplied by Air Liquide with a purity of 99.999 vol–%. Process gases are further purified by pumping on the frozen solids. The residual impurities are out of detection range of the GC. Hydrogen carrier gas for chromatography is continuously purified using a zeolite filter.

A sample volume of 100 µL is injected into a carrier gas flow of 34 mL min\(^{-1}\) and split 1:10 before entering the column at 80°C. Nitrogen and argon are separated in a 5 Å molecular sieve column with a length of 30 m and an inner diameter of 0.53 mm supplied by RESTEK. A thermal conductivity detector heated to 150°C is used to obtain the voltage signal peaks. The GC has been calibrated according to DIN 51899 [5] using the gravimetric method described in ISO 6142 - 1 [6]. In total, 18 calibration points have been used for orthogonal regression of the slope of the calibration line. The recovery

\[
F_{\text{rec}} = \frac{x_{1,\text{cal}}}{x_{1,\text{cert}}} \quad (1)
\]

using a certified gas mixture with molar composition of \(x_{1,\text{cert}} = 0.510\) supplied by Air Liquide yielded 97.4 %, which does not meet our target accuracy of ±1 %.
3.2. Test stand operation

Argon gas is filled into the equilibrium cell at the desired boiling temperature until the cell is filled with liquid to approximately one quarter. Then, the cell temperature is set about 3 K below the triple point temperature for purification by pumping on the frozen solid. After the measurement of the vapor pressure, nitrogen gas is dosed into the cell step-by-step. After each dosage, the vapor phase is circulated until temperature and pressure have reached steady-states. With gas phase circulation turned off, the system is considered in equilibrium when temperature fluctuations remain within ±3 mK and pressure fluctuations within ±1 mbar without drift for at least 1 h. Following Gibbs’ phase rule at these conditions, chemical equilibrium must have set in as well, considering that the changes in composition due to the above fluctuations are below the relative measurement accuracy of 1%.

The first capillary is purged for 20 s and a sample of 200 mbar is taken into a sampling cylinder with a volume of 150 mL. This sampling process leads to equilibrium disturbances below 8 mbar. When temperature and pressure have reached their initial values again, a sample of the remaining phase is taken equally. For each data point, the samples are analyzed five times in the GC. Samples are dismissed if there is a drift in the compositions exceeding measurement uncertainty. Finally, the data is evaluated according to the Guide to the Expression of Uncertainty in Measurement (GUM) [7].

4. Results

The 100 K isotherm has been measured over the whole composition range. The experimental VLE data is listed in Table 1. Unfortunately, one inner temperature sensor failed during experimentation, causing the different uncertainties of \( u(T) = \pm 9 \text{ mK} \) vs. \( \pm 13 \text{ mK} \) in Table 1. The failure has probably been caused by the gas phase circulation, but has not affected the other inner sensor.

The data is plotted in Figure 1 against available literature data at about 100 K listed in Table 2, as well as the reference equation of state (EoS) of Gernert et al. [8] at 100 K taken from REFPROP 10.0 [9]. The EoS represents the literature data within ±0.3 K. Our data fits the available literature data as well as the reference EoS. Compared to the literature data, our data does not scatter and yields smooth boiling and dew point curves.

Table 1: Experimental VLE data for the system nitrogen (1) + argon (2) at temperature \( T \), pressure \( p \), liquid mole fraction \( x \) and vapor mole fraction \( y \) with respective combined uncertainties \( u \) (with coverage factor \( k = 2 \)).

| \( T / \text{K} \) | \( p / \text{bar} \) | \( x_1 / - \) | \( y_1 / - \) | \( u(T) / \text{mK} \) | \( u(p) / \text{mbar} \) | \( u(x_1) / - \) | \( u(y_1) / - \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 100.000         | 3.225           | 0              | 0              | 9               | 1               | 0               | 0               |
| 100.001         | 3.782           | 0.101           | 0.217           | 13              | 1               | 0.002           | 0.003           |
| 100.002         | 4.230           | 0.189           | 0.356           | 13              | 1               | 0.003           | 0.004           |
| 99.999         | 4.781           | 0.303           | 0.496           | 13              | 1               | 0.004           | 0.005           |
| 100.001         | 5.258           | 0.403           | 0.599           | 13              | 1               | 0.005           | 0.005           |
| 100.001         | 5.717           | 0.511           | 0.689           | 13              | 1               | 0.005           | 0.004           |
| 100.002         | 6.225           | 0.630           | 0.776           | 13              | 1               | 0.004           | 0.003           |
| 100.002         | 6.699           | 0.740           | 0.847           | 9               | 1               | 0.004           | 0.003           |
| 100.000         | 7.253           | 0.873           | 0.930           | 9               | 1               | 0.002           | 0.001           |
| 100.001         | 7.509           | 0.934           | 0.964           | 9               | 1               | 0.002           | 0.001           |
| 100.001         | 7.778           | 1              | 1              | 9               | 1               | 0               | 0               |
Figure 1: CryoPHAEQTS measurement data (■) compared against the reference EoS (—), data from Narinskii [10] (◇), from Elshayal and Lu [11] (○), from Mastera [12] (▽) and from Xiao and Liu [13] (△) at 100.0 K, and data from Hiza et al. [14] (☆) at 99.9 K.

Compared to the reference EoS, our data shows an underestimation of the nitrogen fraction in the phases particularly around $x_{1,exp} = 0.5$. Composition analysis in gas chromatography has its highest uncertainty of $u(x, y) = \pm 0.005$ in this range, but still is below the observed deviations of up to $\Delta(x, y) = 0.012$. These deviations may be related to inadequacies in our composition analysis, i.e. the calibration of the gas chromatograph, and/or the reference EoS itself, considering its accuracy of $\pm 0.3$K. For a complete evaluation of the data sets, their thermodynamic consistency is analyzed.

4.1. Thermodynamic consistency

Both our experimental data and the literature data is checked for thermodynamic consistency, using an area test (Redlich-Kister test [26]) and two point-to-point tests (Fredenslund test [27] and Van Ness test [28]). The experimental activity coefficients $\gamma_{i, exp}$ are calculated by

$$\gamma_{i, exp} = \frac{\varphi_i^V}{\varphi_{i,0}^V} \cdot \frac{y_{i, exp}}{x_{i, exp}} \cdot \frac{p_{i, exp}}{p_{i,0,exp}}$$

(2)

where $\varphi_i^V$ denotes the fugacity coefficient of the component $i$ of the mixture in the vapor phase, $\varphi_{i,0}^V$ the fugacity coefficient of the pure component $i$ at saturation and $p_{i,0,exp}$ the vapor pressure of the pure component $i$. Due to low pressures, the Poynting correction is neglected. The
Table 2: Experimental VLE data sources for the argon-nitrogen system including their temperature range $T$, pressure range $p$ and data set type. Literature data, which is far from our work at 100 K, is not compared against and grayed-out.

| Year | Authors            | $T$ / K | $p$ / bar | Type         |
|------|--------------------|---------|-----------|--------------|
| 1916 | Holst et al. [15]  | 74-90   | 0-2       | isothermal   |
| 1956 | Fastovskii et al. [16] | 78-103 | 1-4       | $p,T,x,y$    |
| 1962 | Pool et al. [17]   | 84      | 1-2       | isothermal   |
| 1965 | Wilson et al. [18] | 72-134  | 1-26      | isobaric     |
| 1966 | Narinskii [10]     | 90-120  | 1-24      | isothermal   |
| 1966 | Sprow et al. [19]  | 84      | 1-2       | isothermal   |
| 1968 | Thorpe [20]        | 80-115  | 1-11      | $p,T,x,y$    |
| 1973 | Massengill et al. [21] | 90-113 | 3-13      | $p,T,x,y$    |
| 1973 | Miller et al. [22] | 112     | 8-15      | isothermal   |
| 1975 | Lewis et al. [23]  | 85      | 1-2       | isothermal   |
| 1975 | Elshayal and Lu [11]| 100    | 3-7       | isothermal   |
| 1977 | Mastera [12]       | 85-100  | 1-8       | isothermal   |
| 1990 | Xiao and Liu [13]  | 100     | 3-8       | isothermal   |
| 1990 | Hiza et al. [14]   | 80-100  | 0-8       | isothermal   |
| 1993 | Jin et al. [24]    | 123     | 12-29     | isothermal   |
| 1999 | Baba-Ahmed et al. [25] | 95-121 | 2-27      | isothermal   |

Fugacity coefficients are calculated using the standard Peng-Robinson EoS [29] with Van der Waals mixing rules. To allow consistent fugacity coefficient calculations for all experimental data sets, the parameter $m$ of the $\alpha$-function

$$\alpha(T) = \left[ 1 + m \left( 1 - \sqrt{\frac{T}{T_{\text{crit}}}} \right) \right]^2$$

(3)

is fitted to the respective vapor pressures, if recorded, instead of using the regular acentric factor correlation.

Figure 2 shows a plot of the experimental activity coefficients of our data and the resulting Van Ness residuals based on the Van Laar $g^E$-model [30]. For the Fredenslund test, a third degree Legendre polynomial is used as $g^E$-model. For the Redlich-Kister test, a third degree polynomial is fitted to the data sets using a least squares approach. The consistency tests are performed for all experimental data sets close to 100 K, using critical data from the reference EoS. The results are shown in Table 3, which also includes the average relative deviations

$$ARD = \frac{1}{\sum_{p} |\exp - \text{pref}|}{\sum_{p} \text{pref}}$$

(4)

of the bubble and the dew points, where applicable. The pass criteria are:

- **Redlich-Kister test**
  $$100 \cdot \frac{\int_{x_{1}=0}^{x_{1}=1} \ln \frac{x_{1}}{2} \text{d}x_{1}}{\int_{x_{1}=0}^{x_{1}=1} \ln \frac{x_{1}^{2}}{2} \text{d}x_{1}} \leq 2$$
  (5)

- **Fredenslund test**
  $$\frac{1}{n} \sum_{k=1}^{n} \left| y_{k,1,\exp} - y_{k,1,\text{calc}} \right| \leq 0.01$$
  (6)

- **Van Ness test**
  randomness of the residuals
  $$r = \ln \left( \frac{\gamma_{k,1,\exp}}{\gamma_{k,2,\exp}} \right) - \ln \left( \frac{\gamma_{k,1,\text{calc}}}{\gamma_{k,2,\text{calc}}} \right)$$
  (7)
Figure 2: Activity coefficients $\gamma_1, \text{exp}(\bullet)$ and $\gamma_2, \text{exp}(\blacksquare)$ from our work.

Figure 3: Van Ness point-to-point residual plot of our data.

Table 3: ARDs of the literature data at about 100 K and our data with respect to the reference EoS [8], as well as results of the Redlich-Kister test (RK), the Fredenslund test (Fr) and the Van Ness test (VN).

| Data set       | ARD\text{bubble} / % | ARD\text{dew} / % | RK   | Fr  | VN       |
|----------------|----------------------|-------------------|------|-----|----------|
| Narinskii      | 0.29                 | 0.27              | fail | pass| non-random |
| Elshayal and Lu| 0.38                 | -                 | -    | -   | -        |
| Mastera        | 2.78                 | 3.13              | fail | fail| non-random |
| Hiza et al.    | 0.62                 | 0.37              | fail | fail| non-random |
| Xiao and Liu   | 1.94                 | 1.83              | fail | pass| non-random |
| This work      | 0.57                 | 0.46              | fail | pass| non-random |

As expected for a system of similar molecules, our experimental activity coefficients yield typical symmetrical smooth curves (with the exception of $\gamma_2, \text{exp}\left[x_1 = 0.740\right]$). Both curves can be extrapolated to yield activity coefficients of the infinitely diluted solutions of $\{\gamma_1,\infty; \gamma_2,\infty\} < 1.20$.

The parameters of the reference EoS [8] have been fitted to the original data from Narinskii, Elshayal and Lu and Hiza et al. which explains the low ARDs of this data shown in Table 3. The data sets from Mastera, and Xiao and Liu have not been chosen for the reference EoS, yielding high ARD values. In comparison, our data set performs well and yields reasonably low deviations.

Despite the low deviations from the reference EoS, the data from Hiza et al. fails all consistency tests. In contrast, our data, the data from Narinskii, and from Xiao and Liu pass the averaged residual Fredenslund test. Looking at the Van Ness point-to-point representation of our data, the residuals show non-random behaviour since eight out of nine data points show negative deviations of up to -0.03. None of the investigated data sets show random scattering of their residuals. Regarding the integral Redlich-Kister test, all data sets fail. The denominator in Equation 5 is very small due to the ideality of the system. Therefore, even small errors in the experimental activity coefficients affect the relative area calculations. At $\gamma \to 1$, area tests, such as the Redlich-Kister test, lose their sensitivity.

To conclude, none of the data in the literature, nor our data, pass all consistency test criteria. However, our data, the data of Narinskii, and of Xiao and Liu can be represented by a thermodynamically consistent $g^E$-model, yielding average deviations below 0.01.
5. Conclusion
The vapor-liquid equilibrium of the nitrogen-argon system is measured at 100 K over the whole composition range. The data shows low deviations to the reference EoS and with respect to the available literature data. Assuming correct temperature and pressure measurement, the remaining composition deviations exceed the measurement uncertainty, but their amplitudes correlate with the uncertainty. Common tests for thermodynamic consistency fail due to the ideality of the nitrogen-argon system and consequently small activity coefficients. For future investigations, the gas chromatograph will be recalibrated using different methods to increase the accuracy of the composition analysis.

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**Acknowledgements**

The authors would like to acknowledge the support from the Karlsruhe School of Elementary Particle and Astroparticle Physics: Science and Technology (KSETA) and from the German Research Foundation (DFG) within the project 'Simultaneous description of caloric and thermal properties of cryogenic fluid mixtures' (Gr 4168/2-1).