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Isochoric $p\rho T$ Measurements on Dry and Humid Air

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An isochoric apparatus and a densimeter with a magnetic suspension coupling were used to measure the density of dry air at (10, 30, 75, and 120) kg·m^{-3}. The results are compared with the Zittau database (Kretzschmar, H.-J., et al. *Property Data Base for Humid Air*, version 2.0; 2004) and the work of Lemmon et al. (Lemmon, E. W., et al. *J. Chem. Ref. Data* **2000**, *29*, 331−384) (NIST standard reference database REFPROP 7.0) as well. The humid air was obtained by adding the synthetic air to a gravitationally determined amount of water. It is important to avoid condensation in the part of the apparatus permanently connected to the measuring cell. For that reason, measurements on humid air were carried out using the isochoric apparatus only. Four isochores were measured in the gaseous region at (30, 60, 86, and 107) kg·m^{-3} with a mole fraction of water in humid air of (4.45, 4.46, 4.20, and 1.26) %. The results are compared with the Zittau database.

Introduction

The measurements were part of the EC-project Advanced Adiabatic−Compressed Air Energy Storage (AA-CAES). The aim of this project was to study the storing of electrical energy in the form of compressed air in subterranean caverns. As long as surplus electrical energy is available, a compressor is driven to press humid air from the surroundings into the cavern. When electrical energy is needed, the compressed air from the cavern is used as combustion air in a specially designed gas turbine driving a generator. For the optimization of the compressor and the turbine as well, reliable data were required including the real-gas effects of the humid air.

The measurements of PTB and the partners in the project were used to confirm and set up equations describing the thermophysical behavior of the humid air in the process described above. The best equations at present could be identified in cooperation with the University of Applied Sciences Zittau/Görlitz, Germany, and the University of Rostock, Germany. These commercially available databases can be supplied by the University of Applied Sciences Zittau/Görlitz, Germany.

Materials

Synthetic air produced by LINDE AG (Germany) was used in the measurements. The composition of the synthetic air certified by the manufacturer is as follows:

compound	molar fraction/%	relative uncertainty/%
argon	0.90025	± 0.04
oxygen	20.899	± 0.01
nitrogen	rest	

The water was double distilled and degassed under a vacuum before the experiment.

Apparatus and Procedure

The one-sinker densimeter equipped with a magnetic suspension coupling was used in the EUROMET intercomparison 491 and is described by Weber.[3] Densimeters of that type are described in detail in the review article by Wagner and Kleinrahm.[4]

Description of the Isochoric Apparatus. An isochoric apparatus for pressures up to 40 MPa and temperatures up to 350 °C was used. A schematic diagram is given in Figure 1.

The assembly consists of three major parts: (1) the measuring cell in the thermostat up to the valve V1 and up to the diaphragm in the differential-pressure sensor with the fluid under test, (2) the tubing system between valve V1 and the valve to the supply vessel, and (3) the tubing system above the diaphragm in the differential-pressure sensor for the reference pressure. The closed thermodynamic system consists of the fluid under test in the measuring cell (Autoclave Engineering (US), type AE 0010) with the volume $V_{M0} = 101.442$ cm^3 and the fluid in the tubing which is always open to the measuring cell and in which the temperature is inhomogeneously distributed. This space has a relatively small volume of $V_D = 1.046$ cm^3, known as dead-space volume.

The measuring cell (Figure 2), the valve V1, and the lower part of the differential-pressure sensor are accommodated in an evacuable chamber. An electrically heated steel plate above the lower part of the differential-pressure sensor compensates the heat flux to the upper part and thus allows small temperature gradients in the surroundings of the measuring cell. This chamber is situated in a heat pipe filled with cesium (Dynatherm (US), type IFL 06-60-24 H) in a vertical tube furnace (GERO (Germany), type F-HP0). The chamber is evacuated during measurement and filled with helium when changing the temperature. For the measurements on humid air, two additional heaters are installed along the tubing system from the measuring cell to the differential-pressure sensor and the valve V1 to avoid condensation. An additional electrical heater is installed around the measuring cell to allow faster heating.

The temperature according to ITS-90 is measured using two long-stem platinum resistance thermometers (25 Ω) in openings parallel to the axis of the measuring cell. Into these openings, the sensors are placed at the upper and lower end of the cell. For the resistance measurement, an AC measuring bridge (Automatic System Laboratories (UK), type F17) is used. In

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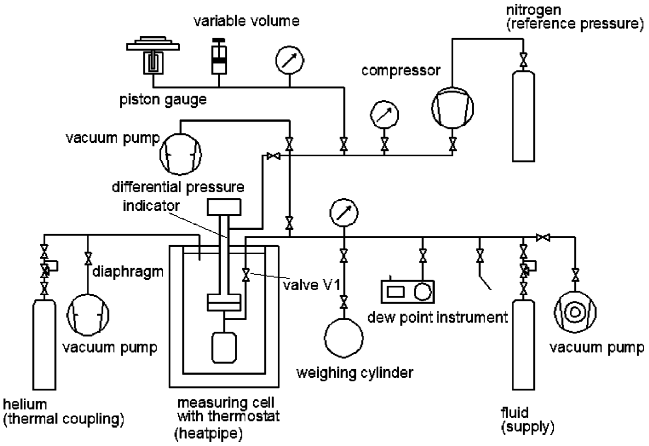

Figure 1. Measuring system for the measurement of isochores.

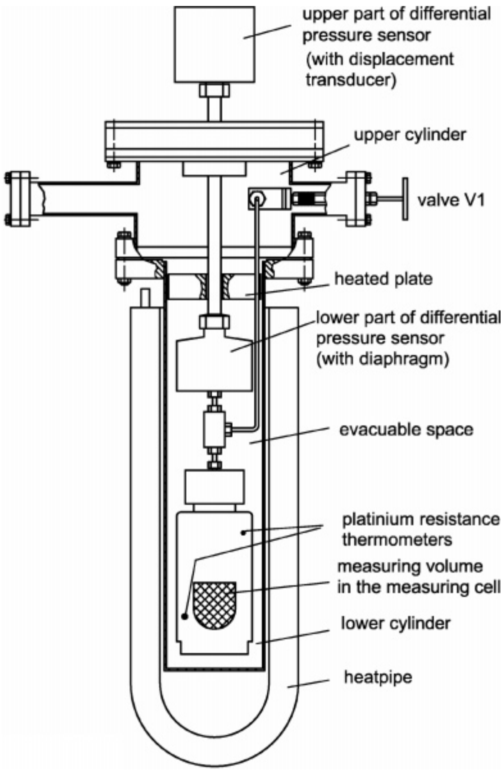

Figure 2. Measuring cell of the isochore assembly. Long-stem platinum resistance thermometers are placed into drill holes parallel to the axis.

the area of the dead space, the temperature is recorded with a digital voltmeter (Prema (Germany), type 6031 A) connected to seven long-stem thermocouples (Heraeus (Germany), K-type). The thermocouples are attached to the lower part of the differential-pressure sensor, the valve V1, and the tubing. The reference junctions have the temperature of ice water. The uncertainty of the temperature differences is 0.1 K.

The pressure is measured using a dead-weight tester (Desgranges & Huot (France), type 5202S) operated with nitrogen. For pressures below 1 MPa, an absolute pressure transducer (Paroscientific (US)) is used.

Coefficients Describing the Isochoric Apparatus. At 20 °C, the apparatus was filled with nitrogen of the purity 5.0 up to 10 MPa. The pressure was measured using the pressure balance. Hereafter, the nitrogen was allowed to flow into an evacuated weighing cylinder with a calibrated inner volume. From the mass difference of the weighing cylinder and the fundamental equation for nitrogen,[5] the sum of the volumes V_{M0} (measuring cell) and V_D (dead volume) was obtained. The experiment was repeated with the measuring cell replaced by a plug to get the dead volume V_D only. The compressibility of the tubing and the cell (see below) was taken into account. $V_{M0} = (101.442 \pm 0.053)$ cm^3 and $V_D = (1.046 \pm 0.053)$ cm^3 was the result.

The thermal expansion coefficient of the measuring cell α was determined experimentally. From the equation

$$V(T,p) = V_{M0}[1 + 3\alpha(T - 293.15\ \mathrm{K})](1 + \kappa p) = \frac{m_{\mathrm{all}}}{\rho} - V_D \quad (1)$$

where V is the volume of the measuring cell depending on pressure p and absolute temperature T; κ is the compressibility of the measuring cell; ρ is the density; and m_{all} is the amount of gaseous mass in the measuring cell and the dead-space volume, we can obtain

$$\alpha = \frac{1}{3(T - 293.15\ \mathrm{K})}\left\{\frac{1}{1 + \kappa p}\left[\frac{m_{\mathrm{all}}}{\rho V} - \frac{V_D}{V}(1 + 3\alpha_D(T_D - 293.15\ \mathrm{K}))(1 + \kappa_D p)\right] - 1\right\} \quad (2)$$

p denotes the absolute pressure, and the index D indicates the dead space. From five measurements at 500 K at densities between (10 and 120) kg·m^{-3}, the mean value $\alpha = (18.49 \pm 0.49)\ 10^{-6}\ \mathrm{K}^{-1}$ was obtained. The uncertainty is stated with a coverage factor $k = 2$ and is estimated according to the Guide.[6]

Due to the thick walls of the measuring cell made from stainless steel A 286, the elastic distortion caused by the pressure is less important. It was sufficient to calculate the compressibility using the Lamé equations with the Young modulus and Poisson ratio taken from the literature: $\kappa = (0.021 \pm 0.0115)\ \mathrm{GPa}^{-1}$.

Experimental. After the desired amount of substance is filled into the measuring cell at about 30 °C, the valve V1 is closed. The measurements are started at that temperature.

After the steady state has been reached, temperature and pressure in the measuring cell are measured ten times at intervals of 2 s. The mean pressure and temperature values calculated for such a measurement series show a standard deviation of 0.2 mK and 0.01 kPa, respectively. In the region of the dead space, the temperatures of the fractional areas are measured and the regional distribution of the amount of substance in the measuring system up to the differential-pressure sensor and valve V1 is calculated using a suitable database (Zittau[1] or Lemmon et al.[2]). The temperature and pressure measurements are repeated at intervals of approximately 10 min. The pressure is corrected for the aerostatic pressure head.

In the experiments with a fixed amount of gas in the system, only quasi-isochores are determined with reference to the measuring cell, because of the expansion of the cell and because the temperature-dependent distribution of the gas between the measuring cell and dead space changes the amount of gas in the measuring cell. The total amount n is determined by

$$n = n_M(T) + \sum_{i=1}^{7} \rho_i(T_i,p)V_i \quad (3)$$

where $n_M(T)$ is the amount of gas in the measuring cell and $\rho_i(T_i,p)$ is the mean density of the amount in the seven single

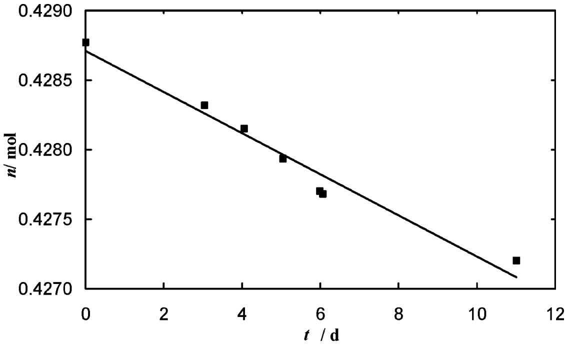

Figure 3. Isochore 120 kg·m^{-3}: long-term leak rate with linear fit.

fractions of the dead space with the volume V_i and the temperature T_i. The amount of gas in the measuring cell is

$$n_M(T) = \rho(p,T)V_{M0}[1 + 3\alpha(T - 293.15\ \text{K}) + \kappa p] \qquad (4)$$

The measurements are continued in steps of 50 K to 230 °C. Hereafter, the measurement at 30 °C is repeated to obtain the very small leak rate, which occurred during these time-consuming measurements. The leak rate caused by the valve V1 is corrected.

Measurements on Dry Air

The measuring cell was filled manometrically.

The first measuring point was repeated at the end of the measurements along one isochore. As an example, Figure 3 shows the decrease of substance in the measuring cell and the dead space with time in the case of the isochore 120 kg·m^{-3}. This effect is corrected using a linear fit.

The densities ρ_i (eq 3) due to differences in temperature and pressure of the dead space from the measuring cell were calculated using the fundamental equation.[2]

Four isochores were measured at (10, 30, 75, and 120) kg·m^{-3} (Figure 4). At the end of each isochoric measurement, the amount of substance from the measuring cell was collected in a weighing cylinder. From the volume of the tubing system from valve V1 to the weighing cylinder and the volume of the weighing cylinder in addition to corresponding temperatures, the amount of substance in the measuring cell and the dead space during measurement could be obtained. In the case of dry air, smaller measurement uncertainties could be obtained using, in addition, the one-sinker densimeter.

The working equation for the densimeter is

$$\rho = \frac{m_0 - m}{V} \qquad (5)$$

where m_0 is the mass of the sinker; m is the apparent mass of the sinker in an atmosphere of density ρ to be measured; and V is the volume of the sinker. The apparatus was used to measure the density of toluene[3] and sulfur hexafluoride. The magnetic effects caused by these samples could be neglected. Oxygen is a paramagnetic substance with a large specific magnetic susceptibility of 1340·10^{-9} m^3·kg^{-1} compared with the other main components of the air (−5.4·10^{-9} m^3·kg^{-1}; −6.1·10^{-9} m^3·kg^{-1} for nitrogen; argon[7]). The magnetic behavior of the gas in the densimeter can be described using the factor c[8]

$$\rho = \frac{m_0 - m}{V}c \qquad (6)$$

For a gas mixture, it is obvious to write

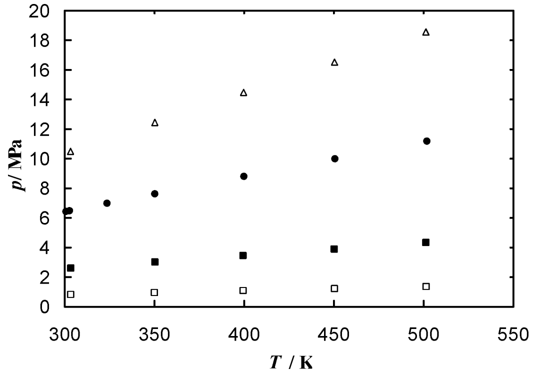

Figure 4. Quasi-isochores of dry air: □, 10 kg·m^{-3}; ■, 30 kg·m^{-3}; ●, 75 kg·m^{-3}; △, 120 kg·m^{-3}.

$$c = 1 + k \sum \Psi_i \chi_i \qquad (7)$$

where Ψ_i is the molar fraction of the component i in the gas and χ_i is the specific magnetic susceptibility. The factor k is temperature-dependent due to the change of the magnetic susceptibility of the upper wall (housing of the magnetic coupling) with temperature. It depends on the vertical adjustment of the electromagnet as well as on the individual magnetic suspension coupling.[8]

The factor k of the magnetic suspension coupling at 30 °C was obtained from measurements on oxygen of high purity (5.0) at (23 and 46) MPa with the density calculated from the fundamental equation.[2]

Prior to every measurement with the densimeter, the measurement cell was evacuated. From this experiment, the mass m_0 is determined. The main contribution to m_0, the mass of the sinker made from quartz glass, is well-known from a PTB certificate. A small cage made from noble steel allows us to measure, in position one, the weight of the permanent magnet and the core of the position sensing element and, in the second position, these weights and in addition the sinker, the spring, and the cave. The cave cannot easily be removed from the suspension balance. The volume V consists of the sinker, the cave, and the spring connecting the two parts. The volume of the cave and the spring is determined from density and mass. The internal automatic calibration routine of the used semimicrobalance METTLER (Swiss) AT 261 was operated just before starting a measurement. The buoyancy corrections were taken into account as well as the thermal expansion and the elastic distortion of the sinker and the cave.

In the case of dry air, temperature and pressure define each measuring point. In the densimeter, temperature and pressure were adjusted according to the last point (30 °C) of the isochoric measurement. The density measured with the densimeter was linked to the last point of the isochore. The density along the other measuring points was calculated as follows

$$\rho(T,p) = \rho(T_{\text{lmp}},p_{\text{lmp}})\frac{b - a\Delta t}{b}[1 - 3\alpha(T - T_{\text{lmp}})][1 - \kappa(p - p_{\text{lmp}})] \qquad (8)$$

The index lmp indicates the last measuring point of the isochore; a/b describe the leak rate; and Δt is the difference in time to the last measuring point. The measurement results are collected in Table 1.

The measurement uncertainties were calculated according to the Guide[6] and the GUM Workbench, respectively. In the case of density measurements on dry air using the densimeter, the relative overall uncertainty is 0.027 % at 120 kg·m^{-3} and 0.048 % at 30 kg·m^{-3}.

Table 1. $p\rho T$ Data of Dry Air[a]

no.	p MPa	ρ mol·dm^{-3}	T K	$2s(\rho)$ mol·dm^{-3}	$2s(\rho)/\rho$ %	$2s(p)$ MPa	$2s(T)$ K	$(\Delta\rho/\rho)_{\mathrm{PTB-LibHuAir}}$ %	H-$\lvert\Delta'_{\mathrm{PTB-LibHuAir}}\rvert$ %
1	10.497	4.1788	303.216	0.00214	0.052	0.000798	0.0115	−0.026	0.087
2	12.446	4.1633	350.236	0.00216	0.052	0.000935	0.0115	−0.046	0.067
3	14.474	4.1502	399.679	0.00222	0.054	0.001087	0.0115	−0.057	0.057
4	16.523	4.1369	450.379	0.00234	0.056	0.001249	0.0115	−0.059	0.056
5	18.558	4.12360	501.335	0.00248	0.060	0.001420	0.0115	−0.058	0.059
6	18.555	4.12350	501.302	0.00248	0.060	0.001419	0.0115	−0.056	0.061
7	10.452	4.16293	303.060	0.00214	0.052	0.000795	0.0115	−0.039	0.074
8	6.4387	2.5992	300.663	0.00107	0.041	0.000538	0.0115	−0.036	0.072
9	6.4847	2.5985	302.619	0.00107	0.041	0.000541	0.0115	−0.029	0.079
10	6.4857	2.5985	302.672	0.00107	0.041	0.000541	0.0115	−0.027	0.081
11	6.9879	2.594	323.523	0.00107	0.041	0.000572	0.0115	−0.070	0.038
12	6.9875	2.5939	323.521	0.00107	0.041	0.000571	0.0115	−0.067	0.041
13	7.6273	2.5895	350.174	0.00108	0.042	0.000611	0.0115	−0.094	0.014
14	8.8058	2.5814	399.874	0.00113	0.044	0.000686	0.0115	−0.094	0.015
15	9.9977	2.5736	450.574	0.00120	0.047	0.000764	0.0115	−0.108	0.002
16	11.184	2.5647	501.805	0.00131	0.051	0.000846	0.0115	−0.107	0.005
17	7.6142	2.5857	350.170	0.00108	0.042	0.000610	0.0115	−0.074	0.034
18	6.4785	2.5901	303.215	0.00107	0.041	0.000541	0.0115	−0.035	0.073
19	2.6074	1.0391	303.377	0.00054	0.052	0.000326	0.0115	−0.038	0.075
20	3.0235	1.0358	350.226	0.00054	0.052	0.000348	0.0115	−0.034	0.079
21	3.4563	1.0322	399.369	0.00056	0.054	0.000371	0.0115	−0.062	0.052
22	3.4565	1.0322	399.354	0.00056	0.054	0.000371	0.0115	−0.076	0.038
23	3.9014	1.0289	450.217	0.00058	0.056	0.000394	0.0115	0.076	0.039
24	4.3432	1.0255	501.264	0.00061	0.060	0.000418	0.0115	−0.071	0.046
25	2.6016	1.0369	303.354	0.00054	0.052	0.000326	0.0115	−0.037	0.076
26	0.829	0.3297	303.330	0.00075	0.23	0.000369	0.0115	0.073	0.178
27	0.9561	0.3286	350.020	0.00074	0.23	0.000404	0.0115	0.043	0.208
28	1.0887	0.3272	399.467	0.00074	0.23	0.000442	0.0115	0.048	0.203
29	1.2245	0.3262	450.359	0.00074	0.23	0.000483	0.0115	0.103	0.148
30	1.3597	0.3251	501.502	0.00074	0.23	0.000525	0.0115	0.168	0.083
31	1.3583	0.32501	501.390	0.00074	0.23	0.000524	0.0115	0.206	0.045
32	0.8267	0.3282	303.483	0.00075	0.23	0.000368	0.0115	−0.046	0.205

[a] $2s(\rho)$ is the measurement uncertainty ($k = 2$) of the density. $u'_{\mathrm{PTB}} = 2s(\rho)/\rho$ is the relative measurement uncertainty of the density. $2s(p)$ is the measurement uncertainty of the pressure. $2s(T)$ is the measurement uncertainty of the temperature. $\Delta'_{\mathrm{PTB-LibHuAir}} = (\Delta\rho/\rho)_{\mathrm{PTB-LibHuAir}}$ is the relative difference in density between PTB and the database LibHuAir. H-$\lvert\Delta'_{\mathrm{PTB-LibHuAir}}\rvert$ is the difference between $H \equiv \sqrt{u'^2_{\mathrm{PTB}} + u'^2_{\mathrm{LibHuAir}}}$ (eq 9) and the absolute value from the neighboring column.

The main contributions to the uncertainty budget according to eq 8 are as follows.

120 kg·m^{-3}:

$$\rho_{\mathrm{lmp}} = (4.1630 \pm 0.00113)\ \mathrm{mol{\cdot}L^{-1}} \Leftrightarrow 19.6\ \%$$

$$(b - a\Delta t)/b = (1.0000 \pm 0.000454) \Leftrightarrow 54.7\ \%$$

$$\alpha = (18.49 \pm 0.00492){\cdot}10^{-6}\ \mathrm{K^{-1}} \Leftrightarrow 23.3\ \%$$

$$\kappa = (0.021 \pm 0.0115)\ \mathrm{GPa^{-1}} \Leftrightarrow 2.3\ \%$$

$$2s(\rho) = 0.00252\ \mathrm{mol{\cdot}L^{-1}};\ 2s(\rho)/\rho = 0.06\ \%$$

30 kg·m^{-3}:

$$\rho_{\mathrm{lmp}} = (1.0369 \pm 0.000496)\ \mathrm{mol{\cdot}L^{-1}} \Leftrightarrow 60.8\ \%$$

$$(b - a\Delta t)/b = (1.0000 \pm 0.000454) \Leftrightarrow 15.8\ \%$$

$$\alpha = (18.49 \pm 0.00492){\cdot}10^{-6}\ \mathrm{K^{-1}} \Leftrightarrow 23.3\ \%$$

$$\kappa = (0.021 \pm 0.0115)\ \mathrm{GPa^{-1}} \Leftrightarrow 0.1\ \%$$

$$2s(\rho) = 0.000628\ \mathrm{mol{\cdot}L};\ 2s(\rho)/\rho = 0.06\ \%$$

The input quantity ± two times the standard deviation is stated. The percentage on the right-hand side of the double arrow is the index of the corresponding input quantity.

The estimated relative density measurement uncertainty for all four isochores as a function of pressure and temperature is shown in Figure 5. The relative density differences between the measurement results of PTB and the Zittau database LibHuAir[1] as a function of temperature and pressure are shown in Figure 6.

According to Bayesian theory,[9] two results, ρ_{PTB} and ρ_{LibHuAir}, do not significantly deviate, if

$$\left|\frac{\rho_{\mathrm{PTB}} - \rho_{\mathrm{LibHuAir}}}{\rho}\right| < \beta{\cdot}\sqrt{\left(\frac{s(\rho_{\mathrm{PTB}})}{\rho_{\mathrm{PTB}}}\right)^2 + \left(\frac{s(\rho_{\mathrm{LibHuAir}})}{\rho_{\mathrm{LibHuAir}}}\right)^2} \equiv H$$

$$\text{with } \rho = \frac{\rho_{\mathrm{PTB}} + \rho_{\mathrm{LibHuAir}}}{2} \quad (9)$$

is valid, where $\beta = 2$. Provided that the relative standard uncertainty in density of the Zittau database LibHuAir is $1{\cdot}10^{-3}$, the relation (9) is fulfilled for all data measured. This corresponds to a positive sign of the values in the last column of Table 1.

Figure 7 shows recent experimental data on dry air,[10,11] for the sake of simplicity compared with the same database.[1] Michels et al.[11] stated the density in Amagat $A = \rho(T,p)/\rho(0°\mathrm{C}, 0.101325\ \mathrm{MPa})$. For the density of the air under standard conditions, the result from the Zittau database was used. The change of the temperature scale from IPTS 48 to ITS 90 was taken into account as well as the change of the pressure unit. Different molar masses were used for the synthetic air mixtures investigated by Howley et al.[10]

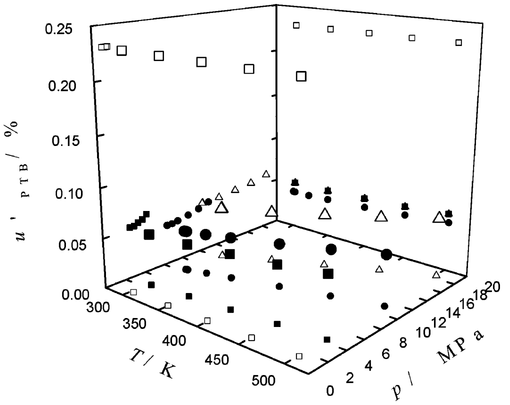

Figure 5. Relative uncertainty of density measurement of dry air along the isochores: □, 10 kg·m^{-3}; ■, 30 kg·m^{-3}; ●, 75 kg·m^{-3}; △, 120 kg·m^{-3}. The small symbols show the projection on the corresponding plane.

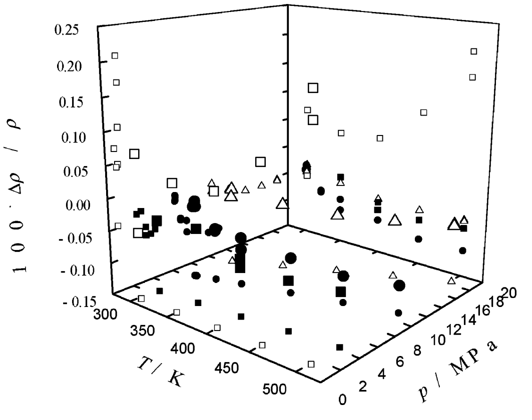

Figure 6. Relative density deviations of dry air. Zittau database LibHuAir[1]/PTB measurements at: □, 10 kg·m^{-3}; ■, 30 kg·m^{-3}; ●, 75 kg·m^{-3}; △, 120 kg·m^{-3}. The small symbols show the projection on the corresponding plane.

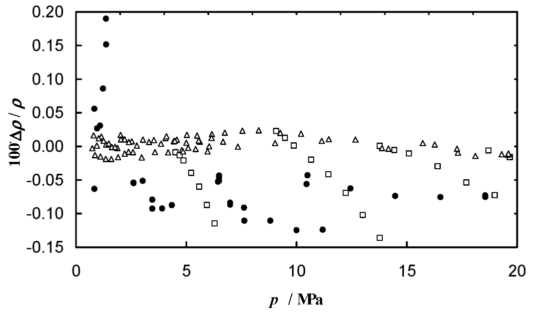

Figure 7. Relative density deviations of different experimental data from the Zittau database LibHuAir:[1] ●, this work; □, Howley et al.;[10] △, Michels et al.[11]

Measurements on Humid Air

Four isochores were measured with densities of (30, 60, 86, and 107) kg·m^{-3} (Figure 8). The mole fraction of the water substance in the humid air Ψ_{H_2O} was (4.45, 4.46, 4.20, and 1.26) %, respectively.

The humid air measurements were regarded as relative measurements. The density of the gas phase at 30 °C was calculated using the Zittau database LibHuAir[1] with the help of the function Rho_ptxw_HuAir(p, ϑ, x_{H_2O}). The quantity $x_{H_2O} = (m_{H_2O})/(m_{air})$ for saturated humid air is obtained from the function xws_pt_HuAir(p,ϑ) of LibHuAir. m_{H_2O} and m_{air} are the mass of water and dry air, respectively. The volume of liquid water in the measuring cell is taken into account. The total amount of air in the isochoric apparatus is determined from the data at 30 °C in the two-phase region (similar to eq 3 for the dry air)

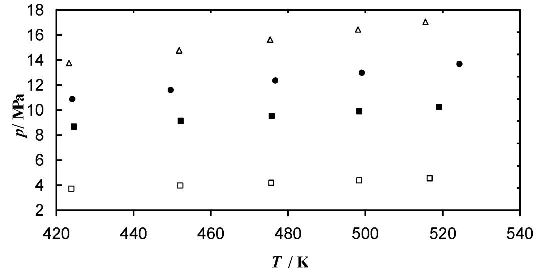

Figure 8. Quasi-isochores of humid air. Parameters: density, ρ/kg·m^{-3}; mole fraction of water, Ψ_{H_2O}/%: □, 30, 4.45; ■, 60, 4.46; ●, 86, 4.20; △, 107, 1.26.

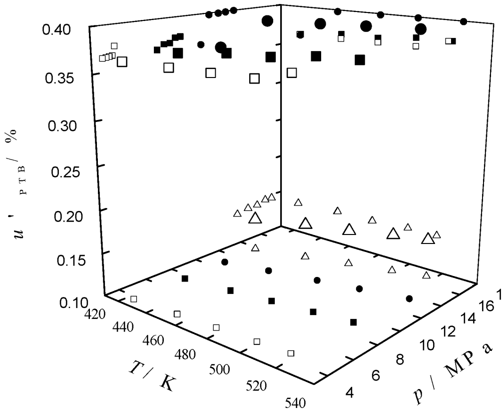

Figure 9. Relative uncertainty of density measurement of humid air along the isochores: □, 30 kg·m^{-3}; ■, 60 kg·m^{-3}; ●, 86 kg·m^{-3}; △, 107 kg·m^{-3}. The small symbols show the projection on the corresponding plane.

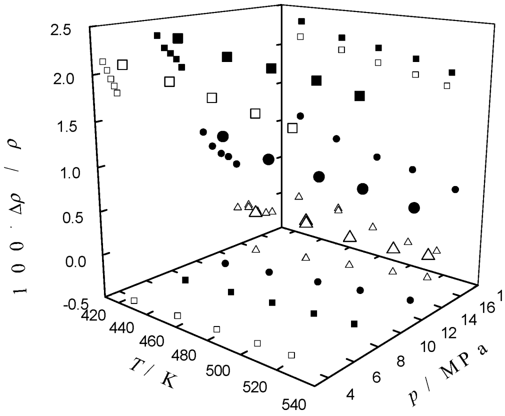

Figure 10. Relative density deviations of humid air. Zittau database LibHuAir[1]/PTB measurements at: □, 30 kg·m^{-3}; ■, 60 kg·m^{-3}; ●, 86 kg·m^{-3}; △, 107 kg·m^{-3}. The small symbols show the projection on the corresponding plane.

$$n = \rho_{M0}(p,\vartheta_{M0},x_{H_2O})\left(V_{M0} - \frac{m_{H_2O}}{\rho_{H_2O}}\right) + \sum_{i=1}^{7} \rho_i(p_i,\vartheta_i,x_{H_2Oi})V_i \quad (10)$$

The index M0 denotes the measuring cell, and all the input quantities p, ϑ, and x are taken at the reference point. In the one-phase region at higher temperatures, the density obtained from the isochoric experiment is

$$\rho = [n - \sum_{i=1}^{7} \rho_i(p_i,\vartheta_i,x_{H_2Oi})V_i]\frac{1}{V_{M0}}\cdot\frac{b - a\Delta t}{b}[1 - 3\alpha(\vartheta - \vartheta_{ref})][1 - \kappa(p - p_{ref})] \quad (11)$$

Table 2. *pρT* Data of Humid Air[a]

	p	ρ	T	Ψ_{H_2O}	$2s(\rho)$	$2s(\rho)/\rho$	$2s(p)$	$2s(T)$	$2s(\Psi_{H_2O})$	$(\Delta\rho/\rho)_{PTB-LibHuAir}$	$H\text{-}\lvert\Delta'_{PTB-LibHuAir}\rvert$
no.	MPa	$mol \cdot dm^{-3}$	K	$mol \cdot mol^{-1}$	$mol \cdot dm^{-3}$	%	MPa	K	$mol \cdot mol^{-1}$	%	%
1	10.87677	3.0201	424.109	0.0420	0.011	0.36	0.000824	0.0115	0.0047	1.10	−0.722
2	11.60037	3.0157	449.569	0.0420	0.012	0.40	0.000875	0.0115	0.0047	0.90	−0.490
3	12.36007	3.0114	476.697	0.0420	0.012	0.40	0.000929	0.0115	0.0047	0.77	−0.359
4	12.97940	3.0076	499.077	0.0420	0.012	0.40	0.000974	0.0115	0.0047	0.71	−0.299
5	13.68388	3.0035	524.328	0.0420	0.012	0.40	0.001027	0.0115	0.0047	0.58	−0.168
6	7.51008	2.1331	424.583	0.0446	0.0078	0.37	0.000604	0.0115	0.0050	2.32	−1.941
7	8.03133	2.1298	452.198	0.0446	0.0079	0.37	0.000636	0.0115	0.0050	2.17	−1.786
8	8.46986	2.1271	475.704	0.0446	0.0079	0.37	0.000664	0.0115	0.0050	2.10	−1.715
9	8.89246	2.1244	498.399	0.0446	0.0080	0.38	0.000691	0.0115	0.0050	2.02	−1.630
10	9.28005	2.1220	519.084	0.0446	0.0080	0.38	0.000716	0.0115	0.0050	1.92	−1.530
11	3.71838	1.0680	423.879	0.0445	0.0039	0.37	0.000384	0.0115	0.0050	2.12	−1.741
12	3.97193	1.0663	452.073	0.0445	0.0039	0.37	0.000398	0.0115	0.0050	2.02	−1.641
13	4.18402	1.0650	475.611	0.0445	0.0039	0.37	0.000410	0.0115	0.0050	1.93	−1.550
14	4.38840	1.0636	498.405	0.0445	0.0039	0.37	0.000421	0.0115	0.0050	1.84	−1.460
15	4.55241	1.0625	516.646	0.0445	0.0040	0.38	0.000430	0.0115	0.0050	1.76	−1.370
16	13.74665	3.7270	423.295	0.0126	0.0052	0.14	0.001032	0.0115	0.0015	0.00	0.172
17	14.75962	3.7210	451.738	0.0126	0.0053	0.14	0.001109	0.0115	0.0015	−0.01	0.164
18	14.76726	3.7210	451.812	0.0126	0.0053	0.14	0.001110	0.0115	0.0015	−0.05	0.124
19	15.61348	3.7162	475.258	0.0126	0.0053	0.14	0.001176	0.0115	0.0015	−0.15	0.024
20	15.61822	3.7162	475.390	0.0126	0.0053	0.14	0.001177	0.0115	0.0015	−0.15	0.024
21	16.42873	3.7114	498.073	0.0126	0.0054	0.15	0.001242	0.0115	0.0015	−0.21	−0.033
22	17.04534	3.7078	515.557	0.0126	0.0054	0.15	0.001292	0.0115	0.0015	−0.23	−0.053

[a] Ψ_{H_2O} is the molar fraction of water in the humid air. $2s(\rho)$ is the measurement uncertainty ($k = 2$) of the density. $u'_{PTB} = 2s(\rho)/\rho$ is the relative measurement uncertainty of the density. $2s(p)$ is the measurement uncertainty of the pressure. $2s(T)$ is the measurement uncertainty of the temperature. $2s(\Psi_{H_2O})$ is the measurement uncertainty of the mole fraction of water in the humid air. $\Delta'_{PTB-LibHuAir} = (\Delta\rho/\rho)_{PTB-LibHuAir}$ is the relative difference in density between PTB and the database LibHuAir. $H\text{-}\lvert\Delta'_{PTB-LibHuAir}\rvert$ is the difference between $H \equiv \sqrt{u'^2_{PTB} + u'^2_{LibHuAir}}$ (eq 9) and the absolute value from the neighboring column.

In eq 10, all the input quantities p, ϑ, and x_{H_2O} are taken at the measuring point. The index ref denotes the reference point at 30 °C. Similar to eq 8, a/b describe the leak rate and Δt is the difference in time to the reference point at the beginning. The reference point is repeated at the end of the measurement series, thus allowing us to determine the leak rate. In the case of the 86 $kg \cdot m^{-3}$ isochore, only a leak rate of $3.5 \cdot 10^{-5}$ $mol \cdot d^{-1}$ was observed.

This experiment starts with small values of x_{H_2O} at 30 °C. x_{H_2O} increases with temperature and remains constant in the measurement range (150 °C to 250 °C). To have an approximation for the change of the density of humid air with x_{H_2O}, the model of the ideal mixture of ideal gases (dry air, steam) is used. Thus, in the uncertainty calculation according to the GUM-Workbench on the right-hand side of the working eq 11, the term

$$\frac{M_{H_2O}R_{H_2O}}{M_{hu.air}R_{hu.air}R_m} \cdot \frac{p}{T}(x_{H_2O} - x_{H_2Oref}) = \frac{M_{H_2O}R_{H_2O}}{R_m^2} \cdot \frac{p}{T}(x_{H_2O} - x_{H_2Oref}) \quad (12)$$

is added. The mass of water is estimated with a relative half-width of 10 %. This pessimistic assumption is used such as in the case of the 107 $kg \cdot m^{-3}$ isochore where only the dew point instrument was used, and in all other cases the mass value of the water before starting the experiment was available. This gives the main contribution in the uncertainty budget. Another important contribution is due to the relative uncertainty of the saturated density at 30 °C according to LibHuAir. For this small content of water, a relative uncertainty in density of 0.1 % with the confidence level $k = 2$ is used. The same value is claimed by Lemmon et al.[2] for dry air.

The main contributions to the uncertainty budget are as follows.

107 $kg \cdot m^{-3}$, measuring point 7:

$$\rho_{ref} = (3.70983 \pm 0.00370)\ mol \cdot L^{-1} \Leftrightarrow 41.7\ \%$$

$$(b - a\Delta t)/b = (1.00000 \pm 0.00024) \Leftrightarrow 2.6\ \%$$

$$\alpha = (18.490 \pm 0.492) \cdot 10^{-6}\ K^{-1} \Leftrightarrow 4.5\ \%$$

$$x_{H_2O} = (7.961 \pm 0.462)\ g \cdot kg^{-1} \Leftrightarrow 46.2\ \%$$

$$2s(\rho) = 0.0054\ mol \cdot L^{-1};\ 2s(\rho)/\rho = 0.15\ \%$$

30 $kg \cdot m^{-3}$, measuring point 1:

$$\rho_{ref} = (1.02994 \pm 0.00100)\ mol \cdot L^{-1} \Leftrightarrow 6.6\ \%$$

$$(b - a\Delta t)/b = (1.00000 \pm 0.00038) \Leftrightarrow 1.0\ \%$$

$$\alpha = (18.490 \pm 0.492) \cdot 10^{-6}\ K^{-1} \Leftrightarrow 0.2\ \%$$

$$x_{H_2O} = (29.01 \pm 3.46)\ g \cdot kg^{-1} \Leftrightarrow 92.0\ \%$$

$$2s(\rho) = 0.0039\ mol \cdot L^{-1};\ 2s(\rho)/\rho = 0.38\ \%$$

The index of the corresponding input quantity is given on the right-hand side of the double arrow. The relative density measurement uncertainty for all four isochors as a function of pressure and temperature is shown in Figure 9.

The differences of the isochoric measurements from the results of the database LibHuAir can be seen in Figure 10. The results of the measurements on humid air are summarized in Table 2. In eq 9, $2s(\rho_{LibHuAir})/\rho_{LibHuAir} = 0.1$ % was again used, which is not enough in the case of humid air. As can be seen from the last column of Table 2, most of the density data show a significant difference (negative sign) from the value obtained from the database LibHuAir. This indicates that a model equation treating humid air as an ideal mixture of the real-gas components dry air and steam is not sufficient, mainly in the case of higher water content.

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Literature Cited

(1) Kretzschmar, H.-J.; Weidner, M.; Buttig, D.; Stöcker, I.; Jähne, I. *Property Data Base for Humid Air*, version 2.0; University of Applied Sciences Zittau: Görlitz, Germany, 2004.

(2) Lemmon, E. W.; Jacobsen, R. T.; Penoncello, S. G.; Friend, D. G. Thermodynamic Properties of Air and Mixtures of Nitrogen, Argon and Oxygen from 60 to 2000 K at Pressures up to 2000 MPa. *J. Chem. Ref. Data* **2000**, *29*, 331−384.

(3) Weber, F. Liquid-density measurements on toluene at elevated temperatures and pressures as part of the EUROMET project 491 “Intercomparison of measurement standards for density” Internal Report (can be obtained from the author by request), 2000.

(4) Wagner, W.; Kleinrahm, R. Densimeters for very accurate density measurements of fluids over large ranges of temperature, pressure, and density. *Metrologia* **2004**, *41*, 24−39.

(5) Span, R.; Lemmon, E. W.; Jacobsen, R. T.; Wagner, W.; Yokozeki, A. A Reference Quality Thermodynamic Property Formulation for Nitrogen *J. Phys. Chem. Ref. Data* **2000**, *29*, 1361−1433.

(6) *Guide to the Expression of Uncertainty in Measurement*, corrected and reprinted; International Organization for Standardization: Geneva, Switzerland, 1995.

(7) Kohlrausch, F. *Praktische Physik* (in German), vol. 3, 24th ed.; B. G. Teubner: Stuttgart, 1996.

(8) Klimeck, J. Weiterentwicklung einer Ein-Senkkörper-Dichtemessanlage und Präzisionsmessungen der thermischen Zustandsgrö*β*en von Kohlendioxid, Argon, Stickstoff und Methan (in German). Thesis, Fakultät für Maschinenbau der Ruhr-Universität Bochum, 1997.

(9) Weise, K.; Wöger, W. Comparison of two measurement results using the Bayesian theory of measurement uncertainty. *Meas. Sci. Technol.* **1994**, *5*, 879−882.

(10) Howley, J. B.; Magee, J. W.; Haynes, W. M. Isochoric (p-ρ-T) Measurements on Liquid and Gaseous Air from 67 to 400 K at Pressures up to 35 MPa. *Int. J. Thermophys.* **1994**, *15*, 881−902.

(11) Michels, A.; Wassenaar, T.; van Seventer, W. Isotherms of Air between 0 °C and 75 °C and at Pressures up to 2200 atm. *Appl. Sci. Res.* **1954**, *4*, 52−56.

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