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Revised formula for the density of moist air (CIPM-2007)

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Abstract

Measurements of air density determined gravimetrically and by using the CIPM-81/91 formula, an equation of state, have a relative deviation of 6.4×10^{-5} .

This difference is consistent with a new determination of the mole fraction of argon x_{Ar} carried out in 2002 by the Korea Research Institute of Standards and Science (KRISS) and with recently published results from the LNE. The CIPM equation is based on the molar mass of dry air, which is dependent on the contents of the atmospheric gases, including the concentration of argon. We accept the new argon value as definitive and amend the CIPM-81/91 formula accordingly. The KRISS results also provide a test of certain assumptions concerning the mole fractions of oxygen and carbon dioxide in air. An updated value of the molar gas constant R is available and has been incorporated in the CIPM-2007 equation. In making these changes, we have also calculated the uncertainty of the CIPM-2007 equation itself in conformance with the *Guide to the Expression of Uncertainty in Measurement*, which was not the case for previous versions of this equation. The 96th CIPM meeting has accepted these changes.

1. Introduction

In the comparison in air of mass standards having different volumes, often the major component of uncertainty is the determination of the density of moist air (buoyancy correction) within the balance. The air density is commonly determined from the recommended equation of state [1,2]. The most recent of these [2] is known as the CIPM-81/91 equation because its use was endorsed by the International Committee for Weights and Measures (CIPM).

A second method developed and used only by a few laboratories is based on the difference in mass of two special artefacts [3–5] having the same nominal mass and surface area but very different volumes. The density of air is then determined gravimetrically by Archimedes' principle. This technique was perfected by Kobayashi *et al* [6] in the 1980s. In 1990, Gläser *et al* were the first to make a systematic comparison between measurements of air density as determined gravimetrically with the CIPM-81 equation of state [7]. Almost 15 years of measurements have now been carried out by four laboratories to compare air density as determined gravimetrically with the density derived from the CIPM-81/91

equation. Detailed results are presented in [8], including those of Euromet project 144 [9]. In typical laboratory atmospheres (air density approximately 1.2 kg m^{-3}), the averaged deviation of these measurements from the value of the CIPM-81/91 equation has a weighted mean of 6.4×10^{-5} with a standard uncertainty of 1.2×10^{-5} . Another independent study has recently confirmed these conclusions [10].

The CIPM-81 and -81/91 equations adopt the mole fraction of argon in air, x_{Ar} , equal to $9.17 \text{ mmol mol}^{-1}$, which was the most recent determination available (see historical section in [11]). However, this value was never adopted by atmospheric scientists, who generally have retained the value $9.34 \text{ mmol mol}^{-1}$ [12] reported in 1903 by Moissan [13]. One of us (RSD) observed that had Moissan's value been used in the CIPM-81/91 equation, then air densities determined by the CIPM formula would be shifted in relative terms by 7×10^{-5} , which has the effect of greatly reducing the difference mentioned above. Thus the choice of the mole fraction for argon that was adopted in 1981 became suspect.

A modern redetermination of the concentration of argon in air was called for by the Consultative Committee for Mass and Related Quantities (CCM) in May 2002. The Gas Analysis

Working Group (GAWG) of the Consultative Committee for Amount of Substance—Metrology in Chemistry (CCQM) were informed and the Korea Research Institute of Standards and Science (KRISS), a member of the GAWG, began in 2002 to make a new study of the mole fraction of argon in air. The value thus obtained by the KRISS [11] of the mole fraction of argon in dry air was $x_{\text{Ar}} = 9.332(3) \text{ mmol mol}^{-1}$, essentially confirming Moisson's value, but with full experimental details and a detailed uncertainty budget. Byproducts of the KRISS work were high-accuracy determinations of the mole fractions of oxygen and carbon dioxide from air sampled on two different continents. These have allowed us to sharpen our uncertainty analysis of the CIPM-2007 equation, as discussed in section 2.2.

The history of argon measurements suggested that a second, independent determination of the concentration of argon in air would be desirable to complement the KRISS result. This has now been provided by a team from the Laboratoire National de Métrologie et d'Essais (LNE, France) [14]. Their result is $x_{\text{Ar}} = 9.330(16) \text{ mmol mol}^{-1}$.

While the KRISS result is based on mass spectrometry, the LNE measurements are based on gas chromatography. In both cases, results are calibrated in terms of synthetic standards prepared gravimetrically. Each group prepared its own gravimetric standards.

In the CIPM-2007 equation derived below, we also include the value of the molar gas constant, R , recommended in CODATA 2006 [15].

We derive the CIPM-2007 equation in section 2.1. The uncertainty evaluation of the equation is presented in section 2.2. We have followed the *Guide to the Expression of Uncertainty in Measurement*, commonly referred to as the *GUM* [16]. We note that the CIPM-81 equation [1] predated the *GUM* and the report of the CIPM-81/91 equation [2] declined to update the uncertainty statements of [1]. In section 3 we compare the CIPM-2007 equation with its immediate predecessor and in section 4 we summarize the essential features and conclusions of this report.

2. The CIPM-2007 equation and its uncertainty

2.1. The CIPM-2007 equation

Formally, the derivation of the CIPM-2007 equation is the same as that of its predecessors [1, 2].

The density of moist air is evaluated using an equation of state

$$\rho_{\text{a}} = \frac{pM_{\text{a}}}{ZRT} \left[1 - x_{\text{v}} \left(1 - \frac{M_{\text{v}}}{M_{\text{a}}} \right) \right], \quad (1)$$

where the quantities and units are p/Pa : pressure, $t/^{\circ}\text{C}$: air temperature, T/K : thermodynamic temperature = $273.15 + t/^{\circ}\text{C}$, x_{v} : mole fraction of water vapour, $M_{\text{a}}/(\text{g mol}^{-1})$: molar mass of dry air, $M_{\text{v}}/(\text{g mol}^{-1})$: molar mass of water, Z : compressibility factor, $R/(\text{J mol}^{-1} \text{K}^{-1})$: molar gas constant.

For the CIPM-2007 formula, we take the value of R to be that recommended by CODATA 2006 [15]:

$$R/(\text{J mol}^{-1} \text{K}^{-1}) = 8.314472(15).$$

The molar mass of dry air is based on the mole fractions found in [12] with the following exceptions:

1. The mole fraction of atmospheric argon, x_{Ar} , is now based on the new results obtained by the KRISS [11] and the LNE, France [14]. A weighted average gives essentially the KRISS result. However, we are much more confident in this result thanks to work carried out at the LNE.

$$x_{\text{Ar}} = 9.332(3) \text{ mmol mol}^{-1}.$$

This new result is close to the value reported in 1903 [13]. However, the previous CIPM equations had assumed a mole fraction for argon of $9.17 \text{ mmol mol}^{-1}$, which in 1981 was thought to be the most reliable estimate [1].

The new value for the mole fraction of argon [11, 14] necessarily changes the accepted mole fraction for atmospheric nitrogen, x_{N_2} . The latter is not directly measured. It is simply determined as the remainder when the mole fractions of all other components of dry air have been subtracted from 1.

2. As in the previous CIPM formulas, the average mole fraction of carbon dioxide in laboratory air, x_{CO_2} , has a default value of 0.00040. The value of x_{CO_2} determines the mole fraction of atmospheric oxygen, x_{O_2} , from the relation

$$x_{\text{O}_2} + x_{\text{CO}_2} = 0.20979 \text{ mol mol}^{-1} = S. \quad (2)$$

Equation (2) assumes that processes of respiration, photosynthesis, combustion, etc are the only processes of importance. Possible inadequacies of this model are addressed in section 2.2.

3. The molar masses of the constituents of dry air are taken from the most recently available compilation of the International Union of Pure and Applied Chemistry [17].

The parameters taken for the CIPM-2007 equation are shown in table 1, which may be compared with table 1 of [1]. The molar masses of the minor constituents of air starting with CO_2 have been rounded for convenience.

As in the previous CIPM equations, the mole fraction of dry air is calculated by

$$M_{\text{a}} = \sum x_i M_i / \sum x_i. \quad (3)$$

The denominator on the right-hand side of (3) is necessary because

$$\sum x_i = 1 - 2.9 \times 10^{-6} \neq 1,$$

presumably due to minor rounding errors in [12]. The value for M_{a} obtained from (3) is

$$M_{\text{a}} = 28.96546 \times 10^{-3} \text{ kg mol}^{-1}.$$

If a measurement of x_{CO_2} is available, then (2) should be used to improve the estimate of the molar mass of dry air:

$$M_{\text{a}} = [28.96546 + 12.011 \cdot (x_{\text{CO}_2} - 0.0004)] \cdot 10^{-3} \text{ kg mol}^{-1}. \quad (4)$$

Table 1. Composition of dry air taken as reference for the air density evaluation.

Constituent	Molar mass $M_i/(10^{-3} \text{ kg mol}^{-1})$	Mole fraction x_i	Contribution $x_i \cdot M_i/(10^{-3} \text{ kg mol}^{-1})$
N ₂	28.0134	0.780 848	21.874 207
O ₂	31.9988	0.209 390	6.700 229
Ar	39.948	0.009 332	0.372 795
CO ₂	44.01	0.000 40	0.017 604
Ne	20.18	18.2×10^{-6}	0.000 367
He	4.0	5.2×10^{-6}	0.000 021
CH ₄	16.0	1.5×10^{-6}	0.000 024
Kr	83.8	1.1×10^{-6}	0.000 092
H ₂	2	0.5×10^{-6}	0.000 001
N ₂ O	44	0.3×10^{-6}	0.000 013
CO	28	0.2×10^{-6}	0.000 006
Xe	131	0.1×10^{-6}	0.000 013

If not measured, one normally assumes a background of $400 \mu\text{mol mol}^{-1}$ for the mole fraction of carbon dioxide in air; but see section 2.2 for cautionary statements concerning this assumption.

The molar mass of moist air includes the amount fraction of water vapour x_v , reducing all other amount fractions proportionately so that the sum is still one and thereby arriving at (1).

Since

$$1 - M_v/M_a = 0.3780,$$

where $M_v/(10^{-3} \text{ kg mol}^{-1}) = 18.015 28(17)$ [17]⁴, then

$$\rho_a/(10^{-3} \text{ kg m}^{-3}) = \frac{[28.965 46 + 12.011 \cdot (x_{\text{CO}_2} - 0.0004)]}{8.314 472} \cdot \frac{P}{ZT} (1 - 0.3780x_v), \quad (5a)$$

$$\rho_a/(10^{-3} \text{ kg m}^{-3}) = [3.483 740 + 1.4446 \cdot (x_{\text{CO}_2} - 0.0004)] \cdot \frac{P}{ZT} (1 - 0.3780x_v). \quad (5b)$$

The quantity x_v is not measured directly but is determined either from the relative humidity h or from the temperature t_d of the dew point; Z is determined from an additional interpolating equation. Complete equations for calculating x_v and Z are given in appendix A.

2.2. Uncertainty of the CIPM-2007 equation

Knowledge of the air density is limited by the uncertainty of the formula itself, which was evaluated by several members of the working group involved in drafting the 1981 equation [1]. In particular Jones [18], Carré [19] and Riéty [20] carried out independent evaluations of the uncertainty due to the equation. We have returned to these references in order to update the uncertainty evaluation of the present equation in the light of new results and current best practice.

⁴ There is a small difference between the molar mass calculated from [17] and that of atmospheric water vapour. In very humid air, we estimate that this difference might lead to a relative systematic offset of order 1×10^{-6} in the calculated air density, and is thus negligible.

Table 2 summarizes the uncertainty evaluation of the air density formula itself exclusive of the measured input parameters: pressure, temperature and dew-point temperature (or relative humidity). Table 2 also assumes that x_{CO_2} is known exactly; there is no requirement that $x_{\text{CO}_2} = 400 \mu\text{mol mol}^{-1}$. Note that the uncertainty budget presented in table 2 takes into account the possibility that, for short periods of time, x_{O_2} might not be perfectly anticorrelated with x_{CO_2} . Rather, each may have some temporary variability not accounted for by (2). Looking at (2), we therefore address three components of uncertainty:

1. The value chosen for S . We assume that S is constant in time. We assign a standard uncertainty $u(S)$ to the value of S that has been adopted in the CIPM-2007 equation.
2. A contribution Δx_{O_2} to x_{O_2} that is not correlated with x_{CO_2} and, therefore, not accounted for by (2). We refer to the standard uncertainty of this component as $u(\Delta x_{\text{O}_2})$ and assume that the long-term average of Δx_{O_2} is zero.
3. A contribution Δx_{CO_2} to x_{CO_2} that is not correlated with correct value of x_{O_2} . Therefore, although x_{CO_2} is known, the calculation of x_{O_2} by means of (2) introduces an error. We assume that the long-term average of Δx_{CO_2} is zero, with a standard uncertainty of $u(\Delta x_{\text{CO}_2})$.

Appendix B shows how these uncertainty components are treated.

We have evaluated these uncertainties from the measurements of x_{O_2} and x_{CO_2} that are reported in [11] on air sampled near sea level from an island in Korea and a measurement on air sampled from a mountain ridge in the United States. Thus, the uncertainty components $u(\Delta x_{\text{O}_2})$ and $u(\Delta x_{\text{CO}_2})$ are based on a limited data set.

As mentioned above, we have followed the *GUM*, whose recommendations were, for the most part, anticipated in [19].

Appendix A shows how to calculate the parameters Z and f and p_{sv} (these are necessary intermediate steps for the determination of x_v). The uncertainty contributions from f , the enhancement factor, and p_{sv} , the vapour pressure of saturated air, are negligible [21]. The compressibility factor Z is derived from the virial coefficients of moist air [18, 21–23]. Hyland and Wexler [21] have provided ‘Estimated Maximum Uncertainties’ (EMU) for their results. Since EMU is not

Table 2. Uncertainty budget for the CIPM-2007 equation when the mole fraction of CO₂ has been assumed to be exactly 400 μmol mol⁻¹.

Parameter	Reference	Standard uncertainty/10 ⁻⁶	Relative contribution	Relative contribution ($u(\rho_a)/\rho_a$)/10 ⁻⁶	
				Type B	Type A
$R/(\text{J mol}^{-1} \text{K}^{-1})$	[15]	15	$u(R)/R$	1.7	0
$M_{\text{N}_2}/(\text{g mol}^{-1})$	[17]	200	$x_{\text{N}_2} \cdot u(M_{\text{N}_2})/M_a$	5.4	0
$M_{\text{O}_2}/(\text{g mol}^{-1})$	[17]	300	$x_{\text{O}_2} \cdot u(M_{\text{O}_2})/M_a$	2.2	0
$M_{\text{Ar}}/(\text{g mol}^{-1})$	[17]	500	$x_{\text{Ar}} \cdot u(M_{\text{Ar}})/M_a$	0.2	0
$M_{\text{CO}_2}/(\text{g mol}^{-1})$	[17]	500	$x_{\text{CO}_2} \cdot u(M_{\text{CO}_2})/M_a$	0.0	0
x_{Ar}	[11, 14]	3	$(M_{\text{Ar}} - M_{\text{N}_2})u(x_{\text{Ar}})/M_a$	1.2	0
$S = x_{\text{O}_2} + x_{\text{CO}_2}$	[11, *]	60	$(M_{\text{O}_2} - M_{\text{N}_2})u(x_S)/M_a$	8.3	0
Δx_{O_2}	[11, 20, *]	60	$(M_{\text{O}_2} - M_{\text{N}_2})u(\Delta x_{\text{O}_2})/M_a$	0	8.3
Δx_{CO_2}	[11, *]	60	$(M_{\text{O}_2} - M_{\text{N}_2})u(\Delta x_{\text{CO}_2})/M_a$	0	8.3
Z	[18, 20, *]	15	Depends on t, p, x_v	15	0
			Quadratic sum	18.2	11.7
			Combined standard uncertainty ($u(\rho_a)/\rho_a$)/10 ⁻⁶	22	

* This paper.

further defined, we believe it prudent to treat it as a standard uncertainty and to treat the virial coefficients themselves as highly correlated. So far the largest uncertainty contribution to Z comes from the second virial coefficient for dry air. The second cross-virial coefficient is the only additional term that makes a significant contribution to the uncertainty of Z . In this regard, we note that the new first-principles calculation of the second cross-virial coefficient [23] is consistent with previous experimental work over the temperature range considered here. The uncertainty of Z was evaluated by Jones to be 17×10^{-6} , based on a 1975 paper by Hyland [18].

Of course there are additional instrumental uncertainties due to the measured input pressure, p , temperature, T , and dew-point temperature, t_d (or relative humidity, h) and mole fraction of carbon dioxide, x_{CO_2} . These must be added in quadrature by users of the CIPM-2007 equation. The appropriate influence factors are as follows:

$$\begin{aligned} \frac{u_p(\rho_a)}{\rho_a} &= \frac{1}{\rho_a} \left(\frac{\partial \rho_a}{\partial p} \right) \cdot u(p) \approx +1 \times 10^{-5} \text{ Pa}^{-1} \cdot u(p), \\ \frac{u_T(\rho_a)}{\rho_a} &\approx -4 \times 10^{-3} \text{ K}^{-1} \cdot u(T), \\ \frac{u_h(\rho_a)}{\rho_a} &\approx -9 \times 10^{-3} \cdot u(h), \\ \frac{u_{t_d}(\rho_a)}{\rho_a} &\approx -3 \times 10^{-4} \text{ K}^{-1} \cdot u(t_d), \\ \frac{u_{x_{\text{CO}_2}}(\rho_a)}{\rho_a} &\approx +0.4 \cdot u(x_{\text{CO}_2}). \end{aligned} \quad (6)$$

A measurement of either h or t_d is required in order to determine x_v , as shown in appendix A. As noted in this appendix, $0 \leq h \leq 1$.

If x_{CO_2} is not measured, but assumed to be 400 μmol mol⁻¹ instead, then $u(x_{\text{CO}_2})$ must be considered with care. This is because it is well known from studies such as Euromet Project 503 [24] that the ambient value of x_{CO_2} varies greatly between laboratories and, in many cases, at different times within the same laboratory. Reference [24] includes data from 11 national metrology institutes and the BIPM.

The average mole fraction of carbon dioxide among the participants was 440 μmol mol⁻¹. However, the average of the maximum values recorded by the 12 participants was 660 μmol mol⁻¹, with some laboratories recording maximum results of 1000 μmol mol⁻¹. An uncertainty component based on (6) should be added to account for known or suspected variability about a reference value for x_{CO_2} .

Note that the coefficient 0.3780 in (5a) and (5b) is treated as a constant. However, (1) shows that the coefficient actually depends on the value of M_a , which is a weak function of x_{CO_2} . An extreme example within the pressure and temperature limits of the CIPM-2007 equation (see appendix A) is $x_{\text{CO}_2} = 0.001$, $p = 600$ hPa, $t = 27^\circ\text{C}$ and $x_v = 0.06$ (100% relative humidity). In this case, the relative error in ρ_a as calculated from (5b) is 9×10^{-6} , which is of the same order as the combined relative uncertainty shown in table 2. Rather than complicate (5b), we simply point out

- The air density ρ_a derived from (5b) is missing an additive term that is approximately equal to $0.26\rho_a x_v(0.0004 - x_{\text{CO}_2})$.
- In a metrology laboratory, the missing term will always be negligible with respect to the combined uncertainty given in table 2.

3. Comparison with the CIPM-81/91 equation

We recall that the CIPM-81/91 equation is [2]

$$\rho_a / (10^{-3} \text{ kg m}^{-3}) = [3.48349 + 1.4446 \cdot (x_{\text{CO}_2} - 0.0004)] \cdot \frac{p}{ZT} (1 - 0.3780x_v). \quad (\text{CIPM-81/91})$$

We may now compare this with (5b), which is the CIPM-2007 equation written in similar form. We first remark that the calculation of Z and x_v is virtually identical for the two equations (see appendix A). Thus the only difference is in the first term, which for the CIPM-2007 equation is increased to 3.483740. This obviously leads to a relative increase of 72×10^{-6} in the calculation of ρ_a . The relative increase is a consequence of new values for x_{Ar} ($+67.7 \times 10^{-6}$) and R ($+4.6 \times 10^{-6}$).

In addition, the uncertainty estimate for the CIPM-2007 equation has been established in conformance with [14], whereas the uncertainty statements in [1, 2] are ambiguous.

4. Discussion and conclusion

Based on the considerations given above, the International Committee for Weights and Measures (CIPM) at its 96th meeting (November 2007) approved an updated formula for the density of moist air, to be known as the CIPM-2007 equation of state for moist air. The CIPM-2007 equation has the following properties:

1. The functional form of all the equations given in previous CIPM equations [1, 2] is unchanged.
2. Some constant parameters used in [1, 2] are amended as follows:

- The value of R is the value recommended by CODATA 2006 [15]:

$$R = 8.314472(15) \text{ J mol}^{-1} \text{ K}^{-1}.$$

- The mole fraction of argon is the value determined in 2002 by the KRISS and in 2006 by the LNE [11, 14]:

$$x_{\text{Ar}} = 9.332(3) \text{ mmol mol}^{-1}.$$

3. The calculation of the uncertainty of the CIPM-2007 equation follows the rules set out in the *GUM* [16].
4. The input parameters to the CIPM-2007 equation are pressure, temperature, relative humidity or dew-point temperature and carbon dioxide fraction. As with both previous CIPM equations, the uncertainties of these parameters must be taken into account according to the sensitivity factors given in (6).
5. If the mole fraction of carbon dioxide in air, x_{CO_2} , is not measured but instead is assumed to be equal to $400 \mu\text{mol mol}^{-1}$ (or any other reference value), an uncertainty component must be added to account for this assumption. The sensitivity factor is shown in (6). The average mole fraction of carbon dioxide and its dispersion within a laboratory may vary greatly from the assumed value. It is therefore advisable for users of the CIPM-2007 equation to base their assumed value for the average mole fraction of carbon dioxide and its dispersion on a survey of the laboratory.
6. Since a significant difference does not exist between measurements of air density as determined gravimetrically by the use of artefacts and proper use of the CIPM-2007 formula, either method can be employed as long as proper account is taken of the uncertainty.

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new argon work. They also acknowledge the valuable advice of Dr A H Harvey (NIST).

Appendix A. Calculation of x_v and Z ; ranges of applicability

Appendix A.1. Calculation of x_v from the measurement of relative humidity or dew-point temperature

The following equations are used to determine x_v from the relative humidity or the dew-point temperature of air [2]. The equations and their constants are unchanged from the CIPM-81/91 equation but are listed here for completeness. Determination of the vapour pressure at saturation, p_{sv} , and the so-called enhancement factor are preliminary steps.

Vapour pressure at saturation, p_{sv} :

$$p_{\text{sv}} = 1 \text{ Pa} \times \exp(AT^2 + BT + C + D/T), \quad (\text{A1.1})$$

with

$$A = 1.2378847 \times 10^{-5} \text{ K}^{-2},$$

$$B = -1.9121316 \times 10^{-2} \text{ K}^{-1},$$

$$C = 33.93711047,$$

$$D = -6.3431645 \times 10^3 \text{ K}.$$

Enhancement factor f :

$$f = \alpha + \beta p + \gamma t^2, \quad (\text{A1.2})$$

with

$$\alpha = 1.00062,$$

$$\beta = 3.14 \times 10^{-8} \text{ Pa}^{-1},$$

$$\gamma = 5.6 \times 10^{-7} \text{ K}^{-2},$$

where t is the temperature in °C.

Using these values,

$$x_v = hf(p, t) \cdot \frac{p_{\text{sv}}(t)}{p} = f(p, t_d) \cdot \frac{p_{\text{sv}}(t_d)}{p}, \quad (\text{A1.3})$$

where h is the relative humidity and t_d is the dew-point temperature. Therefore, either h or t_d can be measured in order to determine x_v . The parameter h has the following range: $0 \leq h \leq 1$. For example, an instrumental relative humidity reading of '53%' is expressed as $h = 0.53$.

Appendix A.2. Calculation of the compressibility factor, Z

The equations for Z and its constants are unchanged from the CIPM-81/91 equation but are listed here for completeness.

$$Z = 1 - \frac{p}{T} \cdot [a_0 + a_1 t + a_2 t^2 + (b_0 + b_1 t)x_v + (c_0 + c_1 t)x_v^2] + \frac{p^2}{T^2} \cdot (d + ex_v^2), \quad (\text{A1.4})$$

where

$$\begin{aligned} a_0 &= 1.581\,23 \times 10^{-6} \text{ K Pa}^{-1}, \\ a_1 &= -2.9331 \times 10^{-8} \text{ Pa}^{-1}, \\ a_2 &= 1.1043 \times 10^{-10} \text{ K}^{-1} \text{ Pa}^{-1}, \\ b_0 &= 5.707 \times 10^{-6} \text{ K Pa}^{-1}, \\ b_1 &= -2.051 \times 10^{-8} \text{ Pa}^{-1}, \\ c_0 &= 1.9898 \times 10^{-4} \text{ K Pa}^{-1}, \\ c_1 &= -2.376 \times 10^{-6} \text{ Pa}^{-1}, \\ d &= 1.83 \times 10^{-11} \text{ K}^2 \text{ Pa}^{-2}, \\ e &= -0.765 \times 10^{-8} \text{ K}^2 \text{ Pa}^{-2}. \end{aligned}$$

Appendix A.3. Appropriate ranges for calculations of p_{sv} and Z

Equations (A1.1) and (A1.4) are interpolating formulas that are valid only for limited ranges of pressure and temperature. These ranges determine the region of validity of the CIPM-2007 equation and its predecessors.

The recommended ranges of temperature and pressure over which the CIPM-2007 equation may be used are unchanged from the original CIPM-81 version [1] and are repeated here for completeness:

$$\begin{aligned} 600 \text{ hPa} &\leq p \leq 1100 \text{ hPa}, \\ 15^\circ \text{C} &\leq t \leq 27^\circ \text{C}. \end{aligned}$$

The second cross-virial coefficient derived in [23] from first principles is consistent with previous experimental results over our recommended temperature range. We note that this temperature range is slightly below the range of data covered in [22]. The uncertainty of the second virial coefficient of water vapour has therefore been increased accordingly. However, as noted above, this coefficient has negligible influence on the value of Z .

Appendix B. Uncertainty components for the mole fractions of carbon dioxide and oxygen

The CIPM-2007 equation assumes that the value of x_{CO_2} is measured or estimated. The equation then infers the value of x_{O_2} to be

$$x_{\text{O}_2} = S - x_{\text{CO}_2}. \quad (\text{A2.1})$$

This model is incomplete if

- x_{CO_2} contains a component Δx_{CO_2} that is not correlated with x_{O_2} or if
- x_{O_2} contains a component Δx_{O_2} that is not correlated with x_{CO_2} .

Thus the exact model is

$$(x_{\text{O}_2} - \Delta x_{\text{O}_2}) + (x_{\text{CO}_2} - \Delta x_{\text{CO}_2}) = S, \quad (\text{A2.2})$$

or

$$x_{\text{O}_2} = (S + \Delta x_{\text{CO}_2} + \Delta x_{\text{O}_2}) - x_{\text{CO}_2}. \quad (\text{A2.3})$$

The additional terms, Δx_{CO_2} and Δx_{O_2} , are each considered to be zero on average. Therefore, the model given in (2) and (A2.1) is still correct for a long-term average. The estimates of the four quantities on the right-hand side of (A2.3) are assumed to be uncorrelated.

To our knowledge, there are no modern data to show that the additional terms must be considered. However, we accept the possibility and estimate the uncertainty of these terms to be consistent with the uncertainty of the data presented in [11]. Although [11] analyses only two air samples, these were selected from different continents and different elevations. Each of the two determinations $x_{\text{O}_2} + x_{\text{CO}_2}$ has an estimated standard uncertainty of $60 \mu\text{mol mol}^{-1}$. Each determination is within $50 \mu\text{mol mol}^{-1}$ of the accepted value for S [1, 2]. Thus for the CIPM-2007 equation we accept the value of S given in [1, 2] and take its standard uncertainty to be $60 \mu\text{mol mol}^{-1}$, which confirms the previous estimate (e.g. [19]) with recent data. Considering the limited data set in [11], we have taken $u(\Delta x_{\text{O}_2})$ and $u(\Delta x_{\text{CO}_2})$ to be $60 \mu\text{mol mol}^{-1}$, each, although there is no compelling evidence to do so. Two of the supporting documents [19, 20] of [1] estimated $u(\Delta x_{\text{O}_2})$ as $170 \mu\text{mol mol}^{-1}$, relying on unconfirmed data published in the 19th century. Although we believe that the previous uncertainty estimate was too pessimistic, we are nevertheless reluctant to ignore this component entirely until such time as a more systematic study of this question becomes available.

The uncertainty components $u(S)$, $u(\Delta x_{\text{CO}_2})$ and $u(\Delta x_{\text{O}_2})$ have been included in table 2. The uncertainty component $u(x_{\text{CO}_2})$, which is due to the measurement or estimate of x_{CO_2} each time that the CIPM-2007 equation is used, is treated separately in (6). Based on the model equation (A2.3), the sensitivity factors for each of these uncertainties are derived in the usual way [16], starting with (3).

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