Equation for the Determination of the Density of Moist Air (1981/91)

metrologia

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Foreword

Mass measurements made in air generally require corrections for the effects of buoyancy. In applying these corrections, the BIPM and most national laboratories now use the same equation for the determination of ρ, the density of moist air [1, 2]. The equation requires input values for the air temperature, pressure, relative humidity (or dew-point temperature), and mole fraction of carbon dioxide. In addition to these variable parameters, the equation includes a number of parameters which are assumed to be constant.

The formalism presented in [1, 2] is often, though unofficially, referred to as the CIPM-81 equation to indicate that its use has been recommended by the Comité International des Poids et Mesures [1] and that 1981 was the year of this recommendation.

In the ten or so years since publication of [1, 2] one of the important constant parameters of the equation, the molar gas constant, has become better known. In addition, updated values for some additional constant parameters have become available. For this reason, the Comité Consultatif pour la Masse et les grandeurs apparentées (CCM), on the advice of the Working Group on Density, at its last meeting (May 1991) considered that it is worthwhile to amend several of the constant parameters given in [1, 2]. It should be emphasized that both the basic form of the 1981 equation as well as the principles by which it was derived remain unchanged.

The CCM has therefore recommended that the 1981 equation incorporating the amended parameters given below be designated as the "1981/91 equation for the determination of the density of moist air", abbreviated in this note to the "1981/91 equation". The amended equation was accepted by the Comité International des Poids et Mesures (CIPM) at its 80th Meeting (September 1991). The 1981/91 equation is valid over the same ranges of pressure, temperature, relative humidity (or dew-point temperature), and carbon dioxide fraction as given in [1, 2].

Differences in numerical results obtained from the 1981 and the 1981/91 equations are small. It may be concluded in fact that: (i) air densities calculated using the 1981/91 equation do not differ significantly from those calculated from the 1981 equation; and (ii) the overall uncertainty of the 1981/91 equation is not significantly improved over that of the 1981 equation. The reason for making the changes is simply to ensure that the values for all constant parameters used in the equation are the best currently available.

1. The 1981 Equation

In essence, the 1981 equation for the density of moist air has the following form:

$$\rho = \frac{p M_{\mathrm{a}}}{ZRT}\left[1 - x_{\mathrm{v}}\left(1 - \frac{M_{\mathrm{v}}}{M_{\mathrm{a}}}\right)\right], \tag{1}$$

where p is the pressure, T the thermodynamic temperature, x_{v} the mole fraction of water vapour, M_{a} the molar mass of dry air, M_{v} the molar mass of water, R the molar gas constant, and Z the compressibility factor.

It is assumed that M_{a} is constant except for local variability of the mole fraction of carbon dioxide. The latter is further assumed to be exactly opposite to variability of the mole fraction of oxygen, leading

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to an auxiliary equation for M_a:

$$M_a = [28{,}963\,5 + 12{,}011\,(x_{CO_2} - 0{,}000\,4)] \times 10^{-3}\ \mathrm{kg/mol}, \quad (2)$$

where x_{CO_2} is the mole fraction of carbon dioxide.

The mole fraction of water vapour x_V is not measured directly. Instead, it is derived either from a measurement of the relative humidity h or from a measurement of the dew-point temperature t_r. In either case, one has need of $p_{SV}(t)$, the saturation vapour pressure of moist air. In [1, 2], this is calculated from the auxiliary equation

$$p_{SV} = 1\ \mathrm{Pa} \times \exp\left(AT^2 + BT + C + \frac{D}{T}\right) \quad (3)$$

Also needed is the enhancement factor f calculated from

$$f = \alpha + \beta p + \gamma t^2, \quad (4)$$

where t is the temperature in degrees Celsius.

Recall that

$$x_V = hf(p, t)\frac{p_{SV}(t)}{p} = f(p, t_r)\frac{p_{SV}(t_r)}{p}.$$

Finally, the compressibility Z is calculated from the following equation:

$$Z = 1 - \frac{p}{T}[a_0 + a_1 t + a_2 t^2 + (b_0 + b_1 t)x_V + (c_0 + c_1 t)x_V^2] + \frac{p^2}{T^2}\cdot(d + ex_V^2). \quad (5)$$

The constant parameters in (3, 4, 5) are specified in [1, 2].

2. The Changes

2.1 *Molar gas constant*

Equation (1) contains R, the molar gas constant. Since the publication of [1, 2], CODATA has recommended an improved estimate of R [3]:

$$R = 8{,}314\,510\,(1 \pm 8{,}4 \times 10^{-6})\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

This value exceeds that used in [1, 2] by 12 parts in 10^6. The uncertainty of the newer estimate is 0,27 times that assigned to the value of R used in [1, 2]. While this is a significant improvement, the overall uncertainty in calculated air density is essentially unchanged.

2.2 *Temperature*

One may also note that temperature, a variable parameter, appears explicitly in the denominator of (1) and implicity in the calculation of p_{SV}, f and Z (3, 4, 5). On 1 January 1990, the ITS-90 [4] superseded the IPTS-68 and it is worthwhile mentioning how this change affects the equation for the density of moist air. Equation (1) is derived by assuming that moist air is an ideal gas and then making the relatively small corrections necessary to take account of non-ideality. Thus the temperature T is meant to be the thermodynamic temperature. Temperatures given on the ITS-90 should therefore be used because temperatures on the ITS-90 are closer to the corresponding thermodynamic temperatures than were those on the IPTS-68.

Since (3, 4, 5) are used for relatively minor corrections, the small change introduced by the adoption of the ITS-90 (about 5 mK at 20°C) is of secondary importance. We have, nonetheless, used the ITS-90 in recomputing the constant parameters for these equations as discussed more fully in the next section.

2.3 *f*, p_{SV}, *Z*

As documented in [1, 2], the formulas for the calculation of p_{SV}, f, and Z are based on the work of Greenspan, Wexler and Hyland. Hyland and Wexler have recalculated this work [5] and we have incorporated their new results. It may be noted that these results depend on R and on T. These authors, anticipating a modification to the IPTS-68, showed how their results could be converted to a different temperature scale. The value of R used in [5] is sufficiently close to the value now recommended by CODATA [3] that their results are insensitive to this change.

3. New Constant Values

The amended constant parameters which are appropriate to the 1981/91 equation for the determination of the density of moist air are given in Table 1. The original parameters of the 1981 equation are also given for comparison purposes. One may note that, in the case of the enhancement factor f, the parameters are unchanged by the new calculations.

In [1, 2], the leading constant of the final equation for the determination of the density of moist air is M_a/R. The calculation of M_a remains unchanged from 1981 but the value of R is now amended as noted in Section 2.1.

4. Effect of the Changes

It is stated in the Foreword that the differences between the 1981 and the 1981/91 equations for the determination of the density of moist air are small. Table 2 illustrates this by comparing the results obtained using each set of constant parameters given in Table 1. The mole fraction of carbon dioxide is as-

Table 1. Constant parameters specified for the 1981 equation for the determination of the density of moist air and their amended 1991 values as recommended in this report for the 1981/91 equation.

	1981	1991
Vapour pressure at saturation		
p_{sv}		
$A/(10^{-5}\,K^{-2})$	1,281 180 5	1,237 884 7
$B/(10^{-2}\,K^{-1})$	−1,950 987 4	−1,912 131 6
C	34,049 260 34	33,937 110 47
$D/(10^{3}\,K)$	−6,353 631 1	−6,343 164 5
Enhancement factor f		
α	1,000 62	1,000 62
$\beta/(10^{-8}\,Pa^{-1})$	3,14	3,14
$\gamma/(10^{-7}\,K^{-2})$	5,6	5,6
Compressibility factor Z		
$a_0/(10^{-6}\,K\,Pa^{-1})$	1,624 19	1,581 23
$a_1/(10^{-8}\,Pa^{-1})$	−2,896 9	−2,933 1
$a_2/(10^{-10}\,K^{-1}\,Pa^{-1})$	1,088 0	1,104 3
$b_0/(10^{-6}\,K\,Pa^{-1})$	5,757	5,707
$b_1/(10^{-8}\,Pa^{-1})$	−2,589	−2,051
$c_0/(10^{-4}\,K\,Pa^{-1})$	1,929 7	1,989 8
$c_1/(10^{-6}\,Pa^{-1})$	−2,285	−2,376
$d/(10^{-11}\,K^{2}\,Pa^{-2})$	1,73	1,83
$e/(10^{-8}\,K^{2}\,Pa^{-2})$	−1,034	−0,765
Gas constant R		
$R/(J\,mol^{-1}\,K^{-1})$	8,314 41	8,314 510
Leading constant M_a (x_{CO_2} = 0,000 4)/R, in equation for the density of moist air		
$M_a R^{-1}/(10^{-3}\,kg\,K\,J^{-1})$	3,483 53	3,483 49

Table 2. Examples comparing results obtained using the 1981 equation and the 1981/91 equation for the determination of the density of moist air. The air density ρ (kg m^{-3}), the vapour pressure at saturation p_{sv} (Pa), and the compressibility factor Z are computed as a function of pressure p, temperature t, and relative humidity h. The ITS-90 is used in all calculations. The mole fraction of carbon dioxide is taken to be 0,000 4 in these examples.

		1981	1981/91
p = 100 000 Pa, t = 20 °C, h = 0,50			
	ρ	1,183 507	1,183 472
	p_{sv}	2 338,6	2 339,2
	Z	0,999 603	0,999 619
p = 110 000 Pa, t = 20 °C, h = 0,10			
	ρ	1,306 622	1,306 582
	p_{sv}	2 338,6	2 339,2
	Z	0,999 590	0,999 608
p = 100 000 Pa, t = 15 °C, h = 0,90			
	ρ	1,202 443	1,202 408
	p_{sv}	1 705,3	1 705,7
	Z	0,999 539	0,999 555
p = 60 000 Pa, t = 25 °C, h = 0,50			
	ρ	0,694 179	0,694 162
	p_{sv}	3 168,8	3 169,8
	Z	0,999 759	0,999 769

sumed equal to 0,000 4 for these calculations and the ITS-90 is used in all cases. The choice of relative humidity rather than dew-point temperature as the input parameter for these illustrative examples was arbitrary.

For all examples given in Table 2, air densities calculated from the 1991 constant parameters are smaller by about 3 parts in 10^5 relative to calculations using the 1981 parameters. While these differences are within the uncertainties ascribed to the equation, they are significant with respect to the precision of tabulated values given in [1, 2]. It may be noted that the change in computed air density due to the introduction of the latest CODATA value for R is roughly equal to the change due to the new Z values.

5. Proposals

Based on the considerations given above, the CCM submitted the following proposals to the CIPM, which approved them at its 80th Meeting (September 1991):

1. In computing the density of moist air, the functional form of all equations given in [1, 2] should be used without change.
2. Some constant parameters given in [1, 2] should be amended as shown in Table 1 of this article.
3. The equation for moist air having the functional form given in [1, 2], but with the amended constant parameters shown in Table 1 of this article, should be referred to as the 1981/91 equation for the determination of the density of moist air.
4. The ITS-90 should be used with the 1981/91 equation.
5. The overall uncertainty for air density as calculated using the 1981/91 equation is essentially the same as if the 1981 equation were used.

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tations and analyses necessary to derive the 1981/91 equation for determination of the density of moist air.

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