Characterisation of a microwave re-entrant cavity resonator for phase-equilibrium measurements and new dew-point data for a (0.25 argon + 0.75 carbon dioxide) mixture

**Gergana Tsankova^a, Markus Richter^{a1}, Adele Madigan^b, Paul Stanwix^b, Eric F. May^b,
and Roland Span^a**

^a *Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, D-44780 Bochum, Germany*

^b *Centre for Energy, School of Mechanical and Chemical Engineering, The University of
Western Australia, Crawley, Western Australia 6009, Australia*

Revised manuscript submitted for publication in *J. Chem. Thermodyn.* (2016).

ABSTRACT

An apparatus based on a microwave re-entrant cavity resonator, originally built for accurate measurements of the dielectric permittivity of natural gas mixtures, was refurbished and extensively characterized. This was done to enable the future investigation of phase equilibria and (p, ρ, T, x) behaviour of fluid mixtures utilizing the present experimental technique. Vacuum resonance frequencies and Q-factors of the resonator's modes were modelled using both analytic and finite element methods, and found to compare well with experimental values. The finite element models helped to identify two whispering gallery-type modes not previously reported for such cavity geometries. The models also predict distributions of the electric and magnetic fields in the re-entrant cavity resonator useful for identifying regions in the cavity more sensitive to the presence of a liquid. Following the resonator's characterisation, its ability to measure dew points was tested using a gravimetrically prepared (0.2501 argon +

---

¹ Corresponding author. Tel.: +49-234-32-26395, E-mail: m.richter@thermo.rub.de.

0.7499 carbon dioxide) mixture over the temperature range from (252 to 280) K at pressures from (2.8 to 6.9) MPa. The combined expanded uncertainty with a level of confidence of approximately 95% ($k = 2$) in dew point temperature and pressure ranged between (0.025 and 0.044) K and from (0.009 to 0.015) MPa, respectively. We compared the experimental dew point pressures with the recently developed multi-parameter equation of state optimised for combustion gases (EOS-CG), showing relative deviations in the range of (0.044 to 0.479)%. In contrast, relative deviations of up to -4% from the GERG-2008 equation of state and two different implementations of the Peng-Robinson equation were observed, although these models are not optimized for dew point calculations of carbon dioxide rich mixtures.

Keywords: argon; carbon dioxide; dew point measurements; finite element model; gas mixture; microwave re-entrant cavity resonator

1. Introduction

Accurate knowledge of the phase behaviour of fluid mixtures containing carbon dioxide is crucial for the development and operation of carbon capture and storage (CCS) systems, which are being investigated to reduce the carbon dioxide emissions from power plants fired with fossil fuels. To that end, Gernert and Span [1] developed a new Helmholtz energy “Equation of State for Combustion Gases and Combustion-Gas-like Mixtures” (EOS-CG) to predict the behaviour of such mixtures, including the phase boundary between liquid and vapour. This model describes most of the mixtures relevant for CCS better than other existing mixture models, including the GERG-2008 equation of state developed by Kunz and Wagner [2], which was developed with an emphasis on natural gas and similar mixtures, as well as cubic equations of state such as that of Peng and Robinson [3], which are commonly used in industry. In all cases, the accuracy of EOS predictions is limited to some degree by the data available at the time of their development; improving the quality and extent of available data, in particular for the description of the phase equilibrium, is a major goal of our ongoing research.

Improving the experimental data base, underlying model predictions for phase equilibria, is both important and challenging, given the technically difficult nature of such measurements. Phase equilibrium (vapour-liquid) measurements of fluid mixtures are often carried out via the analytic method, which involves taking samples from the coexisting phases to analyse the composition (*e.g.*, by gas chromatography, GC) [4]. The uncertainty achievable in the measured composition via the analytic method is, however, limited by both the challenges of sampling repeatability and the accuracy of the GC’s detector calibration [5]. In contrast, the synthetic method, where the phase boundary of a fluid with known composition is measured, does not suffer the disadvantages associated with sampling but it does require a means of

detecting the onset of a phase transition. Such signals can be very small and difficult to resolve; for example, trying to detect a fluid's dew point in a view cell can be very difficult as the small amounts of liquid present can be very difficult to observe or quantify visually. An alternative and promising way to accurately detect the onset of such phase transitions is based on microwave techniques, first introduced by Rogers *et al.* [6] who used an evanescent system. Moldover and co-workers [7,8] described the development of accurate re-entrant cavity resonators for the accurate measurement of fluid thermophysical properties over wide ranges of temperature and pressure, including the determination of dew points via the synthetic method, which was an approach further developed by May *et al.* [9,10,11].

In this work, we have applied a microwave re-entrant cavity to the measurement of dew points of a mixture of importance to CCS applications. The resonator we describe is based on the design of Goodwin *et al.* [7]; it was built at the National Engineering Laboratory (East Kilbride, UK) and was originally used for dielectric permittivity measurements of natural gas [12,13,14]. We refurbished the apparatus at Ruhr-University Bochum for the investigation of phase equilibria (including liquid volume fractions), dielectric permittivity, and (p, ρ, T, x) behaviour of fluid mixtures. The cavity has been extensively characterised to determine the frequency and Q-factor of all resonant modes, which were predicted through both analytical (fundamental mode) as well as finite element modelling (higher order modes) and confirmed experimentally. The finite element modelling was also used to calculate the energy distribution of the electric and magnetic fields within the re-entrant cavity resonator, to identify the internal regions of the resonator sensitive to the presence of a liquid phase (in this case, where the electric field is most intense). To test the current apparatus' suitability for the investigation of the phase behaviour of fluid mixtures, we chose to measure the dew points of a (0.2501 argon + 0.7499 carbon dioxide) mixture since there is a dearth of literature data for this binary system. Isochoric measurements were carried out over the temperature range from

(252 to 280) K at pressures from (2.8 to 6.9) MPa. We compare the experimental results to values calculated with the fundamental equations of state EOS-CG [1] and GERG-2008 [2] as well as with the two different implementations of the cubic Peng-Robinson equation of state [3] and show that the EOS-CG performs best over the range of conditions investigated.

2. Apparatus description

The apparatus used in the present work was originally constructed by the National Engineering Laboratory (NEL, East Kilbride, UK) [12]. Jaeschke [13] and Jaeschke *et al.* [14] established and utilized the resonator for determining the heating value of natural gas samples by dielectric permittivity measurements. For the present work, the device was adapted for the purpose of investigating the phase behaviour of binary mixtures, particularly those rich in carbon dioxide. In the future we plan to also investigate dielectric permittivity and the (p, ρ, T, x) behaviour of fluid mixtures. Below we describe each aspect of the measurement system, from the design of the resonator and determination of its electromagnetic modes, to the preparation and handling of gas mixtures, and the measurement at dew point conditions.

2.1 The re-entrant cavity resonator

The design of the re-entrant cavity resonator, shown as cutaway view in figure 1, is based on the concept described in detail by Goodwin *et al.* [7], where the measuring cell is an electromagnetic cavity resonator for which the principle mode can be represented as a parallel *LCR* circuit. A thin cylindrical neck at the upper part of the resonator expands as a bulbous coaxial extension into a hollow outer cylinder with an inner diameter of 58.5 mm and a wall thickness of 5 mm. The bulbous coaxial extension has a diameter of 54.5 mm and a length of 25.5 mm and fills approximately 1/3 of the outer cylinder's volume. The relatively large toroidal section above the bulbous extension acts as an inductor, and the narrow annular gap of 2 mm between the bulbous extension and the inner surface of the hollow cylinder acts as a capacitor.

A gold-plated copper ring is employed to ensure a reliable low-resistance electrical conduction path between both parts of the resonator when screwed together. The resonator and all required sundries are made from a beryllium-cooper alloy (Brush Alloy 25, Material Nr.: CW101C, Brush Wellman Ltd., UK). After machining, the parts were electroplated with silver, to a nominal thickness of (2 to 3) μm , and then with gold, to a nominal thickness of (5 to 8) μm . When assembled, the total internal volume of the resonator (as a single component) is about 93 cm^3 .

The top part of the resonator is equipped with a sample inlet, a central bore for a standard platinum resistance thermometer reaching down to the bulb and two high-pressure coaxial microwave feedthroughs. The feedthroughs are made of 0.8 mm diameter, gold-plated, nickel-iron alloy wire, fused into a stainless steel component part using a glass-to-metal seal fired at high temperature. The lower end of the wire is formed as a loop and is connected to the stainless steel part through brazing. (No further information about how the feedthroughs were fabricated at NEL can be extracted from reference [12].) The other end of the wire loop passes inside the central hole of the stainless steel part of the feedthrough and leads to an SMA connector. The coupling loop at the bottom of each feedthrough serves either as transmitter or as receiver and couples the magnetic component of the internal field to an external detection system. Two SMA cables lead from the coupling loops to a vector network analyser to measure the resonant frequency (described below).

The resonator is housed in a custom-made pressure vessel fabricated from stainless steel. Thus, the pressure inside and outside the resonator is the same, which largely mitigates the distortion of the cavity when subject to an internal pressure. The outer diameter of the pressure vessel is 95 mm, the length is 160 mm and the wall thickness is 12 mm. When assembled, both the microwave cavity and the pressure vessel have a total internal volume of about 192 cm^3 . We note that this design, with such a large volume and elevated location of the ca-

capitance (*i.e.*, high sensitivity) region is not optimal for dew point measurements because it relies on detecting the change in the vapour phase (other designs have been demonstrated that take these factors into consideration [11]). However, for binary systems with carbon dioxide that exhibit appreciable change in the vapour phase this design is shown to be adequate.

2.2 Measurement of microwave resonant modes

Resonant modes of the cavity, and particularly the resonant frequency, were determined by examination of the transmitted amplitude response measured with a vector network analyser (VNA). The VNA available for the dew point measurements (HP, USA, model 8752C) had a frequency range of (0.3 to 1300) MHz. The long-term stability of the frequency measurement was improved, and the short-term temperature drift of the device was reduced, by using an external oven-controlled crystal oscillator module (HP, USA, type: 10811) with a relative stability in the reference frequency of 0.1×10^{-9} . A second VNA (Keysight, USA, model E5063A), with a maximum operating frequency of 18 GHz was used for the determination of the cavity's higher order modes (but was unavailable for the dew point measurements). The complex resonance frequencies $\mathbf{F}_\alpha = f_\alpha + ig_\alpha$, where f_α is the resonant frequency and g_α is the half-width of a mode enumerated by α , were determined from the complex transmission coefficient S_{21} with a local maximum occurring at $f_\alpha = \text{Re}[\mathbf{F}_\alpha]$. The transmission coefficient was measured at 401 frequencies spanning an interval $f_\alpha \pm 5g_\alpha$. The measured values for the real Re and imaginary Im part are then fitted to the complex Lorentzian function:

$$S_{21}(f) = \frac{Af}{f^2 - \mathbf{F}_\alpha^2} + \mathbf{B} + \mathbf{C}(f - f_*) + \mathbf{D}(f - f_*)^2. \quad (1)$$

The complex constants **A**, **B**, **C**, **D**, and the complex resonant frequency $\mathbf{F}_\alpha = f_\alpha + ig_\alpha$ were treated as fitting parameters; f is the source of frequency and f_* is an arbitrary constant frequency near f_α . A detailed description concerning the fitting procedure is given by Mehl [15]. In this work, the value of f_α was determined with a precision of 10 kHz. However, for (p, T) phase boundary measurements, it is a change in the trend of f_α with T or p that identifies the

onset of a phase transition, as opposed to its absolute value. This discontinuity in the slope of f_a with T or p is caused by the change in the dielectric properties of the fluid under investigation when it undergoes a first order phase transition.

2.3 Mixture preparation and handling

To enable dew point measurements of binary mixtures rich in carbon dioxide, the old gas-dosing system was replaced by a temperature-controlled one, and electrical heating for the tubing and gas mixture supply was installed in an attempt to minimize inadvertent condensation and sorption. The temperature measurement chain, as well as the pressure measurement circuit (including transducers), were renewed completely, and the current status is described in the following sections. New sealing techniques for the pressure vessel and the measuring cell were implemented to enable measurements of carbon dioxide and its mixtures at pressures up to 12 MPa.

The current setup enables measurements over a temperature range from (243 to 353) K at pressures up to 12 MPa. A schematic diagram of the apparatus is shown in figure 2, whereby the comprehensive (electrically heated) sample manifold is deliberately simplified.

The measurements presented here were made on pure carbon dioxide and a binary mixture of argon and carbon dioxide. The pure components we used (also to prepare the mixture) are described in Table 1. The samples were used as received without further confirmation of the purity stated by the supplier. The binary mixture was prepared gravimetrically in house in a 20 L aluminium gas cylinder of Scott Specialty Gases. The inside surface was specifically prepared by the supplier to improve the long-term stability of the mixture composition. We prepared the gas mixture with a comparatively high filling pressure of the sample cylinder of about 19 MPa. The molar mass of the gas mixture was $M_{\text{grav}} = 42.9981 \text{ g}\cdot\text{mol}^{-1}$. The expanded uncertainty ($k = 2$) in composition was estimated to be 0.0004 mole fraction, which corresponds to an uncertainty in molar mass of approximately $0.0019 \text{ g}\cdot\text{mol}^{-1}$. Details about the

mixture preparation system and the preparation procedure are described in detail by Schäfer [16].

2.4 Temperature measurement and control

The temperature of the cavity resonator was measured with a 25 Ω standard platinum resistance thermometer (SPRT, Tinsley, UK, type: 5187L) installed in the central bore of the part of the resonator (see figure 1). A precision AC resistance bridge (Isotech, UK, type: microK 500) was employed to determine of the resistance ratios between the temperature sensor and an external 25 Ω reference resistor (Tinsley, UK, type: 5685A). To determine the accurate resistance value of the reference resistor along its characteristic curve, the temperature of the resistor is measured with a 100 Ω platinum resistance thermometer using a digital multimeter (Tektronix, USA, type: 4040). The temperature measurement chain was calibrated in house in accordance with ITS-90 at the triple points of mercury and water and at the melting point of gallium. The characteristic curve of the 25 Ω reference resistor was determined by comparison to a second reference resistor, which was calibrated at Physikalisch Technische Bundesanstalt. We estimated the combined expanded measurement uncertainty ($k = 1.73$) in temperature to be less than 20 mK. This value includes, *e.g.*, temperature gradients along the measuring cell wall and fluctuations over time, as further described in Section 4.2. (Please note: In line with the "Guide to the Expression of Uncertainty in Measurement" according to ISO/IEC (2008) [17], our basic assumption is that input quantities such as manufacturer specifications, *e.g.*, of the thermometry bridge, and estimates of measurement deviations, *e.g.*, temperature gradients that cannot be directly measured, are described by a symmetric, rectangular probability distribution, thus, the coverage factor can be assumed to be $k = \sqrt{3} \approx 1.73$).

For temperature control of the measuring cell and the pressure vessel, a bath thermostat (Grant, UK, type: LTC-2006-40) and a temperature controller (Eurotherm, UK, type: 2416)

were used. The thermostat was modified with a propeller, a baffle plate and a duct to improve the overall temperature stability. The stability of the temperature regulation was approximately (5 to 10) mK after allowing enough time for equilibration (depending on the target temperature and the stability of the laboratory temperature, this was between 30 min and 3 h).

2.5 Pressure measurement

The pressure was measured utilizing three highly accurate quartz oscillator pressure transducers (Paroscientific, USA, models: 223A-101, 2100A-101 and 42K-CE) and three displays for the signal analysis (Paroscientific, USA, type: 735 Intelligent Display). The pressure sensors cover the operational pressure range of our instrument in three overlapping sub-ranges with maximum pressures of (0.69, 2.7 and 13.8) MPa. The pressure transducers were calibrated with a gas piston gauge by an accredited calibration laboratory (Europascal GmbH, Germany). The expanded uncertainty ($k = 1.73$) in pressure measurement, as specified by the manufacturer, was 0.01% of the maximum value. The pressure transducers were thermostated at a constant temperature of 318.15 K, thus, they were decoupled from changes in the laboratory temperature and condensation as well as sorption effects could be minimized.

3. Modelling

3.1 Electrical modelling of the re-entrant cavity

When characterizing the resonant modes of complex structures such as re-entrant cavities, it is useful to compare experimentally measured modes with those predicted by analytical and numerical modelling. On the one hand, a model of a mode's frequency and electromagnetic field distribution allows the measured response of cavity to a fluid of interest to be correctly interpreted, whilst on the other hand experimental verification of modelled modes is required to categorically exclude numerical solutions that may be inaccessible (because they cannot be coupled into with the probe type and location). To that end, the simplest comparison involves

a calculation of the vacuum resonance frequency of the cavity's fundamental mode, which can be predicted with both an analytical and a finite element numerical model. Additionally, to support our future work aimed at the investigation of dielectric permittivity and (p, ρ, T, x) behaviour of fluid mixtures (including liquid volume fractions), the nature of higher order modes was explored with finite element modelling. Numerical models such as those based on finite element analysis can be constructed to predict the effect of finite losses at the cavity wall (due largely to electrical resistivity) and the distribution of the electromagnetic fields within the cavity for both the fundamental and higher order modes. Both of these characteristics are crucial to assessing the suitability and sensitivity of a particular mode for the purpose of measuring fluid properties.

Before embarking on the finite element analysis, the analytical (waveguide) model was first used to verify the vacuum resonance frequency of the cavity's fundamental mode. While it includes finite-size and dissipative effects, its prediction of the vacuum frequency from the nominal geometry is known to have limitations, particularly for smaller re-entrant cavities [9] because the dimensions of the resonator are not sufficiently well known, and the fringing fields associated with impedance discontinuities in the various waveguide sections can only be estimated approximately. The finite element analysis was then used to correctly predict the first four modes of the re-entrant cavity, as confirmed by measurement. It also predicted that Modes 2 and 3 are whispering-gallery type modes, with both the electric and magnetic fields confined to the annular gap region between the bulb and cavity wall, the existence of which have not previously been reported for re-entrant cavity resonators used for phase equilibrium studies.

3.2 Waveguide model

Using the approach of Goodwin *et al.* [7], the cavity was modelled as two sections of coaxial waveguide, terminated at the lower end by a cylindrical capacitor. The model involved the

equivalent capacitances, inductances and resistances, the circuit components, calculated with the dimensions of the resonator, and the fringing capacitances at the upper and bottom ends of the bulbous extension (where the waveguides terminate). The fringing capacitances were calculated with the formulae from Wadell [18]. The properties of the fluid within the cavity and the electrical properties of the material from which the resonator was made (gold plating) were also included in the model. The equivalent circuit parameters for the waveguide model, together with the dimensions of the re-entrant cavity are shown schematically in figure 3. table 2 contains the calculated values for the capacitances and inductances of each section and the total resistance R . The approximate dimensions of the re-entrant cavity are listed in table 3. The capacitance $C_{\text{gap}} \approx 20$ pF was mostly determined by the annular gap between the bulbous extension and the inner surface of the hollow cylinder. The inductance associated with the relatively large annular gap above the bulbous extension was $L_{\text{neck}} \approx 6.2$ nH. The resistance R was approximately 5.83 m Ω . The vacuum frequency of the fundamental mode $f_{1,\text{vac}}$ was determined by the following equation, given in Goodwin *et al.* [7]:

$$4\pi^2(f_{1,\text{vac}} - ig_{1,\text{vac}})^2 \approx \frac{1 - (1-i)\omega RC^*}{L_{\text{neck}}\left(C^* + \frac{C_{\text{neck}}}{3}\right) + L_{\text{gap}}\left[C_{\text{terminal}} + \frac{C_{\text{gap}}^2}{3C^*} - \frac{C_{\text{terminal}}C_{\text{upfringe}}}{C^*}\right]} \quad (2)$$

Here $C^* = C_{\text{gap}} + C_{\text{upfringe}} + C_{\text{lowfringe}} + C_{\text{bottom}}$, where C_{upfringe} and $C_{\text{lowfringe}}$ are the fringing capacitances at the upper and bottom ends of the bulbous extension, and C_{bottom} is the capacitance at the bottom of the resonator. The vacuum frequency calculated with the equivalent circuit waveguide model was $f_{a,\text{vac}} = 389$ MHz, which is consistent with the measured vacuum frequency at $T = 293.15$ K of $f_{a,\text{vac}} = 394.7$ MHz and thus close to the predicted value.

3.3 Finite element modelling of re-entrant cavity modes

The software COMSOL Multiphysics® [19] was used to create a finite element mesh, solve Maxwell's equations, and calculate the modes of the cavity. The calculated mode's frequencies, Q-factors and the azimuthal mode number m up to 4 GHz are presented in table 4 together with the measured values for the resonant frequency and the Q-factor. The small dif-

ference between the calculated and the measured frequencies can be attributed to at least three factors: (1) small discrepancies between the modelled and actual dimensions of the cavity, (2) modelling of the cavity as an axisymmetric resonator without any antenna or the seals included in the calculations, and (3) a lower experimental Q-factor than that predicted. This last contribution arises because penetration of the electromagnetic field into the bounding metal conductor, which ideally determines the resonance half-width g_α , also ideally shifts the resonance frequency f_α down by an amount equal to g_α relative to the value that would be observed based solely on the cavity's dimensions. The experimental Q-factors were all about a factor of 2 below those predicted based on the penetration depth for the bounding conductor (gold); such a difference is similar to that observed previously [7,9,10,11] for similar re-entrant cavities, and could be attributable to several factors including the presence of the seal between the two parts of the resonator, loading of the resonance by the external circuit, and the similarity between the microwave penetration depths with the thickness of the gold plating applied to the cavity's interior surfaces. These latter two effects were studied in detail by Hamelin *et al.* [20], who found that when their respective contributions were considered, the agreement between the measured and calculated Q-factors was within the combined uncertainties. Hamelin *et al.* [20] calculated the Q-factors of their modes using the formula

$$\frac{1}{Q} = \frac{1}{Q_s} + \frac{1}{Q_e} \quad (3)$$

where $1/Q_s$ is the contribution to the losses due to the surface resistivity of the bounding conductor and $1/Q_e$ is the contribution to the losses due to the external measurement circuit. The $1/Q_s$ contribution associated with the electrical resistivity of the gold plating matched that expected by theory only when Hamelin *et al.* [20] increased the plating thickness to over 30 μm . In part, this was required by their use of non-magnetic stainless steel for the resonator's body (which was also the pressure vessel), and because they conducted measurements with water, which lowered the cavity's resonant frequencies and increased the maximum mi-

microwave penetration depth to about 16 μm . In this work, the nominal gold plating thickness of (5 to 8) μm was close to the 4 μm penetration depth of Mode 1. This may not have been sufficient to prevent completely the surface currents from sampling the silver or beryllium copper metals below, and thus making calculation of the effective surface resistivity difficult.

Hamelin *et al.* [20] measured the $1/Q_e$ contribution associated with the external measurement circuit (VNA) by varying the orientation of their magnetic field coupling loops and reported $1/Q_e \approx 1.5 \times 10^{-4}$ for the lowest mode. In this work, we were unable to manipulate the magnetic field probes but instead determined the loading of the resonance by the external circuit by measuring each of the complex scattering parameters S_{11} , S_{22} , S_{12} , as well as S_{21} both at the resonance frequency and far from it. The analysis method described by Luiten [21] was then used to determine each probe's coupling coefficient, which in turn allowed the value of $1/Q_e \approx 1.7 \times 10^{-4}$ to be calculated for the lowest frequency mode; this is similar to the value found by Hamelin *et al.* [20]. Accounting for this contribution to the losses of Mode 1, the value of $Q_s \approx 1680$ is obtained from the experimental Q-factor measurement of that resonance, which is about 30 % closer to the FEA calculated value. However, while these contributions to the resonance quality factor must be considered for the accurate measurement of dielectric permittivity of fluids contained within the resonator, they are not needed for the determination of phase boundaries, as discussed in Section 4 below.

In figure 4, the first four measured modes (a, top panel) together with the FE-calculated distribution of the electric and magnetic field amplitudes (b, bottom panel) in the cavity for each mode are presented. The FEA confirms that the electric field for the Mode 1 ($m = 0$) is concentrated in the narrow annular gap, and the magnetic field is strongest around the cylindrical neck at the upper part of the cavity, as assumed by the waveguide model. The next higher mode is at 1.8 GHz ($m = 1$). The majority of the electric and magnetic field for Mode 2 and Mode 3 ($m = 2$) is concentrated in the 2 mm annular gap. Figure 5 shows a detailed represen-

tation of the finite element modelled electric and magnetic field components (in cylindrical coordinates r, φ, z (radial, azimuthal, axial)) for Mode 3, (which is similar to that of Mode 2 apart from the increased azimuthal oscillation). This shows that the electric field is largely radial, between the bulb and cavity wall, and the magnetic field is largely axial, corresponding to an azimuthal Poynting vector. The existence of both orthogonal electromagnetic fields in the annular gap region suggests that these modes are in fact Whispering Gallery (WG) type modes, so called for their similarity to the famous acoustic “whispering gallery” phenomena of St Paul’s Cathedral studied by Lord Rayleigh. In electromagnetic resonators, such WG modes typically occur when two counter-propagating electromagnetic fields, guided by a series of internal reflections, form a standing wave around the circumference of a rounded (typically circular) cavity [22,23,24]. To our knowledge, WG modes have not previously been predicted or observed for this type of re-entrant cavity structure, in part because it may have been expected that coupling to them experimentally is difficult given the location of the magnetic field loop probes. However, as shown in figure 5(a), a finite azimuthal H field for Mode 3 exists in the neck region of the cavity which, although small, is sufficient to couple to using the magnetic field probes used in this work.

Mode 4 (with $m = 0$) may be described as a standing wave resonance, because it appears confined to the region between the top of the bulb’s annular gap and the bottom tip of the bulb with electric field anti-nodes in both locations. The magnetic field of Mode 4 has nodes in these locations and is strongest in the annular gap at the bottom corner of the bulb. This resonance is similar in nature to the second mode used by May *et al.* [10,11] to determine liquid levels well into the two phase region of a given mixture.

Knowledge of the electric field distributions of Modes 1-4 and the ability to monitor them during experiments is useful for several reasons and will be the subject of our future research. First, for measurements of single-phase fluid mixtures, the consistency or otherwise of dielec-

tric permittivity determined using different modes provides either a quality check on the measurements *or* potentially, depending on the frequency range accessed, they can be used to quantify dispersion in the refractive index of fluids containing permanent dipole moments such as C_3H_8 [7] or O_2 [25]. For a two-phase mixture the corresponding values of f_α will vary differently as a liquid phase fills the cavity. Once calibrated with a reference fluid, these different responses can be used to determine liquid volume fractions and provide an even more complete picture of the mixture's phase behaviour.

4. Results

4.1 Isochoric determination of dew points

Dew points were determined with respect to temperature decrements along an isochoric pathway. From a starting point approximately 2.5 K above the assumed dew point, the temperature was decreased with 0.2 K steps, and the system was allowed to equilibrate for each step. The system achieved equilibrium when the temperature, pressure and frequency became constant to within pre-set limits of 0.01 K, 0.001 MPa and 0.01 MHz over 30 minutes. The (T, p, f_α) data were measured at each step; for these measurements only the fundamental mode was monitored. After the equilibration period, the temperature was decreased again stepwise to 2.5 K after the assumed dew point. After this overall temperature decrease of about 5 K (from starting point to endpoint), the temperature was increased so as to return back the fluid mixture into the single-phase region. Then, the whole quantity of the sample was released from the system.

When conducting measurements in the described way, we expect an almost constant gas phase density of the sample, which results in a nearly constant resonant frequency. However, as the system enters the two-phase region, sample will condense and collect at the bottom of the pressure vessel. Consequently, the density of the vapour phase remaining in the resonator decreases, and thus the dielectric permittivity of the fluid decreases. For mixtures, the vapour

phase will generally also become enriched in the more volatile component(s), which will further decrease the dielectric permittivity of the fluid remaining in the cavity. As a result, the measured frequency as the dew point is crossed begins to increase. This change in the slope of the frequency vs. temperature curve allows the dew point of the substance under study to be determined. The dew point temperature may then be calculated by the intersection of the straight lines regressed to the single-phase and the two-phase data.

To examine these expectations experimentally, the dew point of a reference fluid, namely carbon dioxide, was measured along an isochoric pathway at temperatures between (270 and 290) K. In figure 6, an example for the measured resonance frequency near the assumed dew point is shown as a function of temperature. The first eight points starting at $T \approx 285$ K down to point A belong to the single gaseous phase, where the slope of the frequency vs. temperature curve is 0.0315 MHz/K. The standard deviation of the experimental data from the linear fit is only 0.0028 MHz. This means that point B, which lies about 0.03 MHz above the fitted line (greater than 10 standard deviations), clearly does not belong to the single phase region anymore but to the two-phase region, and the slope of the frequency vs. temperature curve changes to -0.379 MHz/K. The phase boundary has been crossed between point A at $T = 283.42$ K and point B at $T = 283.22$ K. From the calculation of the intersection of the single-phase and the two-phase lines, the dew point temperature was $T_{\text{dew}} = 283.3733 \pm 0.0217$ K. The relative deviation of the corresponding measured dew point pressure at $T = 283.37$ K was less than 0.046%, which is a reasonable result considering that our apparatus was not optimised for vapour pressure measurements; for example, this deviation is only 0.015 % of the full scale of the pressure transducer used (13.8 MPa). We note that the highly accurate vapour pressure data of Duschek *et al.* [26] were measured with a relative combined expanded uncertainty ($k = 2$) of only 0.012%. The reference equation of state for carbon dioxide by Span and Wagner [27] represents these data within 0.006%.

4.2 Uncertainty analysis

The measurement uncertainty of the dew point pressure and dew point temperature was determined with the "Guide to the Expression of Uncertainty in Measurement" according to ISO/IEC (2008), see [17].

The combined standard uncertainty in the dew point temperature $u_c(T_{\text{dew}})$ can be determined by:

$$u_c(T_{\text{dew}}) = \left[u(T_{\text{meas}})^2 + u(T_{\text{intersect}})^2 + u(T_{\text{repro}})^2 + u(T(x))^2 \right]^{1/2}, \quad (4)$$

where $u(T_{\text{meas}})$ is the standard uncertainty from the temperature measurement chain, $u(T_{\text{intersect}})$ is the uncertainty of the calculated intersection of two fitted lines (see Section 3), $u(T_{\text{repro}})$ takes into account an uncertainty contribution of the reproducibility of the measurements, and $u(T(x))$ corresponds to the uncertainty in dew point temperature resulting from a compositional uncertainty when measurements on mixtures are carried out.

The standard uncertainty of the temperature measurement chain, $u(T_{\text{meas}})$, arises from the individual standard uncertainties of the SPRT and its self-heating, the resistance bridge, the reference resistor (with the 100 Ω platinum resistance thermometer and the digital multimeter), heat dissipation of the test leads, the temperature gradient along the measuring cell wall, the temperature oscillation over the time. For the temperature range from $T = (248 \text{ to } 303) \text{ K}$, at which the phase boundary measurements were carried, the estimated standard uncertainty in temperature measurement varies from $u(T_{\text{meas}}) = (15 \text{ to } 20) \text{ mK} \cdot 1.73^{-1}$.

As mentioned above, the dew point temperature was determined by calculating the intersection of the linear regressions to the single-phase and the two-phase data. The uncertainty $u(T_{\text{intersect}})$ of intersection of the two linear fits was calculated using the method described by Filliben [28].

The reproducibility of the measurement of the dew point temperature is conservatively estimated to be

$$u(T_{\text{repro}}) = 0.001\% \cdot T_{\text{dew}} . \quad (5)$$

For measurements on mixtures, the uncertainty in dew point temperature arising from the uncertainty in mixture compositions needs to be taken into account. A simplified approach was reported by Richter *et al.* [29], and may be transferred to the measurements on a binary (carbon dioxide + argon) mixture in the present work:

$$u(T(x)) = \left(\frac{\Delta T}{\Delta x_{\text{CO}_2}} \cdot u(x_{\text{CO}_2}) \right)^{1/2} . \quad (6)$$

Thereby $u(x_{\text{CO}_2})$ corresponds to the uncertainty of the mole fraction carbon dioxide in the binary mixture, which was prepared gravimetrically in the present work. The standard uncertainty from mixture preparation was 0.0004 mole fraction carbon dioxide. This yields an uncertainty in molar mass of $0.0016 \text{ g} \cdot \text{mol}^{-1}$. Details about the uncertainty analysis of the composition can be found in [29]. Moreover, ΔT is the difference between a dew point temperature calculated with a given mixture compositions and a dew point temperature calculated with a composition changed by Δx_{CO_2} ; for the present work Δx_{CO_2} was set equal to $u(x_{\text{CO}_2})$.

The combined standard uncertainty in the dew point pressure $u_c(p_{\text{dew}})$ is given by the following equation:

$$u_c(p_{\text{dew}}) = \left[u(p_{\text{meas}})^2 + \left(\left(\frac{\partial p}{\partial T} \right)_x \cdot u(T_{\text{meas}}) \right)^2 \right]^{1/2} . \quad (7)$$

The standard uncertainty in pressure measurement $u(p_{\text{meas}})$ depends on the absolute uncertainty of the pressure transducer used and its measuring range. According the manufacturer's specifications, the estimated uncertainty in pressure is $u(p_{\text{meas}}) = 0.010\% \cdot p_{\text{max}} \cdot 1.73^{-1}$, where p_{max} corresponds to the maximum pressure of the respective transducer. The uncertainty due the hydrostatic pressure correction is negligible. The pressure dependence of the temperature is given by the partial derivate $(\partial p / \partial T)_x$ and is calculated from a sensitivity analysis with the experimental values, whereas calculation with an equation of state would be possible as well.

4.3 Experimental results for the (0.25 argon + 0.75 carbon dioxide) mixture

Dew points of a binary (0.2501 argon + 0.7499 carbon dioxide) mixture were measured over the temperature range from (252 to 280) K. The results of the investigation of the (p, T, x) behaviour of the binary mixture with the corresponding uncertainty in the temperature and the pressure measurement are listed in table 5. Figure 7 depicts the phase envelope of the mixture and shows the location of the measured dew points. The phase boundary was calculated with the EOS-CG by Gernert and Span [1].

The relative deviations, shown in figure 8 (a, top panel), of the new experimental dew point pressures for the investigated (argon + carbon dioxide) mixture from values calculated with the EOS-CG (as implemented in [30]) were within 0.48%, which is clearly within the uncertainty of 1% reported by the authors of the equation. The relative deviations of values calculated with GERG-2008 equation of state of Kunz and Wagner [2] (as implemented in [31]) from values calculated with the EOS-CG are also shown, ranging from $(-1.17$ to $-4.65)\%$. The reason for the large deviations is that the GERG-2008 equation of state was not developed with special focus on mixtures with carbon dioxide but on natural gas and similar mixtures; no binary specific departure function was fitted for mixtures of the (argon + carbon dioxide) system, only reducing functions were adjusted, which is why the uncertainty in dew point pressure reported by the authors of the GERG-2008 equation is 5% for this system. In general, the relative deviations of the experimental values from both the EOS-CG and GERG-2008 equation decrease with the decreasing temperature and with decreasing pressure. Figure 8 (a, top panel) also shows the relative deviations of values calculated with two different implementations of the cubic Peng-Robinson equation from values calculated with the EOS-CG are plotted. The relative deviations calculated with the Peng-Robinson (cubic) equation of state [3] (as implemented in [32]) and with the advanced implementation of the Peng-Robinson equation of state (as implemented in [33]) were up to -3.5% and -2.7% respective-

ly. The experimental VLE-data sets available in the literature for the (argon + carbon dioxide) system [34-37] are summarised in table 6, where the measured temperature and pressure ranges, the mole fraction carbon dioxide and the corresponding uncertainties are listed. Figure 8 (b, bottom panel) shows the relative deviations of the dew-point pressures measured in this work and of other experimental literature data [34-37] at different compositions (y_{CO_2} is the mole fraction carbon dioxide in the vapour phase of the VLE-data) from values calculated with the EOS-CG [1]; for the development of the EOS-CG, only the data of Coquelet *et al.* [35] were used. For figure 8 (b) we chose to plot the literature VLE-data in the temperature range relevant for the present work ± 10 K and for the pressure range from (2 to 7) MPa. The resulting compositions range from approximately (0.45 to 0.99) mole fraction carbon dioxide. The relative deviations of the experimental dew-point pressures taken from literature compared to the EOS-CG [1] are between $(-1.2 \text{ and } 7.8)\%$. The data reported by Kaminishi *et al.* [37] with mole fractions carbon dioxide of 0.70 and 0.79 as well as the data of Coquelet *et al.* [35] with mole fractions carbon dioxide of 0.81 and 0.82 are the data closest to our composition (0.75 mole fraction carbon dioxide), and they are in good agreement with our current data. There is only one significant exception for the value reported by Coquelet *et al.* [35] with approximately 0.74 mole fraction carbon dioxide where the data point deviates from the EOS by about 3.5%. Due to the clearly different compositions of the data by Sarashina *et al.* [36] and Ahmad *et al.* [34], these data cannot be compared appropriately with the data measured in this work. However, the data of Sarashina *et al.* [36] agree well with the EOS, whereas the data of Ahmad *et al.* [34] show large scatter with relative deviations up to 7.8%.

5. Conclusions

A microwave re-entrant cavity resonator apparatus has been refurbished and extensively characterised for the purpose of investigating fluid phase equilibria (including liquid volume frac-

tion), dielectric permittivity and (p, ρ, T, x) behaviour of fluid mixtures. Analytical and numerical finite element models have been used to calculate the resonant frequency, Q-factor, and field distribution of the fundamental and first few higher order modes of the resonator. The calculated values for the resonance frequencies are in good agreement with those measured, while the measured Q-factors were generally a factor of two lower than predicted, consistent with previous work and largely attributed to simplifications of the model in respect to coupling probes and the cavity sealing. To determine the sensitivity of the apparatus for liquid formation the same finite element analysis was used to estimate the distribution of the electric and magnetic fields in the re-entrant cavity resonator. Further analysis of the resulting field distribution revealed the existence of whispering-gallery type modes in the annular gap region of the re-entrant cavity resonator, which have not previously been reported for this cavity geometry.

The upgraded apparatus enables measurements over a temperature range from (243 to 353) K at pressures up to 12 MPa. With our current setup, the experimental investigation of phase boundaries of pure substances and fluid mixtures is carried out along an isochoric pathway. To validate our re-entrant cavity resonator, dew points of pure carbon dioxide were measured. The relative deviations of the measured dew point pressures from values calculated with the reference equation of state of Span und Wagner [27] were less than 0.046%. This is within the experimental uncertainty of the present measurements ($\approx 0.2\%$), and more than sufficient for measurements of mixture dew points in CO₂-rich fluids, particularly considering the apparatus was originally designed for measurements of the dielectric permittivity of natural gas samples.

Moreover, dew points of a gravimetrically prepared binary (0.2501 argon + 0.7499 carbon dioxide) mixture were carried out over the temperature range from (252 to 280) K. The relative combined expanded uncertainty ($k = 2$) for the measured dew point temperatures was

estimated to be between (0.025 and 0.044) K and for the measured dew point pressures between (0.009 and 0.015) MPa. The measured results were compared with values calculated from the EOS-CG of Gernert and Span [1,30]. Relative deviations between (0.044 and 0.479)% were observed, which is clearly within the uncertainty of 1% reported by the authors. Relative deviations to other models, *e.g.*, the GERG-2008 equation [2,31] and the Peng-Robinson equation [3,32,33], were up to -4.65% . Furthermore, the dew points measured in this work are consistent with, but generally have less scatter than, those reported in the literature for this binary mixture at comparable conditions.

Acknowledgements

Gergana Tsankova's work at Ruhr-Universität Bochum was supported by the "Forschungsschule für Energieeffiziente Produktion und Logistik" funded by the Ministry of Education, Science and Research of the German State of North-Rhine Westphalia. Moreover, Gergana Tsankova acknowledges the German Academic Exchange Service (DAAD) for funding her research stay at The University of Western Australia. Dr. Markus Richter thanks the institute of advanced studies of the The University of Western Australia for supporting his research fellowship. Dr. Paul Stanwix is supported by an ARC DECRA fellowship (DE140101094). We thank Dr. Mark O. McLinden of NIST for helpful discussions concerning the uncertainty analysis as well as Nils von Preetzmann and Robert Dreiling for supporting the present project within the scope of their student assistantships. This work was supported by the Ruhr-University Research School PLUS, funded by Germany's Excellence Initiative [DFG GSC 98/3].

REFERENCES

- 1 J. G. Gernert, R. Span, *J. Chem. Thermodyn.* 93 (2016), 274-293.
- 2 O. Kunz, W. Wagner, *J. Chem. Eng. Data* 57 (2012) 3032–3091.
- 3 D.-Y. Peng, D. B. Robinson, *Ind. Eng. Chem., Fundam.* 15 (1976), 59-64.
- 4 E. F. May, J. Y. Guo, J. H. Oakley, T. J. Hughes, B. F. Graham, K. N. Marsh, S. H. Huang, *J. Chem. Eng. Data* 60 (2015), 3606-3620.
- 5 M. E. Kandil, M. J. Thoma, T. Syed, J. Guo, B. F. Graham, K. N. Marsh, S. H. Huang, E. F. May, *J. Chem. Eng. Data* 56 (2011), 4301-4309.
- 6 W. J. Rogers, J. C. Holste, P. T. Eubank, K. R. Hall, *Rev. Sci. Instrum.* 56 (1985) 1907-1912.
- 7 A. R. H. Goodwin, J. B. Mehl, M. R. Moldover, *Rev. Sci. Instrum.* 67 (1996), 4294-4303.
- 8 A. R. H. Goodwin, M. R. Moldover, *J. Chem. Thermodyn.* 29 (1997), 1481-1494.
- 9 E. F. May, T. J. Edwards, A. G. Mann, C. Edwards, R. C. Miller, *Fluid Phase Equilib.* 185 (2001) 339-347.
- 10 E. F. May, T. J. Edwards, A. G. Mann, C. Edwards, R. C. Miller, *Int. J. Thermophys.* 24 (2003) 1509-1525.
- 11 E. F. May, T. J. Edwards, A. G. Mann, C. Edwards, *Fluid Phase Equilib.* 215 (2004) 245-252.
- 12 J. T. R. Watson, Report by National Engineering Laboratory, East Kilbride, prepared for Ruhrgas AG, Germany, 2000.
- 13 M. Jaeschke, *Thermochimica Acta* 382 (2001) 37-45.
- 14 M. Jaeschke, P. Schley, R. Janssen-van Rosmalen, *Int. J. Thermophys.* 23 (2002) 1013-1031.
- 15 J. B. Mehl, *J. of the Acoustical Society of America*, 64 (1978), 1523-1525.
- 16 M. Schäfer, Ph.D. Dissertation [Online]. Ruhr-University Bochum, Germany, 2015.
<http://hss-opus.ub.ruhr-uni-bochum.de/opus4/frontdoor/index/index/docId/4542>
(assessed Apr 25, 2016).
- 17 International Organization for Standardization (ISO), ISO/IEC Guide 98-3:2008, Uncertainty of measurement – Part 3: guide to the expression of uncertainty in measurement, Geneva, 2008.
- 18 B. C. Wadell, *Transmission Line Design Handbook*, Artech House: Boston, MA, USA, 1991.
- 19 COMSOL Multiphysics®. Version 5.2. COMSOL, Inc., Burlington, MA, USA, 2015.

- 20 J. Hamelin, J. B. Mehl, M. R. Moldover, *Rev. Sci. Instrum.*, 69 (1998), 255-260.
- 21 A. N. Luiten, *Wiley Encyclopedia of Electrical and Electronics Engineering*, Vol. 17 (1999), 447-491.
- 22 J. R. Wait, *Radio Sci.* 2 (1967), 1005-17
- 23 M. E., Tobar, A.G. Mann, *IEEE Tran. Microw. Theor. Tech.* 39 (1991), 2077-2082.
- 24 P. Wolf, M. E. Tobar, S. Bize, A. Clairon, A. N. Luiten, G. Santarelli, *Gen. Relat. Gravit.* 36 (2004), 2351–2372.
- 25 E. F. May, M. R. Moldover, J. W. Schmidt, *Phys. Rev. A* 78 (2008), 032522.
- 26 W. Duschek, R. Kleinrahm, W. Wagner, *J. Chem. Thermodyn.* 22 (1990), 841-864.
- 27 R. Span, W. Wagner, *J. Phys. Chem. Ref. Data* 25 (1996), 1509-1596.
- 28 J. J. Filiben, J. E. McKinney, *J. of Research of Nat. Bur. Stand. – Math. Sciences* 76 B (1972), 179-192.
- 29 M. Richter, R. Kleinrahm, R. Lentner, R. Span, *J. Chem. Thermodyn.* 93 (2016), 205 - 221.
- 30 R. Span, T. Eckermann, S. Herrig, S. Hielscher, M. Thol. *TREND. Thermodynamic Reference and Engineering Data 2.0*; private communication: Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum: Bochum (Germany), 2015.
- 31 E. W. Lemmon, M. L. Huber, M. O. McLinden, *REFPROP*, NIST Standard Reference Database 23, Version 9.1, Gaithersburg, 2013.
- 32 Aspen Technology, *Aspen HYSYS V8.6*. Aspen Technology, Inc. Copyright 1995-2014.
- 33 *Multiflash™*. DLL Version 4.4.10. September 2014. Infochem/KBC Advanced Technologies plc, London, 2014.
- 34 M. Ahmad, J. Gernert, E. Wilbers, *Fluid Phase Equilib.* 363 (2014) 149-155.
- 35 C. Coquelet, A. Valtz, F. Dieu, D. Richon, P. Arpentinier, F. Lockwood, *Fluid Phase Equilib.* 273 (2008), 38-43.
- 36 E. Sarashina, Y. Arai, S. Saito, S., *J. Chem. Eng. Jpn.* 4 (1971), 379-381.
- 37 G. Kaminishi, Y. Arai, S. Saito, S. Maeda, *J. Chem. Eng. Jpn.* 1 (1968), 109-116.

TABLES

Table 1. Provenance and mass fraction purity of the samples

chemical name	source	purity/mole fraction	purification method
argon	Air Liquide	0.999990 ^a	none
carbon dioxide	Air Liquide	0.999995 ^b	none

^a impurities (stated by supplier): $x(\text{H}_2\text{O}) \leq 2.0 \cdot 10^{-6}$, $x(\text{O}_2) \leq 2.0 \cdot 10^{-6}$, $x(\text{C}_m\text{H}_n) \leq 0.5 \cdot 10^{-6}$, $x(\text{CO}_2) \leq 0.2 \cdot 10^{-6}$, $x(\text{N}_2) \leq 5.0 \cdot 10^{-6}$

^b impurities (stated by supplier): $x(\text{H}_2\text{O}) \leq 2.0 \cdot 10^{-6}$, $x(\text{O}_2) \leq 1.0 \cdot 10^{-6}$, $x(\text{C}_m\text{H}_n) \leq 0.1 \cdot 10^{-6}$, $x(\text{N}_2) \leq 2.0 \cdot 10^{-6}$, $x(\text{CO}) \leq 0.5 \cdot 10^{-6}$, $x(\text{NO}_x) \leq 0.1 \cdot 10^{-6}$

Table 2. Equivalent circuit capacitances C / pF, inductances L / nH and resonance resistance R / m Ω for the re-entrant cavity, as defined in figure 3.

Equivalent circuit parameter	Value	Equivalent circuit parameter	Value
C_{neck}	1.75	C_{terminal}	3.09
C_{upfringe}	2.81	L_{neck}	6.21
C_{gap}	19.99	L_{gap}	0.36
$C_{\text{lowfringe}}$	1.67	R	5.83
C_{bottom}	1.42		

Table 3. The approximate dimensions of the re-entrant cavity.

r / mm	Value	h / mm	Value
r_1	10.99	h_1	30.80
r_2	27.23	h_2	32.82
r_3	29.23	h_3	25.54
r_4	34.25	h_4	14.48

Table 4. Measured and predicted (finite element model) for vacuum frequencies and Q-factors of Modes (1 to 4) at different azimuthal mode numbers, m . No correction has been made to the experimental Q-factors listed here to account for loading by the external measurement circuit (see text and eq. (3) for further discussion).

Mode	Frequency / GHz				Q-factor			
	1	2	3	4	1	2	3	4
Experiment	0.395	1.828	3.507	3.680	1299	1111	1094	1901
FEA	0.389	1.837	3.513	3.534	3373	1392	1757	3705
M	0	1	2	0	0	1	2	0

Table 5. Experimental values of dew point temperatures T_{dew} and dew point pressures p_{dew} for the (0.2501 argon + 0.7499 carbon dioxide) mixture^a. The number following the symbol $\pm$ is the numerical value of the expanded uncertainty ($k = 2$).

$T_{\text{dew}} / \text{K}$	$p_{\text{dew}} / \text{MPa}$
280.338 $\pm$ 0.027	6.9157 $\pm$ 0.0115
280.444 $\pm$ 0.027	6.9448 $\pm$ 0.0121
279.123 $\pm$ 0.027	6.6262 $\pm$ 0.0104
278.028 $\pm$ 0.025	6.3772 $\pm$ 0.0102
277.565 $\pm$ 0.026	6.2815 $\pm$ 0.0100
276.574 $\pm$ 0.025	6.0758 $\pm$ 0.0089
272.895 $\pm$ 0.025	5.3871 $\pm$ 0.0087
270.027 $\pm$ 0.044	4.9133 $\pm$ 0.0148
269.787 $\pm$ 0.043	4.8757 $\pm$ 0.0148
266.866 $\pm$ 0.029	4.4417 $\pm$ 0.0088
263.418 $\pm$ 0.027	3.9790 $\pm$ 0.0074
260.973 $\pm$ 0.025	3.6779 $\pm$ 0.0068
257.800 $\pm$ 0.031	3.3203 $\pm$ 0.0068
252.953 $\pm$ 0.030	2.8320 $\pm$ 0.0076

^a The expanded uncertainty ($k = 2$) in composition is 0.0004 mole fraction carbon dioxide.

Table 6. Review of the VLE-measurements on (argon + carbon dioxide) mixture.

Author	T / K	p / MPa	y_{CO_2}	Uncertainty $T; p; y_{\text{CO}_2}$
This work	252 to 280	2.8 to 6.9	0.75	0.02 K; 0.01% $\cdot p_{\text{max}}$; 0.0004 mole fraction
Ahmad <i>et al.</i> (2014), [34]	278 to 299	4.2 to 7.1	0.95 and 0.98	0.5 K; 0.3%; 0.01%
Coquelet <i>et al.</i> (2008), [35]	233 to 299	1.5 to 14.0	0.25 to 0.99	0.02 K; 0.0003 MPa; 2.4%
Sarashina <i>et al.</i> (1971), [36]	288	5.7 to 9.8	0.79 to 0.94	n/a; n/a; n/a
Kaminishi <i>et al.</i> (1968), [37]	233 to 273	2.6 to 13.2	0.25 to 0.85	n/a; n/a; n/a

FIGURE CAPTIONS

Figure 1. Cutaway view of the microwave re-entrant cavity.

Figure 2. Schematic diagram of the overall apparatus.

Figure 3. Equivalent circuit parameters for the waveguide model. The approximate dimensions of the re-entrant cavity are listed in table 3.

Figure 4. (a) Measured resonances of Modes 1, 2, 3 and 4. (b) Predicted intensity distributions of the electric and magnetic fields for Modes 1, 2, 3 and 4.

Figure 5. (a) Component electric, E , and magnetic, H , vector fields in the azimuthal (ϕ), radial (r) and axial (z) directions for Mode 3 ($m = 2$), predicted using the finite element model. (b) Corresponding plan view of the electric field intensity distribution in the 2 mm gap around the re-entrant bulb, which helps illustrate its “Whispering Gallery” characteristics.

Figure 6. Measured resonant frequency (left axis of ordinates) near the dew point of pure carbon dioxide as a function of temperature. The measured dew point temperature is $T_{\text{dew}} = (283.3733 \pm 0.0217)$ K ($k = 2$). $\circ$, frequency measured in the single gaseous phase; $\square$, frequency measured in the two-phase region; $---$, density (right axis of ordinates) calculated with the equation of state of Span and Wagner [27].

Figure 7. p, T -diagram of the (0.2501 argon + 0.7499 carbon dioxide) mixture. $---$, phase envelope calculated with the EOS-CG by Gernert and Span [1]; $\circ$, dew points measured in the present work.

Figure 8. Relative deviations of the present experimental dew point pressures p_{exp} for the (0.2491 argon + 0.7509 carbon dioxide) mixture from dew point pressures $p_{\text{EOS-CG}}$ calculated with the EOS-CG by Gernert and Span [1] (zero line); (a) relative deviations plotted versus temperature T ; (b) relative deviations plotted versus vapour mole fraction carbon dioxide y_{CO_2} ; $\circ$, dew point pressures measured in this work; $---$, dew point pressures calculated with the GERG-2008 equation of state of Kunz and Wagner [2]; $- \cdot -$, dew point pressures calculated with the PR-EOS [3] as implemented in [32]; $\cdots$, dew point pressures calculated with an advanced implementation of PR-EOS [3] as implemented in [33]; $\diamond$, Ahmad *et al.* [34]; $\times$, Coquelet *et al.* [35]; $\square$, Sarashina *et al.* [36]; $+$, Kaminishi *et al.* [37]; The uncertainty of the EOS-CG (zero line) is 1% as reported in reference [1].

Figure 1

Figure 2
reference resistor

Figure 4

(b)

Figure 5

Figure 6

Figure 7

Pressure p / MPa

*
critical
point

250

260

270

280

290

Temperature T / K

Figure 8