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The Air Density Equation and the Transfer of the Mass Unit

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A new formulation of the equation for calculation of air density has been developed. The Cohen and Taylor value of the gas constant, currently accepted values of the atomic weights, and recent determinations of abundances of the various constituents of air have been used. The abundance of carbon dioxide has been treated as a variable and a factor enabling convenient adjustment of the apparent molecular weight of air for deviation of carbon dioxide abundance from a background value has been derived. A new table of the compressibility factor for the range of pressure and temperature of interest in standards laboratories has been calculated using recently determined values of virial coefficients. The enhancement factor, which has usually been ignored, has been explicitly included. A simple equation for the calculation of enhancement factor has been fitted to values in the range of pressure and temperature of interest. A simple equation for the calculation of saturation water vapor pressure has been fitted. Uncertainties, random and systematic, in the parameters and in the measurement of environmental variables and consequent uncertainties in calculated air density have been estimated.

Application of the equation to air buoyancy determination and the transfer of the mass unit at the various national standards laboratories has been made.

Key words: Air buoyancy; air density; mass unit transfer; real gas equation.

1. Introduction

The transfer of the mass value from one object, such as the International Prototype Kilogram, to another object is accomplished by comparison of the objects by means of a balance. The difference in buoyant force on the two objects is proportional to the difference in their displacement volumes and to the air density. The air density is conventionally calculated using an equation based on the equation of state of an air-water vapor mixture. A new formulation of the air density equation is developed below.

2. Development of the Air Density Equation

The total pressure, P, the total volume, V, and the absolute temperature, T, of a mixture of ideal gases are related by the ideal gas equation,

$$PV = nRT, \tag{1}$$

where n is the number of moles of the mixture and R is the universal gas constant. In terms of density, ρ, rather than volume, eq (1) becomes

$$P = \rho \frac{R}{M} T, \tag{2}$$

where M is the apparent molecular weight of the mixture.

For a mixture of dry air (indicated by subscript a) and water vapor (subscript w), ρ and M are the density and apparent molecular weight respectively of the air-water vapor mixture. Since

$$M = \frac{m}{n} = \frac{m_a + m_w}{n_a + n_w}, \tag{3}$$

where m is the mass of the mixture and n is the number of moles of the mixture,

$$M = \frac{n_a M_a + n_w M_w}{n_a + n_w} = M_a \left(\frac{1 + \dfrac{n_w M_w}{n_a M_a}}{1 + \dfrac{n_w}{n_a}} \right). \tag{4}$$

By introducing the water vapor mixing ratio, r:

$$r = \frac{\text{mass of water vapor}}{\text{mass of dry air}} = \frac{n_w M_w}{n_a M_a}, \tag{5}$$

and by designating the ratio $\dfrac{M_w}{M_a}$ by ϵ, eq (4) becomes

$$M = \frac{M_a(1 + r)}{\left(1 + \dfrac{r}{\epsilon}\right)}. \tag{6}$$

Substituting (6) in (2) and noting that the effective vapor pressure, e', of water *in moist air* is defined [1][1] by:

$$e' = \frac{r}{(\epsilon + r)} P, \tag{7}$$

then

$$P = \rho \frac{R}{M_a} T \left[\frac{1}{1 + (\epsilon - 1)\dfrac{e'}{P}} \right]. \tag{8}$$

Equation (8) is the *ideal* gas equation for a mixture of dry air and water vapor with a vapor pressure of e'. If the air-water vapor mixture behaved as a mixture of ideal gases,

$$\frac{P}{\rho \dfrac{R}{M_a} T \left[\dfrac{1}{1 + (\epsilon - 1)\dfrac{e'}{P}} \right]} = Z = 1, \tag{9}$$

where Z is the compressibility factor. Since the mixture is not ideal the magnitude of the non-ideality is reflected in the departure of Z from 1 and (9) becomes

$$P = \rho \frac{R}{M_a} TZ \left[\frac{1}{1 + (\epsilon - 1)\dfrac{e'}{P}} \right]. \tag{10}$$

Equation (10) is the *real* gas equation for a mixture of dry air and water vapor. By rearrangement of eq (10), the expression for the air density is

$$\rho = \frac{PM_a}{RTZ} \left[1 + (\epsilon - 1)\frac{e'}{P} \right]. \tag{11}$$

3. Specification of the Values of the Parameters in the Air Density Eq (11)

3.1. Universal Gas Constant, R

The value of the molar gas constant, R, listed in a compilation by Cohen and Taylor [2], is 8.31441 ± 0.00026 $\mathrm{JK^{-1}\ mol^{-1}}$. Recently, Quinn et al. [3] made a new determination of R by measuring the speed of sound in argon by means of an acoustic interferometer. Their value was 8315.73 ± 0.17 $\mathrm{JK^{-1}\ kmol^{-1}}$. Gammon [4] recently deduced a value of R from measurements of the speed of sound in helium; his latest reported value is 8315.31 ± 0.35 $\mathrm{JK^{-1}\ kmol^{-1}}$ [5], which is in close agreement with the Quinn et al. value. Rowlinson and Tildesley [6] have recently interpreted the experimental measurements of Quinn et al. and arrived at a value of 8314.8 ± 0.3 $\mathrm{JK^{-1}\ kmol^{-1}}$, which is in agreement with the Cohen and Taylor value within the uncertainties assigned to the values.

We choose at present to use the Cohen and Taylor value with the realization that in the future it might be replaced by a new value.

3.2. Apparent Molecular Weight of Air, M_a

The apparent molecular weight of dry air, M_a, is calculated using the relationship

$$M_a = \sum_{i=1}^{k} M_i x_i \tag{12}$$

where each M_i is the molecular weight of an individual constituent and x_i is the corresponding mole fraction. The molecular weights and typical mole fractions of the constituents of dry air are tabulated in table 1. Other constituents are present in abundances which are negligible for the present application.

The values of the atomic weights of the elements are taken from reference [7] and are based on the carbon-12 scale. The molecular weights are taken to be the sums of the atomic weights of the appropriate elements.

The value for the abundance of oxygen is taken from reference [8]. The value for the abundance of carbon dioxide is taken from a recent unpublished compilation of data on *atmospheric* concentration of carbon dioxide at seven locations throughout the world. It must be emphasized that 0.00033 is the mole fraction of CO_2 in the atmosphere and should be considered to be a "background" value. The mole fraction of CO_2 in laboratories, which is of course the value of interest here, is in general greater than 0.00033 and is *variable*. For example, three samples of air taken from a glove box in the Mass Laboratory at NBS had a mean value of 0.00043, and four samples of laboratory air taken at the National Center for Atmospheric Research in Boulder, Colorado had a mean value of 0.00080. Clearly, then, the optimum utilization of the air density calculation would necessitate a measurement of CO_2 abundance on an air sample taken at the time of the mass comparison.

One of the options one has in dealing with the variability of CO_2 abundance is to select a reference level (for example, 0.00033 or 0.00043) and to provide an adjustment to M_a to account for known departures from the reference level. Gluekauf [9], in discussing the variation of the abundance of oxygen in the atmosphere, stated that "all major variations of the O_2 content must result from the combustion of fuel, from the respiratory exchange of organisms, or from the assimila-

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[1] Figures in brackets indicate references at the end of this paper.

tion of CO_2 in plants. The first process does not result in more than local changes of O_2 content, while the latter two processes, though locally altering the CO_2/O_2 ratio, leave their sum unchanged." The assumed constancy of the sum of the O_2 and CO_2 abundance simplifies the adjustment of M_a to account for departures from the CO_2 reference level and simplifies the estimation of the uncertainty in air density due to an uncertainty in CO_2 abundance. The constancy of the sum is expressed by the equation (for convenience, the subscript i has been replaced by the chemical symbol):

$$x_{CO_2} + x_{O_2} = \text{constant} = 0.20979. \tag{13}$$

The contribution of O_2 and CO_2 to the apparent molecular weight of dry air is

$$M_{O_2}x_{O_2} + M_{CO_2}x_{CO_2} = 31.9988\, x_{O_2} + 44.0098\, x_{CO_2}. \tag{14}$$

From (13),

$$x_{O_2} = 0.20979 - x_{CO_2}, \tag{15}$$

and

$$M_{O_2}x_{O_2} + M_{CO_2}x_{CO_2} = 12.011\, x_{CO_2} + 6.7130. \tag{16}$$

Therefore,

$$\begin{aligned} \delta(M_a) &= \delta\left[M_{O_2}x_{O_2} + M_{CO_2}x_{CO_2}\right] \\ &= 12.011\, \delta(x_{CO_2}), \end{aligned} \tag{17}$$

that is, the variation in M_a due to a variation in CO_2 abundance is equal to 12.011 (the atomic weight of carbon) multiplied by the variation in CO_2 abundance. The variation in M_a due to the difference between the reference levels 0.00033 and 0.00043 is thus 0.0012 g mol^{-1} which corresponds to a relative variation of 41 p.p.m. in M_a and a corresponding relative variation of 41 p.p.m. in air density.

The adjusted M_a accounting for the departure of the CO_2 abundance from the reference level of 0.00033 becomes

$$M_a = M_{a_{033}} + 12.011\left[x_{CO_2} - 0.00033\right], \tag{18}$$

where $M_{a_{033}}$ is the apparent molecular weight of dry air with a CO_2 mole fraction of 0.00033.

The value of the abundance of argon in dry air, 0.00916, is that calculated from the mass spectrometric determination of the ratio of argon to argon and nitrogen by Hughes [10].

The value for the abundance of nitrogen was arrived at by the usual practice of inferring nitrogen abundance to be the difference between unity and the sum of the mole fractions of the other constituents.

The abundances of the constituents neon through nitrous oxide in table 1 were taken to be equal to the parts per volume concentration in U.S. Standard Atmosphere, 1976 [11].

From the data of table 1, the apparent molecular weight of dry air with a CO_2 mole fraction of 0.00033 is calculated by (12) to be 28.963.

TABLE *1. Composition of dry air*

Constituent	Abundance (mole fraction)	Molecular Weight
Nitrogen (N_2)	0.78102	28.0134
Oxygen (O_2)	.20946	31.9988
Carbon Dioxide (CO_2)	.00033	44.0098
Argon (A)	.00916	39.948
Neon (Ne)	.00001818	20.179
Helium (He)	.00000524	4.00260
Krypton (Kr)	.00000114	83.80
Xenon (Xe)	.000000087	131.30
Hydrogen (H_2)	.0000005	2.0158
Methane (CH_4)	.0000015	16.0426
Nitrous Oxide (N_2O)	.0000003	44.0128

3.3. Compressibility Factor, Z

The compressibility factor is computed using the virial equation of state of an air-water vapor mixture expressed as a power series in reciprocal molar volume,

$$Z = \frac{Pv}{RT} = 1 + \frac{B_{\text{mix}}}{v} + \frac{C_{\text{mix}}}{v^2} + \cdot\cdot\cdot\cdot\cdot, \tag{19}$$

and expressed as a power series in pressure,

$$Z = \frac{Pv}{RT} = 1 + B'_{\text{mix}}P + C'_{\text{mix}}P^2 + \cdot\cdot\cdot\cdot\cdot, \tag{20}$$

where v is the molar volume, B_{mix} and B'_{mix} are second virial coefficients and C_{mix} and C'_{mix} are third virial coefficients for the mixture. The virial coefficients of the pressure series are related to the virial coefficients of the volume power series by

$$B'_{\text{mix}} = \frac{B_{\text{mix}}}{RT} \tag{21}$$

and

$$C'_{\text{mix}} = \frac{C_{\text{mix}} - B^2_{\text{mix}}}{(RT)^2}. \tag{22}$$

Each mixture virial coefficient is a function of the mole fractions of the individual constituents and the virial coefficients for the constituents. The latter are functions of temperature only.

The second interaction (cross) virial coefficient of moist air, B_{aw}, is one of the contributors to B'_{mix} and expresses the effects of interaction between an air molecule and a water molecule. The values of B_{aw} used in the calculation of Z are experimental values which strictly apply to CO_2-free air.

Using (28) and (29), below, and the virial coefficients [12, 16] provided by Hyland,, a table of compressibility factor, Z, for CO_2-free air, table 2, has been generated.

In the absence of values for virial coefficients for air-CO_2 mixtures in the temperature range of interest, the effect of the variability of CO_2 abundance on Z has been estimated to be of the order of 1 ppm and, therefore, negligible. Also, the effect of the variability of CO_2 abundance on Z due to the interaction of CO_2 with water vapor has been estimated to be of the order of 0.1 ppm and, therefore, negligible. Consequently, table 2 is applicable to moist air containing reasonable amounts of CO_2.

For temperatures and/or pressures outside the range of table 2, the table of compressibility factor of moist air (also CO_2-free) in the Smithsonian Meteorological Tables [15] can be used, with some loss of precision since the listing there is to the fourth decimal place.

3.4. Ratio of the Molecular Weight of Water to the Molecular Weight of Dry Air

The molecular weight of water is 18.0152 [7]. The ratio, ϵ, of the molecular weight of water to that of dry air is, therefore, 0.62201 for dry air with a CO_2 mole fraction of 0.00033.

4. Uncertainty in Calculation of Air Density

In estimating uncertainties we shall report them as 1 standard deviation and we shall follow the suggested practice of Eisenhart [13, 14] in stating separately the random and systematic components.

4.1. Uncertainty in R

The uncertainty in the value of the molar gas constant is that reported by Cohen and Taylor [2], ± 0.00026 JK^{-1} mol^{-1}. The corresponding random relative uncertainty in ρ is 3.1×10^{-5}.

4.2. Uncertainties in M_a

The uncertainties in M_a will be taken from the estimated uncertainties in particular measurements of the abundances of the constituents of air. The uncertainty in the O_2 abundance (mole fraction) of air [8] is separable into a random component and a systematic component. The random uncertainty is estimated to be ±0.00001, the systematic component is ±0.00006.

TABLE 2. Compressibility factor, Z, for CO_2-free air

Temperature (Celsius)	Pressure (pascals)	Pressure (mm Hg)	Relative Humidity in Percent 0	25	50	75	100
19.0	70000	525.0	.99973	.99972	.99971	.99968	.99966
	75000	562.5	.99972	.99970	.99969	.99967	.99964
	80000	600.0	.99970	.99968	.99967	.99965	.99963
	85000	637.6	.99968	.99967	.99965	.99963	.99961
	90000	675.1	.99966	.99965	.99963	.99961	.99959
	95000	712.6	.99964	.99963	.99961	.99960	.99957
	100000	750.1	.99962	.99961	.99959	.99958	.99956
	101325	760.0	.99962	.99960	.99959	.99957	.99955
	105000	787.6	.99960	.99959	.99958	.99956	.99954
	110000	825.1	.99958	.99957	.99956	.99954	.99952
20.0	70000	525.0	.99974	.99973	.99971	.99969	.99966
	75000	562.5	.99972	.99971	.99969	.99967	.99964
	80000	600.0	.99970	.99969	.99967	.99965	.99963
	85000	637.6	.99969	.99967	.99966	.99964	.99961
	90000	675.1	.99967	.99666	.99964	.99962	.99966
	95000	712.6	.99965	.99964	.99962	.99960	.99958
	100000	750.1	.99963	.99962	.99960	.99958	.99956
	101325	760.0	.99963	.99961	.99960	.99958	.99956
	105000	787.6	.99961	.99960	.99958	.99957	.99954
	110000	825.1	.99959	.99958	.99957	.99955	.99953
21.0	70000	525.0	.99975	.99973	.99971	.99969	.99966
	75000	562.5	.99973	.99972	.99970	.99967	.99964
	80000	600.0	.99971	.99970	.99968	.99966	.99963
	85000	637.6	.99969	.99968	.99966	.99964	.99961
	90000	675.1	.99968	.99966	.99965	.99962	.99960
	95000	712.6	.99966	.99965	.99963	.99961	.99958
	100000	750.1	.99964	.99963	.99961	.99959	.99956
	101325	760.0	.99964	.99962	.99961	.99959	.99956
	105000	787.6	.99962	.99961	.99959	.99957	.99955
	110000	825.1	.99960	.99959	.99958	.99956	.99953
22.0	70000	525.0	.99975	.99974	.99972	.99969	.99966
	75000	562.5	.99974	.99972	.99970	.99968	.99964
	80000	600.0	.99972	.99971	.99969	.99966	.99963
	85000	637.6	.99970	.99969	.99967	.99964	.99961
	90000	675.1	.99968	.99967	.99965	.99963	.99960
	95000	712.6	.99967	.99965	.99963	.99961	.99958
	100000	750.1	.99965	.99964	.99962	.99960	.99957
	101325	760.0	.99965	.99963	.99961	.99959	.99956
	105000	787.6	.99963	.99962	.99960	.99958	.99955
	110000	825.1	.99962	.99960	.99958	.99956	.99954
23.0	70000	525.0	.99976	.99975	.99972	.99969	.99966
	75000	562.5	.99974	.99973	.99971	.99968	.99964
	80000	600.0	.99973	.99971	.99969	.99966	.99963
	85000	637.6	.99971	.99969	.99967	.99965	.99962
	90000	675.1	.99969	.99968	.99966	.99963	.99960
	95000	712.6	.99968	.99966	.99964	.99962	.99959
	100000	750.1	.99966	.99964	.99962	.99960	.99957
	101325	760.0	.99965	.99964	.99962	.99960	.99957
	105000	787.6	.99964	.99963	.99961	.99958	.99956
	110000	825.1	.99963	.99961	.99959	.99957	.99954
24.0	70000	525.0	.99977	.99975	.99973	.99969	.99965
	75000	562.5	.99975	.99973	.99971	.99968	.99964
	80000	600.0	.99973	.99972	.99970	.99967	.99963
	85000	637.6	.99972	.99970	.99968	.99965	.99962
	90000	675.1	.99970	.99969	.99966	.99964	.99960
	95000	712.6	.99968	.99967	.99965	.99962	.99959
	100000	750.1	.99967	.99965	.99963	.99961	.99957
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	105000	787.6	.99965	.99964	.99962	.99959	.99956
	110000	825.1	.99964	.99962	.99960	.99957	.99954
25.0	70000	525.0	.99977	.99976	.99973	.99970	.99965
	75000	562.5	.99976	.99974	.99971	.99968	.99964
	80000	600.0	.99974	.99972	.99970	.99967	.99963
	85000	637.6	.99973	.99971	.99968	.99965	.99962
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	101325	760.0	.99967	.99966	.99963	.99961	.99957
	105000	787.6	.99966	.99964	.99962	.99960	.99956
	110000	825.1	.99965	.99963	.99961	.99958	.99955
26.0	70000	525.0	.99978	.99976	.99973	.99970	.99965
	75000	562.5	.99976	.99975	.99972	.99968	.99964
	80000	600.0	.99975	.99973	.99970	.99967	.99963
	85000	637.6	.99973	.99971	.99969	.99966	.99961
	90000	675.1	.99972	.99970	.99967	.99964	.99960
	95000	712.6	.99970	.99968	.99966	.99963	.99959
	100000	750.1	.99969	.99967	.99964	.99961	.99958
	101325	760.0	.99968	.99966	.99964	.99961	.99957
	105000	787.6	.99967	.99965	.99963	.99960	.99956
	110000	825.1	.99966	.99964	.99961	.99959	.99955

The random component of the uncertainty in the argon abundance is inferred from the precision of Hughes' measurements [10] to be ±0.00003. No assignment of systematic uncertainty was made by Hughes.

The uncertainty in the CO_2 abundance has been mentioned earlier with respect to the variability of the CO_2 abundance in the laboratory. For a sample of air taken at the time a mass comparison is made, the estimated uncertainty in the subsequent mass spectrometric determination of CO_2 abundance is ±0.00003 at the 0.00033 level. Since the measurements made by the mass spectrometric method are considered to be very precise, the estimated uncertainty is considered to be systematic.

Since the N_2 abundance is the difference between unity and the sum of the mole fractions of the other constituents, the random component of the uncertainty in the N_2 abundance is found by combining by quadrature the random components of the uncertainties of the other three major components to be $\pm 1 \times 10^{-5}$. For the systematic component, however, the practice of finding the N_2 abundance by difference provides for very significant reduction of uncertainty. This is shown in the following treatment.

Equation (12) can be written:

$$\begin{aligned} M_a = {} & M_{O_2}x_{O_2} + M_{CO_2}x_{CO_2} \\ & + M_A x_A + M_{N_2}x_{N_2} + \sum_{1=5}^{k} M_i x_i . \end{aligned} \qquad (23)$$

The mole fraction of N_2 is, by difference,

$$x_{N_2} = 1 - x_{O_2} - x_{CO_2} - x_A - \sum_{1=5}^{k} x_i . \qquad (24)$$

If we ignore the last term in (28), differentiate and go to finite differences,

$$\begin{aligned} \Delta(M_a)_{x_i} &= M_{O_2}\Delta x_{O_2} + M_{CO_2}\Delta x_{CO_2} \\ &\quad + M_A \Delta x_A + M_{N_2} \\ &\quad (-\Delta x_{O_2} - \Delta x_{CO_2} - \Delta x_A) \\ &= (M_{O_2} - M_{N_2})\Delta x_{O_2} \\ &\quad + (M_{CO_2} - M_{N_2})\Delta x_{CO_2} \\ &\quad + (M_A - M_{N_2})\Delta x_A . \end{aligned} \qquad (25)$$

With the substitution of the appropriate systematic uncertainties and the molecular weights into (25), the systematic components of the relative uncertainty in M_a due to uncertainties in abundance of the constituents if found to be $\pm 3 \times 10^{-5}$. The random component of the relative uncertainty is found to be $\pm 4 \times 10^{-5}$ by combining by quadrature the product of the molecular weight and the random component of uncertainty in abundance for each of the four major constituents and dividing by M_a. The uncertainty in M_a due to the uncertainty in the value of the atomic or molecular weights of the i-th constituent is

$$\Delta(M_a)_{M_i} = x_i \Delta M_i . \qquad (26)$$

The uncertainties in the values of the atomic or molecular weights are inferred from reference [7].[2] For the four major constituents they are: for O_2, ±0.0002; for CO_2, ±0.0005; for A, ± 0.001; and for N_2, ±0.0001. These uncertainties are considered to be systematic. The sum of the four terms represented by (26) is ±0.0001, corresponding to a relative uncertainty in M_a of $\pm 4 \times 10^{-6}$.

The random component of the *overall* relative uncertainty in M_a is, by quadrature, $\pm 4 \times 10^{-5}$. The systematic component of the overall relative uncertainty in M_a is $\pm 3 \times 10^{-5}$, the sum of the component due to the systematic uncertainty in abundance and that due to the uncertainty in atomic or molecular weight. The corresponding random and systematic components of the relative uncertainty in ρ are $\pm 4 \times 10^{-5}$ and $\pm 3 \times 10^{-5}$, respectively.

4.3. Uncertainty in Z

The uncertainty in Z, the compressibility factor, is estimated from the various uncertainties in Z due to the uncertainties in the virial coefficients [12, 16]. The estimated relative uncertainty in Z at 293.15K, 101325 Pa (1 atmosphere) and 50 percent relative humidity is $\pm 1.7 \times 10^{-5}$. The corresponding relative uncertainty, taken to be systematic, in ρ is $\pm 1.7 \times 10^{-5}$.

4.4. Uncertainty in ϵ

The uncertainty in M_w, the molecular weight of water, is ±0.0005 [7] and is treated here as systematic. The random component of the uncertainty in ϵ, the ratio of M_w to M_a, is calculated to be $\pm 1 \times 10^{-5}$ and the systematic component is estimated to be $\pm 8 \times 10^{-6}$. The corresponding uncertainties in the factor in (11) involving ϵ,

$$\left[1 + (\epsilon - 1)\frac{e'}{P} \right], \qquad (27)$$

at 293.15K, 101325 Pa and 50 percent relative humidity are $\pm 1 \times 10^{-7}$ and $\pm 9 \times 10^{-8}$, respectively. The corresponding relative uncertainties in the term and consequently in ρ are $\pm 1 \times 10^{-7}$ and $\pm 9 \times 10^{-8}$, respectively.

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[2] The uncertainty assigned in the reference is divided by 3 to estimate the uncertainty at 1 standard deviation.

4.5. Combined Relative Uncertainties in ρ Due to the Uncertainties in M_a, R, Z and ϵ

The random and systematic components of the relative uncertainty in ρ at 293.15K, 101325 Pa and 50 percent relative humidity, due to the uncertainties in M_a, R, Z and ϵ are tabulated in table 3.

TABLE 3. *Components of the relative uncertainty in ρ due to uncertainties in* M_a, R, Z and ϵ

Parameter	Random	Systematic
Ma	$\pm 4 \times 10^{-5}$	$\pm 3 \times 10^{-5}$
R	$\pm 3.1 \times 10^{-5}$	------------
Z	------------	$\pm 1.7 \times 10^{-5}$
ϵ	$\pm 1 \times 10^{-7}$	$\pm 9 \times 10^{-8}$
Combined	$\pm 5 \times 10^{-5}$	$\pm 5 \times 10^{-5}$

The random components were combined by quadrature, the systematic components were combined by addition. These components of uncertainty can be considered to represent the uncertainty "intrinsic" to the air density equation, that is, that which is contributed by the limitations on the present knowledge of M_a, M_w, R and Z. With these uncertainties must, of course, be combined the uncertainties in the environmental variables: P, T and relative humidity, and in the knowledge of the carbon dioxide abundance.

5. Measurement of P, T and Relative Humidity

In order to estimate the uncertainties in ρ due to uncertainties in the measurements of the environmental variables, P, T and relative humidity, we shall estimate the uncertainties in these measurements when made using the best applicable instrumentation and procedures. Therefore, the estimated uncertainties in ρ will be those contributed by the *best possible* measurements.

5.1. Pressure Measurement

The state-of-the-art in pressure measurement [17] permits the measurement of the pressure in a laboratory with a random relative uncertainty of less than $\pm 2 \times 10^{-4}$. Calibration of pressure measuring instruments against a primary standard of pressure contributes a systematic relative uncertainty of about $\pm 3 \times 10^{-5}$. The corresponding $\Delta\rho/\rho$'s contributed by uncertainties in the measurement of pressure in a laboratory in the vicinity of a balance case are $\pm 2 \times 10^{-4}$ and $\pm 3 \times 10^{-5}$.

5.2. Temperature Measurement

The measurement of temperature in a balance case, that is the temperature which determines the buoyant forces, is potentially the most critical measurement in terms of its effect on the uncertainty in the calculated air density. In the absence of experimental results, it is possible at this time to make only a rough estimate of the temperature uncertainty to be expected. If the balance case were instrumented with a network of thermopile junctions, for example, the measurements would be expected to have a standard deviation of about ±0.05K [18]. The systematic uncertainty is estimated to be of the order of ±0.01K. At a temperature of 293.15K, these uncertainties correspond to relative uncertainties of $\pm 2 \times 10^{-4}$, and $\pm 3 \times 10^{-5}$, respectively. The corresponding $\Delta\rho/\rho$'s are $\pm 2 \times 10^{-4}$ and $\pm 3 \times 10^{-5}$, respectively.

5.3. Humidity Measurements

The state-of-the-art in humidity measurement [19] permits the measurement of humidity in a balance case with a random uncertainty of ±0.5 percent relative humidity and a systematic uncertainty of ±0.3 percent relative humidity. These uncertainties correspond to relative uncertainties in the water vapor pressure factor $[1 + (\epsilon - 1)e'/P]$, in (11) and, therefore, to $\Delta\rho/\rho$, of $\pm 4 \times 10^{-5}$ and $\pm 3 \times 10^{-5}$ at 293.15K, 101325 Pa and 50 percent relative humidity.

Since e' is the effective vapor pressure of water in *moist air*, a word of caution with regard to inferring e' from measurements of relative humidity is in order. Relative humidity, U, can be defined [20] by

$$U = \frac{e'}{e'_s} \times 100 \text{ percent}, \tag{28}$$

where e'_s is the *effective* saturation vapor pressure of water in moist air. e'_s is greater than e_s, the saturation vapor pressure of pure phase (i.e., water vapor without the admixture of air or any other substance) over a plane surface of pure ordinary liquid water, since the introduction of a second gas (air in this case) over the surface of the water increases the saturation concentration of water vapor above the surface of the water. This "enhancement" of water vapor pressure is expressed by the enhancement factor, f, which is defined by

$$f = \frac{e'_s}{e_s}. \tag{29}$$

The most recently published [16] experimentally derived value of f at 293.15K and 100000 Pa is 1.00400. Therefore, the common practice of inferring e' from measured U and tabulated values of e_s introduces a significant error in e' if f has been ignored. The corresponding relative error in ρ at 293.15K, 101325 Pa and 50 percent relative humidity is about 1.7×10^{-5}.

f is a function of temperature and pressure. In the present work, Hyland's values of f [16] have been fitted to a three-parameter equation in the pressure and temperature (t, °C) ranges of interest in national standards laboratories. The resulting equation is

$$f = 1.00070 + 3.113 \times 10^{-8}P + 5.4 \times 10^{-7}t^2. \quad (30)$$

The expression for e' is found by combining (28) and (29) to be

$$e' = \frac{U}{100} f e_s. \quad (31)$$

The systematic relative uncertainties in ρ due to the uncertainties assigned to f [16] and e_s [22] are approximately $\pm 1 \times 10^{-6}$ and $\pm 2 \times 10^{-7}$, respectively.

For the temperature range of interest in the present application, any of several tables of e_s, for example, references [21], [22], and [23], can be used. Besley and Bottomley [24] have recently published experimental values of e_s in the temperature range 272.60 to 298.04K.

In the present work, the data of Besley and Bottomley in the temperature range 288.15 to 298.04K and calculated values [22] for the remainder of the temperature range to 301.15K, have been fitted to a two-parameter equation. The resulting equation is

$$e_s = 1.7526 \times 10^{11} \exp(-5315.56/T). \quad (32)$$

Values calculated using (32) are sufficiently close to experimental and calculated values, within ±0.1 percent, to be used in the present application.

5.4. Random and Systematic Components of the Relative Uncertainty in ρ Due to Anticipated Uncertainties in State-of-the-Art Measurements of P, T and Relative Humidity

The random and systematic components of the relative uncertainty in ρ at 293.15K, 101325 Pa and 50 percent relative humidity due to anticipated uncertainties in state-of-the-art measurements of the environmental variables are tabulated in table 4. The random components were combined by quadrature, the systematic components were combined by addition.

It is clear from inspection of tables 3 and 4 that the dominant uncertainty in the calculation of air density is that contributed by the measurement of pressure, temperature and relative humidity, even when the measurements are made using the *best* instrumentation and procedures. Considerable care must therefore be taken in making measurements of these environmental variables in order to attempt to approach the precision and accuracy represented in table 4.

To illustrate the effect of errors in the measurement of the environmental variables, at 293.15K, 101325 Pa and 50 percent relative humidity, an error of 0.1 percent in calculated air density results from an error of 0.29K in temperature measurement or a 101 Pa error in pressure measurement or an 11.3 percent relative humidity error in the measurement of relative humidity.

TABLE 4. *Components of the relative uncertainty in ρ due to anticipated uncertainties in state-of-the-art measurements of P, T and relative humidity*

Variable	Random	Systematic
P	$\pm 2 \times 10^{-4}$	$\pm 3 \times 10^{-5}$
T	$\pm 2 \times 10^{-4}$	$\pm 3 \times 10^{-5}$
Relative Humidity	$\pm 4 \times 10^{-5}$	$\pm 3 \times 10^{-5}$
Combined	$\pm 3 \times 10^{-4}$	$\pm 9 \times 10^{-5}$

5.5. Carbon Dioxide Abundance

As stated in section 3.2, the CO_2 abundance in laboratory air and consequently in the air in balance cases is in general variable. A variation of 0.0001 in CO_2 mole fraction is equivalent to a relative variation of 4×10^{-5} in calculated air density. Consequently, for optimum utilization of the air density calculation, the CO_2 abundance should be known. Equation (18) enables adjustment of M_a for departures from the reference level, 0.00033, of CO_2 abundance.

6. Overall Uncertainty in ρ Due to Uncertainties in the Parameters and Variables in the Air Density Equation

The random and systematic components of the relative uncertainties in ρ in tables 3 and 4 when combined provide estimates of the components of the overall relative uncertainty in ρ. The random component, by quadrature, is $\pm 3 \times 10^{-4}$; the systematic component, by addition, is $\pm 1 \times 10^{-4}$. The relative uncertainty due to the variation of CO_2 abundance (4×10^{-5} per 0.0001 in CO_2 mole fraction) is necessarily not included in this estimate.

At 293.15K, 101325 Pa (1 atmosphere), and 50 percent relative humidity, the estimated overall relative uncertainties in p correspond to uncertainties in mass in the transfer between platinum-iridium and stainless steel kilogram artifacts (volume difference of ~80 cm³) of approximately 30 μg random and 10 μg systematic.

7. Air Density at Standard Conditions, ρ_0

The air density, ρ_0, at standard conditions (P_O, M_{a_O}, R, T_O, Z_O), for dry air is expressed by an equation of the form of (11) as

$$\rho_O = \frac{P_O M_{a_O}}{R T_O Z_O}. \quad (33)$$

By dividing (11) by (33) we arrive at

$$\rho = \rho_0 \left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)\left(\frac{Z_0}{Z}\right)\left(\frac{M_a}{M_{a_0}}\right) \cdot \left[1 + (\epsilon - 1)\frac{e'}{P}\right]. \tag{34}$$

The gas constant, R, has been eliminated but M_a has not unless the apparent molecular weight of the dry air in the standard state, M_{a_0} is equal to M_a. For example, if the ρ_0 is determined by experiment, M_{a_0} is not necessarily equal to M_a.

If an experimental value of ρ_0 of sufficient accuracy were available in the determination of which R was not used, R and its associated uncertainty would be eliminated. In the absence of such an experimental value, as is the present case, the use of an equation combining (11) with (18) is preferred to an equation of the form of (34).

If standard conditions are taken to be T_0 = 273.15K, P_0 = 101325 Pa, M_{a_0} = 28.963, and relative humidity = 0, for which Z_0 = 0.99940, ρ_0 is calculated by (33) to be 1.2930 kg m^{-3}. The same result is obtained for M_a = 28.964 (i.e., for a CO_2 mole fraction of 0.00043).

8. Air Density Equation

By combining (11) and (31) and substituting $\frac{M_w}{M_a}$ for ϵ, the air density equation developed in this work becomes

$$\rho = \frac{PM_a}{RTZ}\left[1 - \left(1 - \frac{M_w}{M_a}\right)\frac{U}{100}\frac{fe_s}{P}\right]. \tag{35}$$

By substituting the Cohen and Taylor value of R, 8314.41 (J K^{-1} kmol^{-1}), the value 18.0152 for M_w and the value 28.963 for $M_{a_{033}}$ in (18), (35) becomes

$$\rho = 0.000120273\,\frac{PM_a}{TZ} \left[1 - \left(1 - \frac{18.0152}{M_a}\right)\frac{U}{100}\frac{fe_s}{P}\right], \tag{36}$$

where

$$M_a = 28.963 + 12.011\,[x_{CO_2} - 0.00033]. \tag{37}$$

For T = 293.15K, P = 101325 Pa, 50 percent relative humidity and M_a = 28.964 g mol^{-1}, the air density calculated using (36) is 1.1993 kg m^{-3}.

8.1. Use of Constants in the Air Density Equation

In this section we shall investigate the effect on mass comparisons of the use of appropriate constant values of f, Z and M_a in (36).

The buoyant effect of the displacement of air by a mass artifact is proportional to the density of the air, ρ, and the displacement volume, V_m, of the artifact. We define here the buoyancy correction, m_b, to be added to the observed mass, by the following equation:

$$m_b = \rho V_m = \rho\,\frac{m}{\rho_m}, \tag{38}$$

where m and ρ_m are the mass and density, respectively, of the artifact.

The variation, Δm_b, in m_b due to a relative uncertainty, $\Delta\rho/\rho$, in air density can be written

$$\Delta m_b = \frac{m}{\rho_m}\left(\frac{\Delta\rho}{\rho}\right)\rho. \tag{39}$$

By substituting a nominal value of ρ, 1.2 kg m^{-3}, in (39) we arrive at

$$\Delta m_b = 1.2\,\frac{m}{\rho_m}\left(\frac{\Delta\rho}{\rho}\right). \tag{40}$$

We shall return to this equation to estimate the uncertainty in mass comparisons due to the use of certain constants in (36) for the calculation of air density.

To estimate the effect of a variation in f about a selected constant value, nominal values of P, T, M_a, Z, relative humidity and e_s are substituted in (36) and the resulting equation is differentiated with respect to f. Nominal values appropriate to the Mass Laboratory of NBS are P = 100000 Pa, T = 298.15K, M_a = 28.964 g mol^{-1}, 30 percent relative humidity and e_s = 3169 Pa. The resulting equation is

$$\rho = 1.1688\,(1 - 0.003594\,f) \tag{41}$$

and

$$\frac{\Delta\rho}{\rho} = -\,0.0036\,\frac{\Delta f}{f}. \tag{42}$$

The values of f range from 1.0030 to 1.0046, therefore the maximum $\Delta f/f$ for a nominal value of f of 1.0042 is equal to 1.2×10^{-3}. The corresponding $\Delta\rho/\rho$ is equal to 4.3×10^{-6}.

To estimate the effect of a variation of Z about a selected constant value, from (36),

$$\frac{\Delta\rho}{\rho} = \frac{-\Delta Z}{Z}. \tag{43}$$

To estimate the expected variation in Z, it is necessary to estimate the ranges of the environmental variables, P, T and relative humidity. The maximum and minimum of the atmospheric pressure at NBS, taken from climatological records of the National Weather Service of the National Oceanic and Atmospheric Administration and adjusted to the elevation of the Mass Laboratory, are 103850 and 96160 Pa. The expected ranges in temperature and relative humidity are taken to be 18 to 28 °C and 10 to 50 percent, respectively. For the nominal values given in this section, the expected variations in the environmental variables result in a variation of Z between 0.99957 and 0.99971. These extremes in Z correspond to relative variations in Z about the nominal value, 0.99966 of -9×10^{-5} and 5×10^{-5}, respectively. The corresponding $\frac{\Delta\rho}{\rho}$'s are 9×10^{-5} and -5×10^{-5}.

As was shown in section 3.2, a variation of 0.0001 in CO_2 mole fraction corresponds to a relative variation in M_a of 4×10^{-5} and to a $\Delta\rho/\rho$ of 4×10^{-5}.

Combining by quadrature the maximum values of $\Delta\rho/\rho$ due to expected variations in f and Z and variation of 0.0001 in CO_2 mole fraction, the result is 9.9×10^{-5}. This is the value to be used in (39). Since the values combined are maximum values, the combined value can be considered loosely to approximate 3 standard deviations.

For various materials of interest in the comparison of mass artifacts, Δm_b in micrograms (μg) has been calculated using (39) and 1 kg and 100 g artifacts and tabulated in table 5.

TABLE 5. *Variation in the buoyancy correction, Δm_b, resulting from the use of constant values of f, Z and M_a in (36)*

Material	Δm_b (μg)	Δm_b (μg)
	1 kg	100 g
Platinum-iridium	5.5	0.55
Stainless steel	15	1.5
Silicon	54	5.4
Brass	14	1.4
Aluminum	44	4.4
Tantalum	7.1	0.71
Water	119	12

The variation in the apparent mass difference between mass artifacts due to the use of constant values of f, Z and M_a is equal to the difference in Δm_b for the artifacts. For example, for a comparison of kilogram artifacts of platinum-iridium and stainless steel the variation in the apparent difference in their masses is $15 - 5.5 = 9.5$ μg.

On the basis of the values calculated using table 5 and the precision of the balance used for mass comparisons, a judgment can be made concerning the adequacy of the use of constant values of f, Z and, M_a in (36). The precision of the balance used for the comparisons of 1 kg mass artifacts at NBS is 25 μg at the 1 standard deviation level. Thus it can be concluded, for example, that constant values can be used in the comparison of platinum-iridium and stainless steel artifacts, and stainless steel and brass kilogram artifacts, but not for comparison of platinum-iridium and silicon kilogram artifacts. The precision of the kilogram balance at the Bureau International des Poids et Mesures (BIPM) is 1.5 μg at the 1 standard deviation level, therefore it could be concluded that the use of constants would not be appropriate in mass comparisons made using that balance.

For mass comparisons in the Mass Laboratory of NBS for which the values in table 5 indicate that the use of constant values of f (1.0042), Z (0.99966) and M_a (28.964) in (36) is adequate, the resulting equation is

$$\rho = \frac{0.0034848}{T}(P - 0.0037960\, Ue_s). \tag{43}$$

For pressure in millimeters of mercury and temperature, t, in °C, (43) becomes

$$\rho = \frac{0.46460}{(t + 273.15)}(P - 0.0037960\, Ue_s). \tag{44}$$

For saturation water vapor pressure, e_s, in millimeters of mercury (32) becomes

$$e_s = 1.3146 \times 10^9 \exp\left(-5315.56/(t + 273.15)\right). \tag{45}$$

9. Conclusions

The following are recommendations concerning the transfer of the mass unit at the various national standards laboratories: 1) eq (36) should be adopted for use for all national standards laboratories to provide both uniformity and the best available calculation of air density; 2) the CO_2 concentration should be treated as a variable and *at least* a "background" value should be determined for each of the laboratories; 3) instrumentation and practices representing the state-of-the-art in the measurement of the environmental variables should be applied.

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