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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 $6.4 \times 10^{-5}$.

This difference is consistent with a new determination of the mole fraction of argon $x_{\mathrm{Ar}}$ 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 $1.2\,\mathrm{kg\,m^{-3}}$), the averaged deviation of these measurements from the value of the CIPM-81/91 equation has a weighted mean of $6.4 \times 10^{-5}$ with a standard uncertainty of $1.2 \times 10^{-5}$. Another independent study has recently confirmed these conclusions [10].

The CIPM-81 and -81/91 equations adopt the mole fraction of argon in air, $x_{\mathrm{Ar}}$, equal to $9.17\,\mathrm{mmol\,mol^{-1}}$, 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 $9.34\,\mathrm{mmol\,mol^{-1}}$ [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 $7 \times 10^{-5}$, 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 $x_{\mathrm{Ar}} = 9.332(3)\ \mathrm{mmol\ mol^{-1}}$, 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 $x_{\mathrm{Ar}} = 9.330(16)\ \mathrm{mmol\ mol^{-1}}$.

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

$$\rho_{\mathrm{a}} = \frac{pM_{\mathrm{a}}}{ZRT}\left[1 - x_v\left(1 - \frac{M_v}{M_{\mathrm{a}}}\right)\right], \qquad (1)$$

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

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

$$R/(\mathrm{J\ mol^{-1}\ K^{-1}}) = 8.314\,472(15).$$

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, $x_{\mathrm{Ar}}$, 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.

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

   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 $9.17\ \mathrm{mmol\ mol^{-1}}$, 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, $x_{\mathrm{N_2}}$. 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, $x_{\mathrm{CO_2}}$, has a default value of 0.000 40. The value of $x_{\mathrm{CO_2}}$ determines the mole fraction of atmospheric oxygen, $x_{\mathrm{CO_2}}$, from the relation

   $$x_{\mathrm{O_2}} + x_{\mathrm{CO_2}} = 0.209\,79\ \mathrm{mol\ mol^{-1}} = S. \qquad (2)$$

   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 $\mathrm{CO_2}$ have been rounded for convenience.

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

$$M_{\mathrm{a}} = \sum x_i M_i \Big/ \sum x_i. \qquad (3)$$

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 $M_{\mathrm{a}}$ obtained from (3) is

$$M_{\mathrm{a}} = 28.965\,46 \times 10^{-3}\ \mathrm{kg\ mol^{-1}}.$$

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

$$M_{\mathrm{a}} = [28.965\,46 + 12.011 \cdot (x_{\mathrm{CO_2}} - 0.0004)] \cdot 10^{-3}\ \mathrm{kg\ mol^{-1}}. \qquad (4)$$

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

| Constituent | Molar mass $M_i/(10^{-3}\,\mathrm{kg\,mol^{-1}})$ | Mole fraction $x_i$ | Contribution $x_i \cdot M_i/(10^{-3}\,\mathrm{kg\,mol^{-1}})$ |
|---|---|---|---|
| $N_2$ | 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 | $18.2 \times 10^{-6}$ | 0.000 367 |
| He | 4.0 | $5.2 \times 10^{-6}$ | 0.000 021 |
| $CH_4$ | 16.0 | $1.5 \times 10^{-6}$ | 0.000 024 |
| Kr | 83.8 | $1.1 \times 10^{-6}$ | 0.000 092 |
| $H_2$ | 2 | $0.5 \times 10^{-6}$ | 0.000 001 |
| $N_2O$ | 44 | $0.3 \times 10^{-6}$ | 0.000 013 |
| CO | 28 | $0.2 \times 10^{-6}$ | 0.000 006 |
| Xe | 131 | $0.1 \times 10^{-6}$ | 0.000 013 |

If not measured, one normally assumes a background of $400\,\mu\mathrm{mol\,mol^{-1}}$ 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 $M_v/(10^{-3}\,\mathrm{kg\,mol^{-1}}) = 18.015\,28(17)$ [17][4], then

$$\rho_a/(10^{-3}\mathrm{kg\,m^{-3}}) = \frac{[28.965\,46 + 12.011 \cdot (x_{CO_2} - 0.0004)]}{8.314\,472} \cdot \frac{p}{ZT}(1 - 0.3780 x_v), \qquad (5a)$$

$$\rho_a/(10^{-3}\mathrm{kg\,m^{-3}}) = [3.483\,740 + 1.4446 \cdot (x_{CO_2} - 0.0004)] \cdot \frac{p}{ZT}(1 - 0.3780 x_v). \qquad (5b)$$

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.

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 $x_{CO_2} = 400\,\mu\mathrm{mol\,mol^{-1}}$. 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 $\Delta x_{O_2}$ 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 $u(\Delta x_{O_2})$ and assume that the long-term average of $\Delta x_{O_2}$ is zero.
3. A contribution $\Delta x_{CO_2}$ 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 $\Delta x_{CO_2}$ is zero, with a standard uncertainty of $u(\Delta x_{CO_2})$.

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 $u(\Delta x_{O_2})$ and $u(\Delta x_{CO_2})$ 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

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[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 $1 \times 10^{-6}$ in the calculated air density, and is thus negligible.

**Table 2.** Uncertainty budget for the CIPM-2007 equation when the mole fraction of $CO_2$ has been assumed to be exactly 400 $\mu$mol mol$^{-1}$.

| Parameter | Reference | Standard uncertainty/$10^{-6}$ | Relative contribution | Relative contribution $(u(\rho_a)/\rho_a)/10^{-6}$ Type B | Type A |
|---|---|---|---|---|---|
| $R/(\mathrm{J\,mol^{-1}\,K^{-1}})$ | [15] | 15 | $u(R)/R$ | 1.7 | 0 |
| $M_{N_2}/(\mathrm{g\,mol^{-1}})$ | [17] | 200 | $x_{N_2}\cdot u(M_{N_2})/M_a$ | 5.4 | 0 |
| $M_{O_2}/(\mathrm{g\,mol^{-1}})$ | [17] | 300 | $x_{O_2}\cdot u(M_{O_2})/M_a$ | 2.2 | 0 |
| $M_{Ar}/(\mathrm{g\,mol^{-1}})$ | [17] | 500 | $x_{Ar}\cdot u(M_{Ar})/M_a$ | 0.2 | 0 |
| $M_{CO_2}/(\mathrm{g\,mol^{-1}})$ | [17] | 500 | $x_{CO_2}\cdot u(M_{CO_2})/M_a$ | 0.0 | 0 |
| $x_{Ar}$ | [11, 14] | 3 | $(M_{Ar}-M_{N_2})u(x_{Ar})/M_a$ | 1.2 | 0 |
| $S = x_{O_2} + x_{CO_2}$ | [11, ∗] | 60 | $(M_{O_2}-M_{N_2})u(x_S)/M_a$ | 8.3 | 0 |
| $\Delta x_{O_2}$ | [11, 20, ∗] | 60 | $(M_{O_2}-M_{N_2})u(\Delta x_{O_2})/M_a$ | 0 | 8.3 |
| $\Delta x_{CO_2}$ | [11, ∗] | 60 | $(M_{O_2}-M_{N_2})u(\Delta x_{CO_2})/M_a$ | 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 $17 \times 10^{-6}$, 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:

$$\frac{u_p(\rho_a)}{\rho_a} = \frac{1}{\rho_a}\left(\frac{\partial \rho_a}{\partial p}\right)\cdot u(p) \approx +1\times 10^{-5}\,\mathrm{Pa^{-1}}\cdot u(p),$$

$$\frac{u_T(\rho_a)}{\rho_a} \approx -4\times 10^{-3}\,\mathrm{K^{-1}}\cdot u(T),$$

$$\frac{u_h(\rho_a)}{\rho_a} \approx -9\times 10^{-3}\cdot u(h),$$

$$\frac{u_{t_d}(\rho_a)}{\rho_a} \approx -3\times 10^{-4}\,\mathrm{K^{-1}}\cdot u(t_d),$$

$$\frac{u_{x_{CO_2}}(\rho_a)}{\rho_a} \approx +0.4\cdot u(x_{CO_2}). \tag{6}$$

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, $0 \leqslant h \leqslant 1$.

If $x_{CO_2}$ is not measured, but assumed to be 400 µmol mol$^{-1}$ instead, then $u(x_{CO_2})$ 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 (5*a*) and (5*b*) 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 $x_{CO_2} = 0.001$, $p = 600$ hPa, $t = 27\,°\mathrm{C}$ and $x_v = 0.06$ (100% relative humidity). In this case, the relative error in $\rho_a$ as calculated from (5*b*) is $9 \times 10^{-6}$, which is of the same order as the combined relative uncertainty shown in table 2. Rather than complicate (5*b*), we simply point out

- The air density $\rho_a$ derived from (5*b*) is missing an additive term that is approximately equal to $0.26\rho_a x_v(0.0004 - x_{CO_2})$.
- 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]

$$\rho_a/(10^{-3}\,\mathrm{kg\,m^{-3}}) = [3.483\,49 + 1.4446\cdot(x_{CO_2} - 0.0004)] \cdot\frac{p}{ZT}(1 - 0.3780x_v). \qquad \text{(CIPM-81/91)}$$

We may now compare this with (5*b*), 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 3.483 740. This obviously leads to a relative increase of $72 \times 10^{-6}$ in the calculation of $\rho_a$. 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]:

     $$R = 8.314\,472(15)\ \mathrm{J\,mol^{-1}\,K^{-1}}.$$

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

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

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, $x_{\mathrm{CO_2}}$, is not measured but instead is assumed to be equal to 400 µmol 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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## Appendix A. Calculation of $x_{\mathrm{v}}$ and $Z$; ranges of applicability

### *Appendix A.1. Calculation of $x_{\mathrm{v}}$ from the measurement of relative humidity or dew-point temperature*

The following equations are used to determine $x_{\mathrm{v}}$ 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, $p_{\mathrm{sv}}$, and the so-called enhancement factor are preliminary steps.

Vapour pressure at saturation, $p_{\mathrm{sv}}$:

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

with

$$A = 1.237\,884\,7 \times 10^{-5}\ \mathrm{K^{-2}},$$

$$B = -1.912\,131\,6 \times 10^{-2}\ \mathrm{K^{-1}},$$

$$C = 33.937\,110\,47,$$

$$D = -6.343\,164\,5 \times 10^{3}\ \mathrm{K}.$$

Enhancement factor $f$:

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

with

$$\alpha = 1.000\,62,$$

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

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

where $t$ is the temperature in °C.

Using these values,

$$x_{\mathrm{v}} = hf(p,t)\cdot\frac{p_{\mathrm{sv}}(t)}{p} = f(p,t_{\mathrm{d}})\cdot\frac{p_{\mathrm{sv}}(t_{\mathrm{d}})}{p}, \qquad \text{(A1.3)}$$

where $h$ is the relative humidity and $t_{\mathrm{d}}$ is the dew-point temperature. Therefore, either $h$ or $t_{\mathrm{d}}$ can be measured in order to determine $x_{\mathrm{v}}$. The parameter $h$ has the following range: $0 \leqslant h \leqslant 1$. 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.

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

where

$$a_0 = 1.581\,23 \times 10^{-6}\,\mathrm{K\,Pa^{-1}},$$

$$a_1 = -2.9331 \times 10^{-8}\,\mathrm{Pa^{-1}},$$

$$a_2 = 1.1043 \times 10^{-10}\,\mathrm{K^{-1}\,Pa^{-1}},$$

$$b_0 = 5.707 \times 10^{-6}\,\mathrm{K\,Pa^{-1}},$$

$$b_1 = -2.051 \times 10^{-8}\,\mathrm{Pa^{-1}},$$

$$c_0 = 1.9898 \times 10^{-4}\,\mathrm{K\,Pa^{-1}},$$

$$c_1 = -2.376 \times 10^{-6}\,\mathrm{Pa^{-1}},$$

$$d = 1.83 \times 10^{-11}\,\mathrm{K^2\,Pa^{-2}},$$

$$e = -0.765 \times 10^{-8}\,\mathrm{K^2\,Pa^{-2}}.$$

### *Appendix A.3. Appropriate ranges for calculations of $p_{\mathrm{sv}}$ 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:

$$600\,\mathrm{hPa} \leqslant p \leqslant 1100\,\mathrm{hPa},$$

$$15\,^\circ\mathrm{C} \leqslant t \leqslant 27\,^\circ\mathrm{C}.$$

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 $x_{\mathrm{CO_2}}$ is measured or estimated. The equation then infers the value of $x_{\mathrm{O_2}}$ to be

$$x_{\mathrm{O_2}} = S - x_{\mathrm{CO_2}}. \tag{A2.1}$$

This model is incomplete if

- $x_{\mathrm{CO_2}}$ contains a component $\Delta x_{\mathrm{CO_2}}$ that is not correlated with $x_{\mathrm{O_2}}$
  or if
- $x_{\mathrm{O_2}}$ contains a component $\Delta x_{\mathrm{O_2}}$ that is not correlated with $x_{\mathrm{CO_2}}$.

Thus the exact model is

$$(x_{\mathrm{O_2}} - \Delta x_{\mathrm{O_2}}) + (x_{\mathrm{CO_2}} - \Delta x_{\mathrm{CO_2}}) = S, \tag{A2.2}$$

or

$$x_{\mathrm{O_2}} = (S + \Delta x_{\mathrm{CO_2}} + \Delta x_{\mathrm{O_2}}) - x_{\mathrm{CO_2}}. \tag{A2.3}$$

The additional terms, $\Delta x_{\mathrm{CO_2}}$ and $\Delta x_{\mathrm{O_2}}$, 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 $x_{\mathrm{O_2}} + x_{\mathrm{CO_2}}$ has an estimated standard uncertainty of 60 µmol mol$^{-1}$. Each determination is within 50 µmol 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 µmol mol$^{-1}$, which confirms the previous estimate (e.g. [19]) with recent data. Considering the limited data set in [11], we have taken $u(\Delta x_{\mathrm{O_2}})$ and $u(\Delta x_{\mathrm{CO_2}})$ to be 60 µmol mol$^{-1}$, each, although there is no compelling evidence to do so. Two of the supporting documents [19, 20] of [1] estimated $u(\Delta x_{\mathrm{O_2}})$ as 170 µmol 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 $u(S)$, $u(\Delta x_{\mathrm{CO_2}})$ and $u(\Delta x_{\mathrm{O_2}})$ have been included in table 2. The uncertainty component $u(x_{\mathrm{CO_2}})$, which is due to the measurement or estimate of $x_{\mathrm{CO_2}}$ 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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