Density Measurements on Binary Helium + Neon Mixtures over the Temperature Range from (100 to 233) K at Pressures up to 10 MPa[#]

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ABSTRACT

Densities of two binary (Helium + Neon) mixtures were measured along six isotherms in the temperature range from (100 to 233.15) K and at pressures of up to 10 MPa, using a low-temperature single-sinker magnetic suspension densimeter. The mixtures were prepared gravimetrically yielding molar Helium fractions of approximately 0.50 and 0.25, respectively. The measurements were carried out at T = (100, 120, 140, 170, 200, and 233.15) K in the homogenous gas region. In total, densities at 72 (T, p) state points were determined. The relative expanded combined uncertainties (k = 2) of the experimental densities were estimated to be within (0.023 and 0.055)%. The largest uncertainty contributions result from the weighing of the sinker and the composition of the prepared mixtures. The experimental results were compared with available experimental literature data as well as with a preliminary mixture model of Lemmon and with a fundamental equation of state of Tkaczuk *et al*.

Keywords: cryogenic state, density measurement, magnetic suspension coupling, noble gas mixtures, single-sinker densimeter, hydrogen liquefaction

NOMENCLATURE

Abbreviations	
AARD	Average absolute relative deviation
EOS	Equation of State
exp	Experimental
FTE	Force Transmission Error
LH_2	Liquid Hydrogen
VLE	Vapor-Liquid Equilibrium
Symbols	
α	Balance Calibration Factor
ε	Force Transmission Error
m	Mass / Weighing Value
ρ	Density
V	Volume

1. INTRODUCTION

Hydrogen, used for energy supply, transport, and storage, is considered in basically all CO_2-mitigation plans [1,2]. Hydrogen roadmaps have been published by many regions and countries, including the United States [3] and the European Union [4,5]. To meet the respective demands on available hydrogen, not only the production capacities must be scaled up extensively, but likewise, the capacity of hydrogen liquefaction [2] to support economic long-distance transport. Current hydrogen liquefaction plants feature energy demands of (11.9 to 15.0) kWh/kg$_{LH2}$ [1]. Novel concepts for advanced large-scale liquefaction plants predict a reduction to about 6 kWh/kg$_{LH2}$ [1,6]. Many of these concepts apply Brayton cycle pre-cooling stages that utilize mixtures of Helium and Neon as refrigerants [7–9]. Besides the application in hydrogen liquefaction processes, mixtures of Helium and Neon are also used for other cryogenic cooling concepts; *e.g.* for the Future Circular Collider [10].

Accurate simulations and detailed designs of respective technical processes require likewise accurate predictions of the thermophysical properties of the involved fluids. Here, equations of state (EOS) are being used to calculate various properties like densities and speeds of sound. These models, however, rely on comprehensive experimental data sets. For the development of an equation of state for mixtures of Helium and Neon, Tkaczuk *et al.* faced the problem of scarce data in the literature [11]. The existing data sets are old and in the temperature range of 41 K < T < 233 K, no experimental (p, ρ, T) data is available at all. Accordingly, the model of Tkaczuk *et al.* has been developed merely predictive in this temperature region and the accuracy of the model may be rather limited in some technically relevant regions.

In this work, we present first results of precise density measurements on two (Helium + Neon) mixtures in the temperature range of (100 to 233.15) K at pressures up to 10 MPa. This data constitutes the initial stage of expanding the database for fluid mixtures that

are relevant for hydrogen liquefaction processes. This data can then serve for the validation of existing models or the development of new equations of state.

2. EXPERIMENTAL SECTION

2.1 Apparatus *Description*

The density measurements presented in this work were performed using a low-temperature single-sinker densimeter that has been designed for precise density measurements on liquefied gas mixtures; *i.e.* natural gases and similar mixtures. It covers a temperature range from (100 to 300) K at pressures of up to 12 MPa. The densimeter is based on the buoyancy principle, utilizing a silicon sinker in conjunction with a magnetic suspension coupling. Its design and the implementation of a so-called "VLE-cell" are described in detail by Richter *et al.* [12] and Lentner *et al.* [13]. In the following, we only give a brief overview of the densimeter. General descriptions of this type of densimeter are given by Wagner and Kleinrahm [14] and by McLinden [15].

The single-sinker principle in conjunction with a load-compensation method and a magnetic suspension coupling is illustrated in Fig. 1. A sinker of known volume $V_S(T,p)$ and known mass m_S is weighed while being submerged in the fluid of interest. The weighing forces are, without contact, transferred to an analytical balance by the magnetic suspension coupling. To compensate for a zero-drift of the balance, the magnetic suspension coupling alternates between the tare position, where the sinker is not attached to the coupling, and the measuring position, where the sinker is lifted. Typically, 15 to 20 weightings are recorded at the tare and measurement positions respectively. Their averaged difference is considered the weighing force of the sinker. With this, the density of the fluid under survey ρ_{fluid} can be determined by

$$\rho_{\text{fluid}} = \frac{m_{S,\text{vac}}^* - m_{S,\text{fluid}}^*}{V_S(T,p)}.$$

Here, $m_{S,\text{fluid}}^*$ is the weight of the sinker suspended in the fluid under survey and $m_{S,\text{vac}}^*$ is the weighing of the sinker in the evacuated measuring cell. The latter is slightly different to m_S due to a small force transmission error (FTE) that is introduced by the magnetic suspension coupling. The effect of the FTE and its correction are described in detail by Kleinrahm *et al.* [16]. Furthermore, the balance calibration factor $\alpha = 1/(1 - \rho_{\text{air}}/\rho_{\text{cal}})$ needs to be considered. Here ρ_{air} is the air density during calibration and ρ_{cal} is the density of the 100 g standard mass that is being used for the balance calibration. Considering both, the FTE and

the balance calibration factor, the final working equation for the determination of the fluid density is

$$\rho_{\text{fluid}} = \frac{\left(m_{\text{SD,vac}}^* - m_{\text{SD,fluid}}^*\right)/\alpha}{V_S(T,p)} \cdot (1 + \varepsilon_{\text{vac}} + \varepsilon_{\text{fse}})^{-1}.$$

Here, ε_{vac} and ε_{fse} are the apparatus contribution and the so-called "fluid specific effect" of the FTE, respectively (refer to [16]). The index "SD" accounts for the utilization of compensation masses that are used to operate the analytical balance near its tare point, even when the sinker is lifted at the measuring position (see Fig. 1) to minimize the linearity error of the balance.
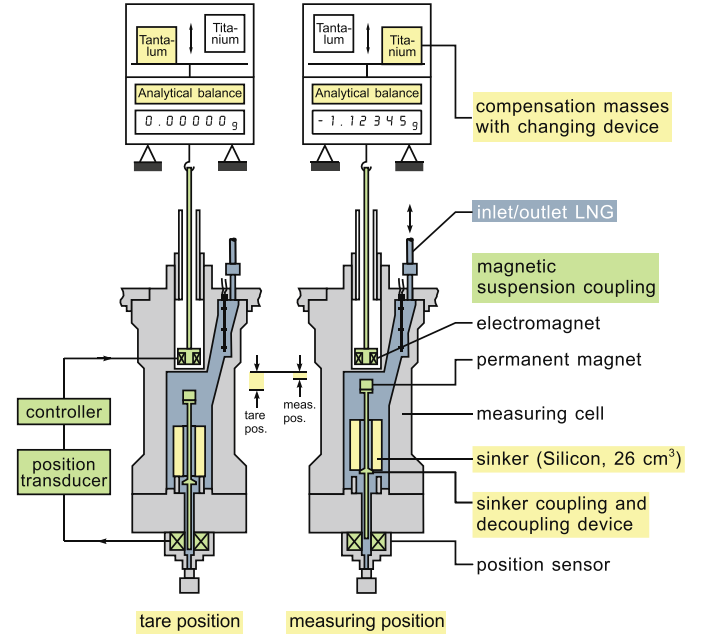

Fig. 1 Principle of the utilized single-sinker densimeter. Schematic as given in Richter *et al.* [12].

2.2 Experimental Material

Two binary (Helium + Neon) mixtures were prepared gravimetrically in aluminum cylinders with an internal volume of 20 dm³. Using a custom-made gravimetric mixture preparation system [17], the pure components, described in Table 1, were sequentially filled into the cylinders. The mixture preparation system consists of a mass comparator (Sartorius, CCE60K3, maximum load 61 kg, resolution 0.002 g) to determine the mass of the evacuated cylinder and likewise the added masses of the pure components. The expanded uncertainty of the respective cylinder weightings was estimated to be 0.200 g. Details of the mixture preparation procedure are given by Schäfer [17]. With a target cylinder filling pressure of approximately 12.5 MPa, the required masses of each component were determined beforehand. The obtained molar fractions of the two studied mixtures and their respective uncertainties in composition are given in Table 2.

Table 1 Molar purities of the pure components used for the mixture preparation.

Component	Source	Purity
Helium	Air Liquide	0.999990[a]
Neon	Messer Industriegase	0.999990[b]

[a] $x(H_2O)<2ppm$, $x(C_nH_m)<0.2ppm$, $x(N_2)<5ppm$, $x(O_2)<2ppm$.

[b] $x(He)<6ppmv$, $x(H_2O)<1ppmv$, $x(C_nH_m)<0.1ppmv$, $x(N_2)<2ppmv$, $x(CO_2)<0.5ppmv$, $x(O_2)<1ppmv$.

Table 2 Compositions, molar masses M and uncertainty in composition $U(x_{Ne})$ (k = 2) of the studied mixtures.

Mixture	0.25/0.75	0.50/0.50
x_{He} / mole fraction	0.250238	0.499861
x_{Ne} / mole fraction	0.749762	0.500139
M / (g·mol^{-1})	16.1316	12.0934
$U(x_{Ne})$ / mole fraction (k = 2)	0.000148	0.000148

2.3 Experimental Procedure

The single-sinker densimeter used for the density measurements presented in this work was originally designed for measurements on liquefied gases. In this regard, a special VLE-cell was implemented as a buffer for the unavoidable phase transition from the liquid in the measuring cell to vapor in the pressure measuring circuit (refer to [12,13]. With a low-temperature limit of 100 K, however, the apparatus is only capable of measurements in the homogenous gas phase when studying (Helium + Neon) mixtures. Therefore, the functionality of the VLE-cell was not applied and the filling procedure could be simplified compared to the elaborate technique described by Richter *et al.* [12].

The density measurements were performed along six isotherms. For each isotherm, the evacuated apparatus was filled to the maximum pressure of 10 MPa, starting at ambient temperature. Since the measurements are performed only in the gas phase, crossing the vapor-liquid equilibrium (VLE) is of no concern. Thus, to save some time, the core apparatus could be cooled down simultaneously to the gradual filling to 10 MPa. When the target temperature was reached and the sample was in a sufficient equilibrium state, the first density measurement was performed at $p \approx 10$ MPa. Subsequently, further state points along the respective isotherm at $p \approx (8.0, 6.0, 4.0, 2.0,$ and 1.0) MPa were approached by venting sample from the system. Densities for each state point were recorded at least twice to ensure representative conditions of the sample.

After each investigated isotherm the system was exhausted and heated up to ambient temperature. Then it was alternately evacuated and filled with the respective mixture several times before the actual filling for the next measurements at a new temperature commenced.

2.4 Uncertainty Analysis

The uncertainty in density was estimated for each (p, ρ, T, x) state point individually, considering the respective sensitivity coefficients. The expanded combined uncertainty $U(\rho)$ is determined in line with the GUM [18] (ISO/IEC Guide):

$$U(\rho) = k \cdot \left[u(\rho)^2 + \left(\left(\frac{\delta\rho}{\delta p} \right)_T \cdot u(p) \right)^2 + \left(\left(\frac{\delta\rho}{\delta T} \right)_p \cdot u(T) \right)^2 \\ + u(\rho(x))^2 + u(\rho_{repro})^2 + u(\rho_{corr})^2 \right]^{\frac{1}{2}},$$

where $u(\rho)$, $u(T)$, and $u(p)$ are the standard uncertainties in density, temperature, and pressure, respectively. The uncertainty in composition of the prepared mixtures is represented by $u(\rho(x))$, and $u(\rho_{repro})$ and $u(\rho_{corr})$ consider the reproducibility and the correction of the FTE, respectively.

The uncertainty of the density measurement $u(\rho)$ was estimated by Richter *et al.* [12] to be 0.0080% for liquids. Von Preetzmann *et al.* [19] were the first to publish gas densities determined with the single-sinker densimeter used in this work. They estimated the uncertainty contribution of the weighing to be 0.0030 kg/m^3 or 0.0080%, whichever is greater. For the pressure measurement, a rotary piston gauge (Fluke, PG-7601-CE) was used; its expanded uncertainty (k = 1.73) is (0.0035%·p + 20 Pa). The ambient pressure was recorded via an external barometer with an expanded uncertainty of 11 Pa (k = 1.73). The uncertainty of the temperature measurement is 15 mK (k = 1.73). The contributions of the reproducibility and the FTE correction are 0.0100% and 0.0030%, respectively. Considering all contributions in line with the GUM [18], the expanded combined relative uncertainties of the 72 measured densities are in the range of (0.023 to 0.055)%. The largest contributions come from the uncertainty in composition and the density measurement itself.

3. RESULTS AND DISCUSSION

Our experimental densities are compared with two equations of state; the preliminary equation of state by Lemmon [20] for mixtures composed of Helium and Neon and the new equation of state by Tkaczuk *et al.* [11] for binary mixtures of Helium, Neon, and Argon. Moreover, our results of the (0.499861 Helium + 0.500139 Neon) mixture at $T = 233.15$ K are compared to the data of Vogl and Hall [21]. They reported compressibility data and virial coefficients for

temperatures from (233 to 313) K. We included measurements along the T = 233.15 K isotherms in our investigations, to allow for a comparison with their reported data for a binary (Helium + Neon) mixture with a molar Helium fraction of 0.494. The relative deviations of experimental densities from densities calculated with the equations of state are plotted in Fig. 2 and Fig. 3.
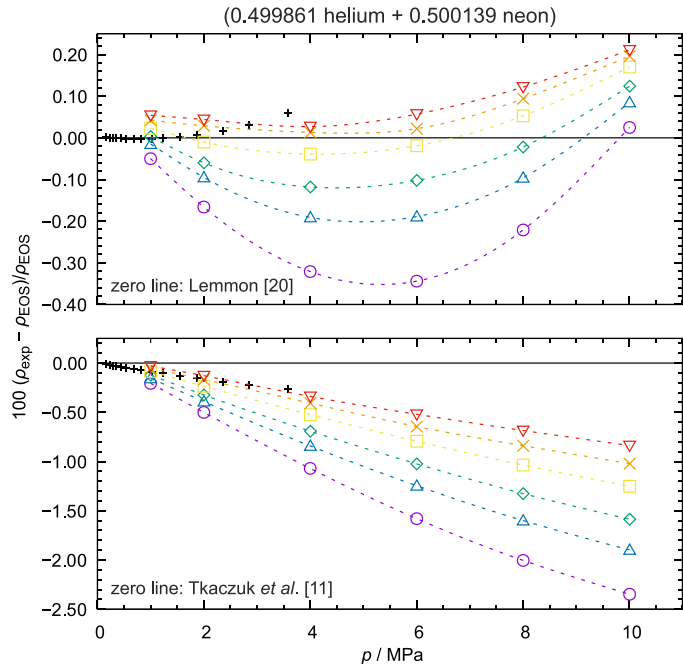
that Tkaczuk *et al.* focused on the prediction of the VLE behavior as this is a crucial region concerning hydrogen liquefaction and cryogenic cooling processes. This can also be seen by comparing the data of Vogl and Hall [21] at $T \approx 233$ K to both models. The average absolute relative deviation (AARDs) is 0.097% to the model of Tkaczuk *et al.* and only 0.009% to the model of Lemmon.
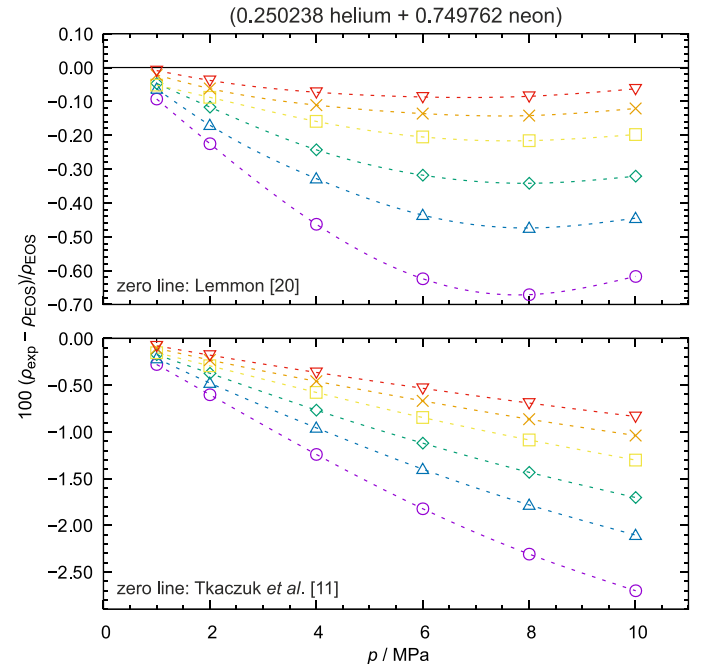

Fig. 2 Relative deviations of experimental densities ρ_{exp} for the (0.499861 Helium + 0.500139 Neon) mixture from densities ρ_{EOS} calculated with the equations of state of Lemmon [20] (top) and Tkaczuk *et al.* [11] (bottom): ○, T = 100 K; △, T = 120 K; ◇, T = 140 K; □, T = 170 K; ×, T = 200 K; ▽, T = 233.15 K; +, Vogl and Hall [21] at T = 233.158 K for a (Helium + Neon) mixture with x_{He} = 0.494.

Fig. 3 Relative deviations of experimental densities ρ_{exp} for the (0.250238 Helium + 0.749762 Neon) mixture from densities ρ_{EOS} calculated with the equations of state of Lemmon [20] (top) and Tkaczuk et al. [11] (bottom): ○, T = 100 K; △, T = 120 K; ◇, T = 140 K; □, T = 170 K; ×, T = 200 K; ▽, T = 233.15 K.

It can be seen that the model of Lemmon [20] predicts the homogenous gas densities significantly better than the newer equation of Tkaczuk *et al.* [11]. The experimental densities for the (0.499861 Helium + 0.500139 Neon) mixture deviate between (−0.35 and 0.22)% from values calculated with the model of Lemmon, and between (−2.35 and −0.03)% from densities calculated with the model of Tkaczuk *et al.* The deviations of the (0.250238 Helium + 0.749762 Neon) mixture are within (−0.67 to −0.09)% and (−2.71 to −0.08)%, respectively. We would like to point out that deviations in the observed magnitude can impair the accuracy when designing facilities and technical processes, yielding lower achievable effectivities or profitability. This can be of relevance for cryogenic refrigerators where mixtures of Helium and Neon are used as working fluids at temperatures of up to 80 K [22] as well as for the pre-cooling stages in hydrogen liquefaction processes [1]. Here, it shall be mentioned

When comparing our densities of the (0.499861 Helium + 0.500139 Neon) mixture at T = 233.15 K to the data of Vogl and Hall [21], it can be seen that the experimental data sets are consistent within their experimental uncertainties. Vogl and Hall state uncertainties of (0.02 to 0.04)% in the compressibility factor which implies the same uncertainty in density, derived from the compressibility factor. The combined uncertainties (k = 2) of our data are within (0.029 and 0.055)% for T = 233.15 K at pressures up to 4.0 MPa.

Fig. 2 and Fig. 3 show that the experimental densities approximately approach a relative deviation of zero with decreasing pressure. This is due to the fact, that the gas mixtures exhibit an ideal gas behavior at the zero-density limit at p = 0. The models are built to meet this ideal gas condition. Consequently, the deviations of our data to the models at zero-density can be used to validate our experimental data. It can be seen that the densities of the investigated isotherms do not exactly extrapolate to a relative deviation of zero, at p = 0, but a value of about

0.05% or 0.10%. This could be explained by the experimental uncertainty to some extent. For the state points of all 12 recorded isotherms, at $p \approx 1.0$ MPa, the expanded uncertainties ($k = 2$) range from (0.032 to 0.055)%. Moreover, the uncertainty of extrapolated densities increases exponentially with decreasing pressure. As an example, the uncertainty of the weighing of at least 0.003 kg/m^3 (see section 2.4) alone would translate to a relative uncertainty of 0.2%, when extrapolating the $T = 100$ K isotherm of the 0.50/0.50 mixture to $p \approx 0.1$ MPa.

The ultimate cause for the offset at the zero-density limit and if it can be reduced for future investigations is yet unclarified. It may be caused by a minor error in measurement that just becomes discernible when dealing with densities as low as those of the (Helium + Neon) mixtures studied in this work and is negligible when measuring liquid densities. Systematic errors in the temperature or pressure measurement can be excluded as they would manifest differently. Other potential sources can be the weighing (*e.g.* the vacuum data), or the composition of the mixtures. Further considerations and experimental tests will be performed to further examine and evaluate this subject. However, this offset at the zero-density limit does not change the overall conclusions that can be made when comparing our results to the models; *i.e.* that both models are not capable of accurately predicting the homogenous gas densities. Hence, further improvements to the equations of state are of interest; *e.g.* to support the efficiency goals for large-scale hydrogen liquefaction plants [1,6].

4. CONCLUSION AND OUTLOOK

Accurate homogenous gas density measurements on two gravimetrically prepared (Helium + Neon) mixtures were carried out along the six isotherms T = (100, 120, 140, 170, 200, and 233.15) K at pressures up to 10 MPa. For the study, a single-sinker densimeter was used, which was originally developed for density measurements on cryogenic liquids. In total, 72 state points were measured in the homogenous gas phase. The combined uncertainty in density ($k = 2$) was estimated to be within (0.023 and 0.055)%. The main contributions are the uncertainty in composition and the uncertainty of the weighing.

The new results presented in this work were compared to the mixture models of Lemmon [20] and Tkaczuk *et al.* [11]. The relative deviations, plotted in Fig. 2 and Fig. 3, show that the new model of Tkaczuk *et al.*, shows significant cutbacks when considering the homogenous gas region in the investigated temperature range, while the model of Lemmon performs noticeably better. Since no density data was available in the

temperature range from (41 to 233) K so far, with our new data, a validation of the equations of state in a large section of this region was possible for the first time. For the (0.499861 Helium + 0.500139 Neon) mixture the deviations of our experimental densities were between (−0.35 and 0.22)% from values calculated with the model of Lemmon, and between (−2.35 and −0.03)% from the model of Tkaczuk *et al*. For the (0.250238 Helium + 0.749762 Neon) mixture, the deviations are within (−0.67 to −0.09)% and (−2.71 to −0.08)%, respectively.

Our results demonstrate the need for further improvements to the available equations of state to support the accurate designing of efficient processes that apply mixtures of Helium and Neon [7−10,[22]. In this regard, further extensions of the experimental database will significantly facilitate this objective. For this purpose, in near future, we will carry out accurate density measurements on a (0.75 Helium + 0.25 Neon) mixture with the apparatus utilized for the investigations presented in this work. Moreover, to extend the database towards temperatures lower than 100 K, the set-up of a new densimeter is projected, that aims for density and speed of sound measurements at temperatures as low as 20 K.

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