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Volume ratio determination in static expansion systems by means of a spinning rotor gauge

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Abstract

Static or volume expansion systems are used to generate accurately known pressures in the high and medium vacuum range for vacuum gauge calibrations. To determine the volume ratios in such systems, different methods can be used. We have tested the method of using a spinning rotor gauge for measuring pressures before and after an expansion for several gases and compared it with two other independent methods. The results of the volume ratios obtained with the spinning rotor gauge method were in agreement (relative differences $\leq 3 \times 10^{-4}$) with the results obtained with either of the two other methods. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Vacuum primary standard; Static expansion; Spinning rotor gauge; Expansion ratio

1. Introduction

Static expansion systems (also called volume or series expansion systems) are used as primary standards for generating pressures in the high and medium vacuum range for vacuum gauge calibrations [1–4]. In such systems, known pressures are generated by expanding a known gas amount enclosed in a small volume into a much larger evacuated volume by opening a valve in between the two volumes. Under isothermal conditions, the gas pressure is reduced by the ratio of the small volume to the sum of the small and large volume. This ratio is called expansion ratio, its inverse, volume ratio. In most static expansion systems several different expansion ratios are available, and expansions are carried out in series to generate very low pressures. The expansion ratios are the crucial parameters in all static expansion systems and have to be determined very accurately.

Two main types of methods are used for the accurate determination of expansion ratios:

- In the gravimetric technique the unknown volume is filled with a suitable liquid of known density, the weight of which is measured. When each volume has been determined in this way, the expansion ratios can be calculated.
- In the expansion technique the pressures before and after the expansion are used for direct determination of the expansion ratio. The pressure ratio has to be measured with high accuracy. It is possible to use two calibrated gauges [5] or a single uncalibrated gauge with strictly linear pressure response [6].

A third method, the constant pressure technique [3], is rarely applied and mainly suitable for volumes <100 cm^3 and is not under concern in this investigation.

In 1986 Berman and Fremerey applied the expansion technique by using a single uncalibrated spinning rotor gauge (SRG) [6] to measure expansion ratios of down to 1/257. The same SRG is used to measure the pressure both before and after the gas expansion. The problem of using a SRG for low expansion ratio measurements (large pressure reductions) is that the useful linear range of the SRG is relatively small: At pressures above about 0.1 Pa the deceleration rate of the rotor becomes non-linear with pressure due to viscosity effects and at low pressures of a few mPa the accuracy of reading is affected by the offset fluctuations of the SRG [7–9]. Berman and Fremerey [6] solved this problem with a linearization procedure and claimed a relative total standard

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uncertainty of 2×10^{-4} for the determination of the above- mentioned expansion ratio.

In this investigation we compared results obtained with the SRG method after Berman and Fremerey with results obtained with two independent methods to detect any systematic unrecognised problems associated with at least one of the methods.

At the Physikalisch-Technische Bundesanstalt (PTB), two static expansion systems, SE1 and SE2, are available [4]. At SE1 we measured an expansion ratio of roughly 1/25 by the SRG method and by the gravimetrical method, at SE2 we applied the SRG method and the expansion method with two calibrated gauges [5] (in the following called gas accumulation method) for a ratio of about 1/109.

2. Experimental set-up and measurement procedure

Figs. 1 and 2 show schematically the static expansion systems SE1 and SE2. At SE1 the initial pressure before the first expansion is measured by a quartz Bourdon spiral (QBS), at SE2 either a QBS or a piston gauge can be chosen. The SE1 system is used for generating calibration pressures from 10^{-6} Pa up to 1 kPa in volume V_5, while SE2 is regularly used for generating pressures in the range 0.1 Pa up to 1 kPa in V_6.

At SE1 we have determined the expansion ratio

$$f_4 = \frac{V_6}{V_5 +} \qquad (1)$$

with an approximate value of $1/250 = 4 \times 10^{-3}$ (nominally 1/234), at SE2 the expansion ratio

$$f_1 = \frac{V_1}{V_1 + V_3 +} \qquad (2)$$

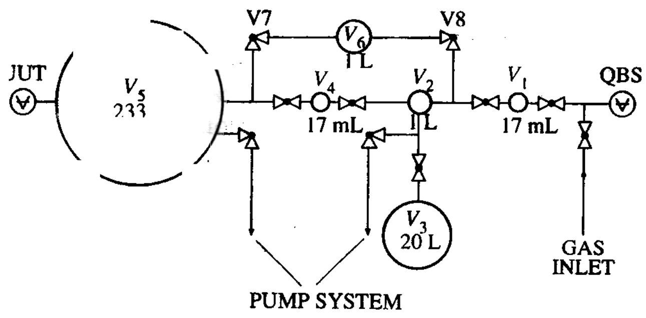

Fig. 1. Scheme of the static expansion system SE1 used at PTB, which is used as primary standard to generate pressures in vacuum from 10^{-6} Pa to 1 kPa. Volumes are denoted with slanted letters plus subscribed numbers, valves with normal letters and numbers. QBS: Quartz Bourdon spiral manometer. UUT: Unit under test.

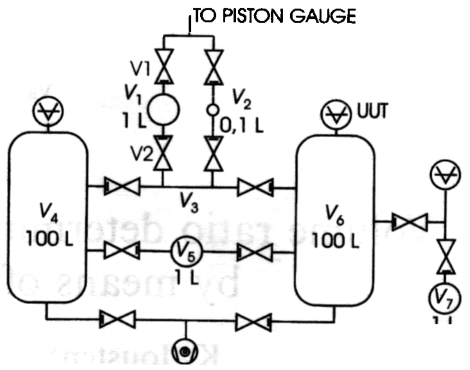

Fig. 2. Scheme of the static expansion system SE2 used at PTB, which is used as primary standard to generate pressures in vacuum from 0.1 Pa to 1 kPa. Volumes are denoted with slanted letters plus subscribed numbers, valves with normal letters and numbers. UUT: Unit under test.

with an approximate value of $1/109 = 9.2 \times 10^{-3}$ (nominally 1/101). The notations of the expansion ratios are the usual notations in our laboratory.

We compared the SRG method with the gravimetric method in the case of f_4 and with the gas accumulation method in the case of f_1.

2.1. Determination of f_1 with the gas accumulation method

For the measurement of f_1 with the gas accumulation method [5] a piston gauge was used to establish the initial pressure in V_1 and a newly calibrated quartz Bourdon spiral (QBS) for measuring the pressure in V_6 after repeated expansions. To correct for temperature gradients between the vessels and temperature changes over time (temperature drifts), 7 calibrated PT100 sensors were attached to the vessels. The temperature correction term was calculated in a different way as compared to Ref. [5], as discussed in the appendix.

The measurement procedure was the following: Before the first expansion, with valve V1 open and valve V2 closed, a pressure of 100.39 kPa nitrogen was established in V_1 with the piston gauge. After slowly closing V1 (the pressure is kept constant by the piston gauge), the temperature of V_1 was measured, and by opening of valve V2 the gas was expanded into the evacuated volumes V_3 and V_6. After pressure relaxation, the temperatures of the sensors on V_6 were read out and the reading of the QBS taken. For the following expansion valve V2 was closed, the pressure of 100.39 kPa was re-established, the temperature of V_1 was measured and the amount of gas expanded again. Since V_3 and V_6 were not evacuated between the expansions, the pressure contributions of all expansions add up to the final pressure. Under isothermal conditions, the pressure in V_3 and V_6 after n expansions is [5]

$$p_n = p_i[\qquad (1 - f_1)^n] \qquad (3)$$

In our case, $n = 25$ expansions were carried out ($p_{25} = 20.59$ kPa) to improve the accuracy of the pressure measurement and to reduce the standard deviation of f_1.

2.2. Determination of f_1 with the SRG method

The deceleration rate $(-\dot{\omega}/\omega)$ (*DCR*-reading) of the rotor of an SRG corresponds to a pressure reading by [7]

$$p = K\frac{-\dot{\omega}}{\omega} \tag{4}$$

with

$$K = \frac{\pi\rho d\bar{c}}{20\sigma} \tag{5}$$

ρ and d are the mass density and diameter of the rotor, $\bar{c}$ the mean thermal velocity and σ the effective accommodation coefficient of tangential momentum on the rotor surface of the gas particles. In Eq. (4) the deceleration rate $(-\dot{\omega}/\omega) \equiv DCR$ is corrected for an pressure independent offset OFF (also called residual drag) [7–9]:

$$\frac{}{\omega} \equiv DCR \quad DCR' \quad OFF \tag{6}$$

where DCR' is the indicated deceleration rate including the offset.

f_1 was determined with the SRG method in the following manner (cf. Fig. 2): An SRG was installed on vessel V_6 (in the position of UUT in Fig. 2). Before the measurements, its offset was measured over a longer period of time (several hours) at a pressure below the resolution limit of the SRG (10^{-6} Pa). For the measurements, a pressure between 0.3 and 30 Pa was established in volumes V_1, V_3 and V_6, while the valves between the volumes were open. The deceleration rate DCR_1 of the SRG was taken. Then V_1 was isolated by slowly closing valve V2, and V_3 and V_6 were evacuated to a level where the DCR signal showed its typical offset fluctuations.

The gas retained in V_1 was then expanded into V_3 and V_6, and a second reading DCR_2 was taken. Under isothermal conditions and with a perfectly linear DCR vs. pressure characteristic (i.e. $K = \text{const.}$ in Eq. (4)), the ratio DCR_1/DCR_2 would give the volume ratio $R_1 = f_1^{-1}$. Both requirements were not fulfilled; however, We had typical temperature differences between V_1 (temperature T_1) and V_6 (T_6) of $T_1 - T_6 = 0.3$ K. We corrected for isothermal conditions by

$$\left(\frac{DCR_1}{DCR_2}\right)_{\text{corr}} = \left(\frac{DCR_1}{DCR_2}\right)_{\text{meas}} \frac{T_6}{T_1}. \tag{7}$$

The non-linear DCR vs. pressure characteristic was linearised as described in Section 3.2. Three different gas species (He, N_2, Ar) were used with the SRG method, and for each gas about 40 DCR data pairs were taken in the pressure range above mentioned.

Since relative short-term fluctuations of the offset are typically of the order of 0.5%, we measured the offset before the measurements over a period of time of several hours to improve the statistical uncertainty. This procedure has the advantage that the offset can be measured with low uncertainty caused by random fluctuations, but the disadvantage that possible offset drifts and short-term changes during the measurements cannot be detected. Therefore we decided to measure the offset in a different way at SE1 (see below).

Before each series of measurement we checked thoroughly that neither leaks nor outgassing would significantly affect the succeeding measurements.

2.3. Determination of f_4 with the SRG method

The SRG method was applied to the determination of f_4 in the same manner as described in the preceding section. The SRG was installed at the vessel V_5 (cf. Fig. 1). In this case the offset was determined separately for each measured point, so that the measurements were made in the following order: Measurement of offset at residual pressure below 10^{-6} Pa, expansion of gas from V_6 into V_5 to generate the higher pressure p_1 to be measured with the SRG (DCR_1), closing of valve V7 and pumping down V_5 to residual pressure, taking the offset reading again, isolating V_5 from the pump system, opening valve V7 to generate the lower pressure to be measured with the SRG (DCR_2), evacuation of V_6 and V_5 and starting again. 10 data pairs were taken in each measurement series with p_1 in the range from 0.4 to 4 Pa. As test gases we used helium, neon, nitrogen, argon and xenon.

2.4. Determination of f_4 with the gravimetric method using distilled water

The large volume V_5 of SE1 (Fig. 1) had been determined, when the system was commissioned in 1969. First of all, the vessel was weighed empty (air filled). Then the vessel was filled with distilled water to about $\frac{3}{4}$ of its volume and evacuated for 48 h by a water jet pump for degassing. Finally, the volume was completely filled with distilled water and evacuated again for several hours. All flanges were positioned on top of the vessel and remained open to avoid air enclosures. Since the flanges were not on the same height, sealed Plexiglas tubes were mounted on the flanges, so that the water was completely filling the stainless steel vessel. The additional volume in the Plexiglas tubes was later subtracted from the result. After measuring the temperature and temperature gradient of the water in the vessel, the weight of the water filled vessel was measured. Part of the water was then used to determine its density. After correcting for different buoyancy of the stainless steel vessel and the weights in air, the volume could be determined with a total standard uncertainty of 1×10^{-4}, including the uncertainty due to volume changes of the vessel under air pressure, when the vessel is evacuated. These changes were also measured.

In a similar manner, the smaller volume V_6 was measured three times. The results are shown in Table 4.

3. Evaluation of data

3.1. Gas accumulation method for determination of f_l

Eq. (3) gives the correct expansion ratio only under ideal conditions (ideal gas, isothermal conditions). The measured data, however, have to be corrected for temperature differences between the vessels and temperature drift (see the appendix) and for deviations from the ideal gas law. This latter correction was carried out according to

$$f_{\text{corr}} \quad \left(1 - \frac{B}{V_{\text{m}}}\right), \tag{8}$$

where B is the second virial coefficient [10] and V_{m} the molar volume before expansion. For B we used -4.7 cm^3/mol, which is the recommended value [10] for nitrogen at the measurement temperature of 25°C.

For easy comparison of the different methods, the expansion ratio f_1 was calculated for V_6 without the additional volume V_{g} of the different test gauges in different methods. V_{g} was either measured by gas expansions [2] or determined geometrically. f_1 was calculated by

$$f_1 = \frac{1}{1/f_1' - V_{\text{g}}/V_1}, \tag{9}$$

from the expansion ratio f_1' (already corrected) including all additional volumes. The variable volume in valve V2 has not to be considered, because the valve is in the same state during the expansion ratio determination and during its use in the generation of standard pressures for calibrations.

3.2. SRG method for determination of f_l and f_4

Above 0.1 Pa the deceleration rate DCR of the SRG becomes increasingly non-linear in pressure, so that K in Eq. (4) is no longer a constant. As a result, f^{-1} is not simply given by the measured (and temperature corrected) ratio $(\text{DCR}_1/\text{DCR}_2)_{\text{corr}}$. However, up to 1 Pa, K (or σ, respectively) can be approximated by linear functions of p, and above 1 Pa up to 30 Pa by a polynomial of second order. Therefore, as suggested by Berman and Fremerey [6], the temperature corrected DCR ratio

$$g(DCR_1) = (DCR_1/DCR_2)_{\text{corr}} \tag{10}$$

was fitted by a second order polynomial

$$g(DCR_1) = a_0 + a_1 DCR_1 + a_2 DCR_1^2 \tag{11}$$

with a least-squares formalism (Marquard–Levenberg algorithm [11]). This function was used to extrapolate each DCR ratio to zero pressure by

$$\left(\frac{DCR_1}{DCR_2}\right)_{\text{lin}} = \left(\frac{DCR_1/DCR_{2\text{corr}}}{g(DCR_1)}\right) a_0. \tag{12}$$

The final DCR ratios were virtually independent of the initial pressure or DCR_1 value. Their mean value gives the final result for f^{-1}:

$$= \overline{\left(\frac{DCR_1}{DCR_2}\right)_{\text{lin}}}. \tag{13}$$

As already mentioned, a reason for erroneous results could be that the offset of the SRG changed during the measurements or was not measured correctly. We measured the offset, but found during evaluation of the data of SE2 that more accurate results can be achieved if the offset itself is taken as variable to be fitted. Since the offset affects only the DCR_2 value significantly (DCR_1 is hundred times larger) it is sufficient to adjust the offset for DCR_2 and to use the measured value for DCR_1. Therefore the following function was fitted instead of the one in Eq. (11):

$$h(DCR_1) = 0 = a_0 + a_1 DCR_1 + a_2 DCR_1^2 - \frac{DCR_1}{DCR_2' - OFF}. \tag{14}$$

Here DCR_2' is the measured deceleration rate including the offset (see Eq. (6)).

4. Results

In Table 1 the result of the recent determination of f_1 at SE2 with the gas accumulation method is compared with the results of previous determinations. The measurements until 1988 lacked of an appropriate temperature

Table 1

Expansion factor f_1 (Eq. (2)) in the static expansion system SE2 as determined in this and previous investigation with the gas accumulation method

f_1	Year
$(9.188 \pm 0.005) \times 10^{-3}$	This investigation
$(9.183 \pm 0.005) \times 10^{-3}$	1993
$(9.184 \pm 0.005) \times 10^{-3}$	1992
$(9.176 \pm 0.011) \times 10^{-3}$	1988
$(9.168 \pm 0.011) \times 10^{-3}$	1987
$(9.192 \pm 0.011) \times 10^{-3}$	1985

Table 2
Uncertainty budget of the determination of $f_1 = 9.188 \times 10^{-3}$ with the gas accumulation method (this investigation)

Uncertainty due to	Standard uncertainty	Relative standard uncertainty
Repeatability	1.4×10^{-7}	1.6×10^{-5}
Initial pressure	7×10^{-7}	7.6×10^{-5}
Final pressure	1.1×10^{-6}	1.2×10^{-4}
Temperature correction	1.4×10^{-6}	5.1×10^{-4}
Additional volume	5.5×10^{-7}	6.0×10^{-5}
Total	4.4×10^{-6}	5.3×10^{-4}

Table 3
Expansion factor f_1 (Eq. (2)) in the static expansion system SE2 as determined with the SRG and the gas accumulation method. $R' = (f_1^{-1})'$ is the value including the additional volumes during the measurements and is therefore identical to the mean linearised *DCR* ratio (Eqs. (12) and (13)). The uncertainty given is the experimental standard deviation of the mean for all gases

Method	R'	f_1
SRG mean	108.924 ± 0.014	$(9.187 \pm 0.001) \times 10^{-3}$
Gas accumul.		9.188×10^{-3}

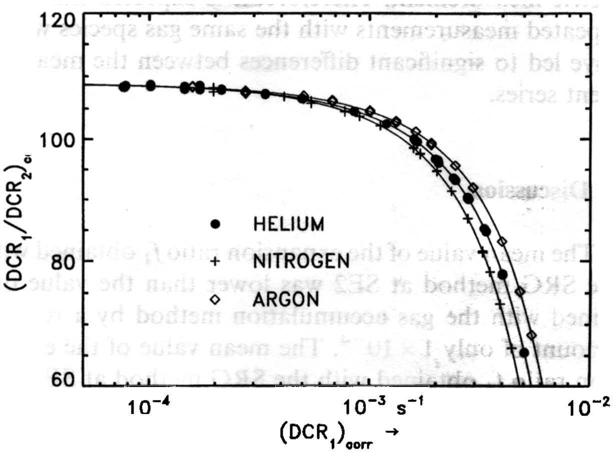

Fig. 3. Measured temperature-corrected DCR_1/DCR_2 ratios for three gases in dependence of DCR_1 with the offset value fitted. The measurements were made to determine the expansion ratio f_1 (Eq. (2)) at SE2.

measurement and have considerable higher uncertainties. Table 2 shows the uncertainty budget of the present determination according to the ISO guideline [12].

Fig. 3 shows the corrected *DCR* ratios according to Eq. (7) for helium, nitrogen and argon. The curves could be fitted with the following polynomials of second order:

$$\begin{aligned} g(\mathrm{He}) &= (108.90 \pm 0.09) - (4343 \pm 70)DCR_1 \\ &\quad - (8.49 \pm 0.12) \times 10^5\, DCR_1^2, \\ g(\mathrm{N_2}) &= (108.99 \pm 0.11) - (4902 \pm 95)DCR_1 \\ &\quad - (1.089 \pm 0.018) \times 10^6\, DCR_1^2, \\ g(\mathrm{Ar}) &= (108.88 \pm 0.14) - (3724 \pm 99)DCR_1 \\ &\quad - (6.86 \pm 0.15) \times 10^5\, DCR_1^2. \qquad (15) \end{aligned}$$

The first, constant terms (a_0) of the polynomials agree within their statistical uncertainties. Therefore, the *DCR* ratios extrapolated to zero pressure are not significantly different between the gases and it is justified to calculate the mean from all data.

Table 3 lists the mean values of the corrected and linearised *DCR* ratios according to Eqs. (11) and (12), the experimental standard deviation of the mean, the resulting expansion ratio without additional volumes, and the value obtained here with the gas accumulation method for comparison. The relative difference of the expansion ratios obtained with the two different methods is 1×10^{-4} and smaller than the combined statistical uncertainties of the two methods let alone their total uncertainties (see Discussion).

The good agreement could only be achieved because the offset *OFF* could be accurately fitted in Eq. (14). The fitted offset values were $(1.964 \pm 0.001) \times 10^{-6}\,\mathrm{s}^{-1}$ for helium, $(1.961 \pm 0.002) \times 10^{-6}\,\mathrm{s}^{-1}$ for nitrogen, and $(1.962 \pm 0.002) \times 10^{-6}\,\mathrm{s}^{-1}$ for argon. Before the expansion measurements, we measured an offset value of $(1.969 \pm 0.003) \times 10^{-6}\,\mathrm{s}^{-1}$ (unfortunately a rather high value). The typical short-term variations were $0.015 \times 10^{-6}\,\mathrm{s}^{-1}$. No frequency dependence of the offset was found between 405 and 415 Hz within the statistical uncertainties. At the end of the measurement series, we determined an offset of $(1.961 \pm 0.003) \times 10^{-6}\,\mathrm{s}^{-1}$, so that all fitted offset data lie within the range of the two measured values. If the offset in these measurements is deliberately changed by $+1 \times 10^{-8}\,\mathrm{s}^{-1}$ (a relatively change of 0.5%) the a_0 value of the fit polynomial changes by +0.9 (0.8%). This shows the importance of a correct offset value determination. It should be noted that the offset value is about equal to the measurement signal DCR_2 for the lower starting pressures at 0.3 Pa. A presupposition of the determination of the offset value by the fit is that the offset does not change significantly during the measurement series, so that it must not have any significant frequency dependence and no temperature drift on the rotor.

For the second experiment at SE1 we had decided to measure the offset after each measured pressure point and to subtract it from the signal.

Since the expansion ratio f_4 in SE1 was lower valued than f_1 in SE2, the range of suitable starting pressures before expansion to be measured with the SRG was reduced. In the case of SE1 we used two SRGs

Table 4
The results of the gravimetric measurements of volumes V_5 and V_6 at SE1. The volumes are given for a temperature of 23°C

Year	V_5 (cm^3)	V_6 (cm^3)	$f_4 = V_6/V_5 + V_6$
This investigation		930.94 ± 0.28	$(3.9760 \pm 0.0015) \times 10^{-3}$
1984		931.01 ± 0.28	$(3.9767 \pm 0.0015) \times 10^{-3}$
1979		931.29 ± 0.29	$(3.9775 \pm 0.0015) \times 10^{-3}$
1969	233207 ± 55		

Table 5
The expansion ratio f_4 (Eq. (1)) as measured with the SRG method. Two SRG (SRG1 and SRG2) were used at the same time. Each value is the mean of 10 data pairs. The experimental standard deviations are in the range of 4×10^{-7} to 1.2×10^{-6} and corresponding relative deviations range from 1×10^{-4} to 3×10^{-4}. The weighted mean of SRG1 and SRG2 is $(3.9750 \pm 0.0034) \times 10^{-3}$

Gas species	SRG1	SRG2
He	3.9675×10^{-3}	3.9514×10^{-3}
Ne	3.9751×10^{-3}	3.9748×10^{-3}
N_2	3.9680×10^{-3}	3.9675×10^{-3}
Ar	3.9839×10^{-3}	3.9772×10^{-3}
Xe	3.9868×10^{-3}	3.9891×10^{-3}
Mean	$(3.9763 \pm 0.0040) \times 10^{-3}$	$(3.9720 \pm 0.0062) \times 10^{-3}$

simultaneously and five gases (helium, neon, nitrogen, argon, and xenon).

The results of the gravimetric measurements are shown in Table 4. Table 5 presents the results obtained for f_4 with the SRG method.

Table 5 shows that there are significant differences between the values obtained with different gases, the largest difference existing between the lightest (He) and the heaviest (Xe) gas, which differ by a relative amount of 1% for SRG2. On the other hand, the mean values of all gases of 3.9763×10^{-3} for SRG1 and 3.9720×10^{-3} for SRG2 are in good agreement with the gravimetric method (3.9760×10^{-3}). The value obtained with SRG1 is relatively higher by 8×10^{-5} than the value obtained with the gravimetric method, the value of SRG2 by 1×10^{-3} lower.

Unfortunately, the data obtained at SE1 did not allow to fit the offset and to use the fit function of Eq. (14), as the Marquardt–Levenberg algorithm did not converge for these data. Several reasons may be responsible for this: At SE1 only 10 data pairs were taken in each measurement series instead of 40 at SE2, so that for 4 fit parameters the numbers of redundant points is too small. The pressure range at which the DCR_2 values were taken was lower and covered only one order of magnitude (1,6 mPa ... 16 mPa) instead of two (SE2: 3 mPa ... 300 mPa). At higher pressures the offset plays a less dominant role and the coefficients a_0 ... a_2 of the fit polynomial can be fitted more accurately. Finally, the offset values were not very stable at SE1. Unfortunately, we had not checked, whether the offset of the two SRGs used at SE1 had a frequency dependence.

We do not think that the differences between the measurement series with different gases at SE1 are caused directly by any physical property of the gas species. Rather, since the measurements were carried out at the same nominal pressures, the influence of the gas independent offset changed due to the variation of the deceleration rate which depends on the molecular mass of the gas species. In addition, the probably erroneous offset measurements are apparently randomly distributed, since the mean value of all data agrees reasonably well with the value obtained by the gravimetric measurement. Therefore, it is expected that even repeated measurements with the same gas species would have led to significant differences between the measurement series.

5. Discussion

The mean value of the expansion ratio f_1 obtained with the SRG method at SE2 was lower than the value obtained with the gas accumulation method by a relative amount of only 1×10^{-4}. The mean value of the expansion ratio f_4 obtained with the SRG method at SE1 was lower than the value obtained with the gravimetric method by a relative amount of 3×10^{-4}. Although the results of the different methods agree within their statistically determined uncertainties in both cases, we discuss the uncertainties associated with the SRG method in detail. For the gas accumulation method and the gravimetric method this has already been done in Section 4 (Table 2), respectively, Section 2.4 (Table 5).

The following uncertainties are associated with the SRG method:

(i) The experimental standard deviation of DCR_1 and DCR_2, which include the standard deviation of the offset, since the offset is subtracted from the signal. Its effect on the mean value can be estimated by the experimental standard deviation of the mean $(DCR_1/DCR_2)_{\text{lin}}$ as given in Tables 3 and 5. The typical relative standard deviation of the mean for the DCR ratio or f of all data at SE2 was 1×10^{-4}, similar to the value found by Berman and Fremerey (2×10^{-4}), but was 8.5×10^{-4} in the case of SE1.

(ii) The standard deviation of the mean also includes uncertainties due to an insufficient fit polynomial. We have checked that the residuals are normally distributed (Fig. 4) in dependence on DCR_1 and that the use of higher-order polynomials does not lead to further improvement in the fit, respectively, linearization procedure. Accordingly, uncertainties due to insufficient linearization are smaller than the experimental standard deviations.

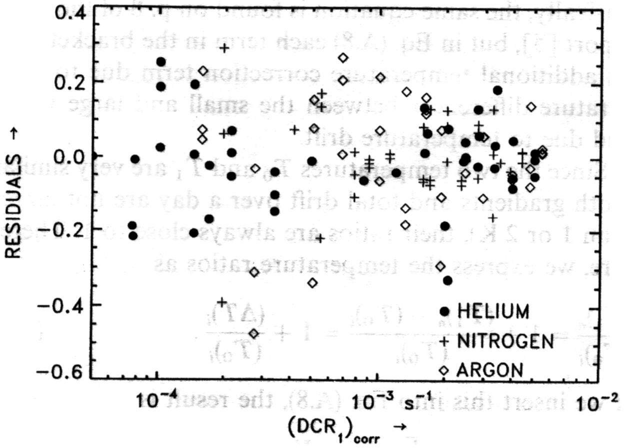

Fig. 4. Residuals of the measured and temperature-corrected DCR_1/DCR_2 ratios of Fig. 3 to the values predicted by the fit (Eq. (15)) in dependence of DCR_1. The Gaussian distribution indicates that the second-order polynomial is sufficient as fit curve.

(iii) The temperatures of the two vessels (see Eq. (6)) can be determined only with a standard uncertainty of about 0.1 K. This gives an additional relative uncertainty of 5×10^{-4} of f.

(iv) The uncertainties related to the offset determination have already been described in the previous sections. The importance of the uncertainty of the offset can also be seen from Fig. 4, where the residuals at lower DCR values (lower pressures) are clearly larger than at higher values. However, when there is no frequency dependence of the offset and no temperature drift on the rotor, the uncertainty of the offset determination is purely random and due to the evaluation (Eqs. (6) and (7)) procedure already considered in the standard deviation of the mean of $(DCR_1/DCR_2)_{\text{lin}}$ (Eq. (12)). Therefore, by fulfilling the requirements of temperature stability and frequency independence of the offset, the uncertainty can be strongly reduced by taking many data points.

(v) Other uncertainties resulting, for example, from deviations from the ideal gas law, gas impurities, leaks, adsorption on the walls of the chambers or outgassing could be neglected in the considered range of pressures. Also, since the fit curve is determined for each individual gas and measurement series, gas specific accommodation effects (e.g. a change of surface roughness of the rotor with gas and pressure) cannot falsify the results.

In summary, a total relative standard uncertainty of 5×10^{-4} and 1×10^{-3} for the results obtained with the SRG method at SE2, respectively, SE1 can be estimated. The differences of the results obtained with the different methods were considerably smaller, so that it can be concluded that the different methods are in full agreement. This holds true, even if it is considered that the temperature measurements in the gas accumulation and SRG method were highly correlated, as the same temperature sensors at the same positions were used.

Berman and Fremerey [6] have claimed a total relative standard uncertainty of 2×10^{-4} not discussing the influence of the accuracy of offset measurement and the influence of temperature gradients between the vessels. Their data show that similar differences occurred between the expansion ratios obtained with different gases or in different measurement series as in our results (cf. Eq. (15) and Table 5).

6. Conclusions

Measurements of the expansion ratio with the so called SRG method [6] were found to be in full agreement with the gas accumulation method [5] developed at NPL and the gravimetric method. In the SRG method, a single spinning rotor gauge is used to measure the pressures both before and after an expansion. In the gas accumulation method, two different gauges are being used to measure pressures before and after expansion, where expansions are repeated without intermediate pumping to obtain higher pressures which can accurately be measured.

In the SRG method, most accurate results can be achieved using a rotor with stable offset, where the offset should have no frequency dependence. In this case it is possible to determine the offset as variable in a fit function, when many data points over about two decades of pressure (0.3 Pa … 30 Pa) are taken. The higher pressure range is necessary to accurately fit the coefficients of first- and second-order of a second-order polynomial to the data points, the lower pressure range is required to accurately fit the offset and the pressure-independent fit variable of the polynomial.

Appendix

The NPL report [5] describing the gas accumulation method proposes an inaccurate correction for temperature drift. For the calculation of the correction term for drift, the report (p. 10) assumes that no temperature differences between the vessels exist initially and that after each expansion the vessels' temperatures are continuously changed by $\mathrm{d}T$. After the second expansion, approximately half of the mass of the gas (the amount injected during the first expansion), has changed its temperature by $\mathrm{d}T$ and the observed pressure shows a relative change of $\mathrm{d}T/2T$ as compared to constant temperature conditions. This is correct.

In the following, however, the report states that the pressure changes by $(n-1)\mathrm{d}T/2T$ after the nth expansion. According to this expression, the pressure changes by $\mathrm{d}T/T$ after the third expansion. What really happens, however, is that half of the mass of gas changes its temperature by $\mathrm{d}T$ between the 1st and 2nd expansion $\frac{2}{3}$

(not $\frac{1}{2}$) of the gas changes by an additional $\mathrm{d}T$ between the 2nd and 3rd expansion. This sums up to $\frac{1}{2}\cdot \mathrm{d}T/T + \frac{2}{3}\cdot \mathrm{d}T/T = \frac{7}{6}\,\mathrm{d}T/T$, which is different from $\mathrm{d}T/T$. The more expansions are done, the larger the error becomes.

In the following, we deduce a temperature correction which includes both gradients between vessels and drift:

As in the NPL report, we assume that the initial pressure p_0 is constant. After the first expansion we have

$$\frac{p_0 V_0}{(T_0)_1} = \frac{(p_1)_1 (V_1 + V_0)}{(T_1)_1}. \tag{A.1}$$

All quantities indexed with 0 refer to the initial small volume, all quantities indexed with 1 to the large volume.

$(T_0)_1$ denotes the temperature of the small vessel before expansion 1 when p_0 is determined, $(T_1)_1$ the temperature of the large vessel after the first expansion when p_1 is measured as $(p_1)_1$.

From Eq. (A.1) we find

$$(p_1)_1 = \frac{V_0}{V_0 + V_1}\left(\frac{T_1}{T_0}\right)_1 \tag{A.2}$$

The 2nd expansion results in:

$$\frac{p_0 V_0}{(T_0)_2} + \frac{(p_1)_1 V_1}{(T_1)_1} = \frac{(p_1)_2 (V_1 + V_0)}{(T_1)_2}. \tag{A.3}$$

Solving for $(p_1)_2$ we obtain

$$(p_1)_2 = p_0 \frac{V_0}{V_0 + V_1}\left(\frac{T_1}{T_0}\right)_2 + (p_1)_1 \frac{V_1}{V_0 + V_1}\frac{(T_1)_2}{(T_1)_1} \tag{A.4}$$

Insertion of Eq. (A.2) into Eq. (A.4) yields:

$$(p_1)_2 = p_0 \frac{V_0}{V_0 + V_1}\left[\left(\frac{T_1}{T_0}\right)_2 + \frac{V_1}{V_0 + V_1}\frac{(T_1)_2}{(T_0)_1}\right] \tag{A.5}$$

For the 3rd expansion we find

$$\frac{p_0 V_0}{(T_0)_3} + \frac{(p_1)_2 V_1}{(T_1)_2} = \frac{(p_1)_3 (V_1 + V_0)}{(T_1)_3}, \tag{A.6}$$

and if Eq. (A.5) is inserted becomes

$$(p_1)_3 = p_0 \frac{V_0}{V_0 + V_1}\left[\left(\frac{T_1}{T_0}\right)_3 + \frac{V_1}{V_0 + V_1}\frac{(T_1)_3}{(T_0)_2} + \left(\frac{V_1}{V_0 + V_1}\right)^2 \frac{(T_1)_3}{(T_0)_1}\right] \tag{A.7}$$

If this procedure is continued until the nth expansion, the result for $(p_1)_n$, the pressure in the large volume after the nth expansion is

$$(p_1)_n = p_0 \frac{V_0}{V_0 + V_1}\left[\left(\frac{T_1}{T_0}\right)_n + \frac{V_1}{V_0 + V_1}\frac{(T_1)_n}{(T_0)_{n-1}} + \left(\frac{V_1}{V_0 + V_1}\right)^2 \frac{(T_1)_n}{(T_0)_{n-2}} + \cdots + \left(\frac{V_1}{V_0 + V_1}\right)^{n-1} \frac{(T_1)_n}{(T_0)_1}\right] \tag{A.8}$$

Basically, the same equation is found on p. 8 of the NPL report [5], but in Eq. (A.8) each term in the brackets has an additional temperature correction term due to temperature differences between the small and large vessel and due to temperature drift.

Since the two temperatures T_0 and T_1 are very similar (both gradients and total drift over a day are not larger than 1 or 2 K), their ratios are always close to 1. Therefore, we express the temperature ratios as

$$\frac{(T_1)_n}{(T_0)_i} = 1 + \frac{(T_1)_n - (T_0)_i}{(T_0)_i} = 1 + \frac{(\Delta T)_i}{(T_0)_i}. \tag{A.9}$$

If we insert this into Eq. (A.8), the result is

$$(p_1)_n = p_0 \frac{V_0}{V_0 + V_1}\left[1 + \frac{V_1}{V_0 + V_1} + \left(\frac{V_1}{V_0 + V_1}\right) + \left(\frac{V_1}{V_0 + V_1}\right)^{n-1} + \alpha\right], \tag{A.10}$$

where $\alpha \ll 1$ is given by

$$\alpha = \left[\left(\frac{\Delta T}{T_0}\right)_n + \frac{V_1}{V_0 + V_1}\frac{(\Delta T)_n}{(T_0)_{n-1}} + \left(\frac{V_1}{V_0 + V_1}\right)^2 \frac{(\Delta T)_n}{(T_0)_{n-2}} + \cdots + \left(\frac{V_1}{V_0 + V_1}\right)^{n-1} \frac{(\Delta T)_n}{(T_0)_1}\right]. \tag{A.11}$$

Eq. (A.10) without the small term α was solved in the NPL report. To calculate the temperature-corrected volume ratio R or expansion ratio $f = R^{-1}$, we need a few more equations:

$$R = \frac{V_0 + V_1}{V_0} \qquad \frac{V_0}{V_0 + V_1} \tag{A.12}$$

$$\frac{V_1}{V_0 + V_1} = \quad - f \tag{A.13}$$

From Eq. (A.10) (and the geometric series):

$$\frac{(p_1)_n}{p_0} \quad \left(\frac{-(1-f)^n}{f} + \alpha \right) = \quad -(1-f)^n + f\alpha \tag{A.14}$$

or

$$f = \quad \left(+ f\alpha - \frac{(p_1)_n}{p_0} \right) \tag{A.15}$$

If $\alpha = 0$, this simplifies to

$$f = \quad \left(1 - \frac{(p_1)_n}{p_0} \right)^{1/n} \tag{A.16}$$

which is basically Eq. (1) for $R = f^{-1}$ on p. 8 of the NPL report.

The easiest way to solve Eq. (A.15) for f is to carry out the following algorithm:

Calculate f without the temperature correction term ($\alpha = 0$) according to Eq. (A.16).

Use this approximate value of f to calculate α according to Eqs. (A.11) and (A.13).

Insert α and the uncorrected f in the right-hand side of Eq. (A.15) to obtain the temperature-corrected f.

This procedure works well, because $f\alpha$ is much smaller than both 1 and the pressure ratio p_1/p_0 (α is typically of the order of 10^{-4} while p_1/p_0 is of the order of $0.01 \ldots 0.1$). The relative error due to this approximate algorithm is of the order of 10^{-8} for $\alpha = 1.3 \times 10^{-3}$ and $f = 10^{-2}$ and can therefore be neglected.

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