Approximate equations for some acoustical and thermodynamic properties of standard air

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This paper describes an investigation into the variation with humidity and carbon dioxide content in air of the speed of sound, characteristic impedance, specific heats, the ratio of specific heats, air density and the molar mass. The theoretical model is an approximation, which is based on standard air over a temperature range of 0 to 30 degrees Celsius and at a barometric pressure of 101.325 kPa. Empirical equations for the computation of the above physical properties are provided together with uncertainty estimations.

Keywords: Standard air, Acoustical, thermodynamic properties

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1. INTRODUCTION

The effects of humidity on most of the following acoustical and thermodynamic properties of air, such as the sound speed c , characteristic impedance ρc , specific heat at constant pressure C_p and at constant volume C_v , and their ratio γ , air density ρ , and the molar mass M have been investigated.¹⁻⁸⁾ For the speed of sound, a prediction¹⁾ has been given for the variation of c with carbon dioxide content. However, there is no comprehensive information available on the combined effects of CO₂ and humidity on the above physical properties of air.

In mass measurement standards and high precision weighing applications, the density of air has to be taken into consideration for air buoyancy correction.^{8,9)} In order to have an uncertainty of a few micrograms during the comparison of standard kilograms, the uncertainty of the density of air should be known to within 10^{-4} and possibly 10^{-5} in relative terms (Ref. 9), p. 12). Since the above measurements are normally performed in air, a knowledge on the variation of air density with

humidity and CO₂ is essential. For laboratory experiments, the CO₂ content in air may approach 1% (Ref. 10), p. 316), and the effects of CO₂ on the air specific heats C_p and C_v have some influence on the thermodynamic performance of heat engines and furnaces. In acoustical standards, the numerical values for γ , c and ρ are required in precision calibration of condenser microphones with the reciprocity method.^{11,12)}

It is the aim here to provide theoretical predictions for the effects of humidity and carbon dioxide content on the above acoustical and thermodynamic properties of standard air. For temperatures at 10, 20 and 25 degrees Celsius, the variation of γ with humidity has been confirmed experimentally⁷⁾; and the theoretical data given in this investigation may help to prepare future experiments for the confirmation of the above remaining physical properties of air. Unless otherwise stated, the theoretical data presented here are applicable to the range of temperatures t from 0 to 30 degrees Celsius; relative humidity h from 0 to 1; and CO₂ concentration from 0 to 10%. A constant barometric pressure P_0 of 101.325 kPa is used.

2. THEORY

The constituents of air for the following calculation are initially based on the standard air mixture.¹³⁾ The characteristics of the constituents, as listed in Table 1, with the inclusion of a minute trace of carbon monoxide, are the same as given in Refs. 13) and 14). The standard air CO₂ concentration is 314 ppm, and the concentration (mole fraction) of each constituent, shown in Table 1, is modified in proportion to the change in CO₂ content, such that the sum of the mole fractions x_i remains unity. Comprehensive discussions on the computation method have been described,¹⁵⁾ and a brief summary of the theory is given here:

The mole fraction x_w of water vapor in humid air is

$$x_w = hfP_{sv}/P \quad (1)$$

where h is the relative humidity (dimensionless), f is the enhancement factor (Ref. 8), Eq. 23) to correct for the departure of behavior of humid air from that of an ideal gas. At pressure P , the standard vapor pressure P_{sv} is a function of the absolute temperature T (273.15 + temperature t in degrees Celsius). See Ref. 16), p. 5.2, Eq. 4.

With the inclusion of humidity, for a particular value of h , after the CO₂ content has been selected, the mole fraction of water x_w is derived from Eq. (1), and the mole fractions of the constituents are again

modified in proportion (this time without changing the current concentration of CO₂), such that the sum of the modified mole fractions $x'_i = x_i(1 - x_w)$, equals unity. The molar mass of air is given by

$$M = \sum x'_i M_i \quad (2)$$

where M_i is the molar mass of the constituent (i), and the density of air is

$$\rho = PM/(ZRT) \quad (3)$$

where R is the universal gas constant whose numerical value is 8,314.51 J kmol⁻¹ K⁻¹ (Ref. 17), p. 11), and Z is the compressibility factor which is a function of P , x_w , and T . An approximate equation for the computation of the compressibility factor has been published (Ref. 8), Eq. 24).

Touloukian and Makita¹⁸⁾ provided the real-gas equations to calculate the specific heats $C_{p(i)}$ of the constituents at pressure P_0 . Where possible, the real-gas equations are used in this investigation (see list in Appendix A of Ref. 15)). The fractional contributions of the constituents to the specific heat of humid air at 1 atmosphere, C_p^1 are added to give a mean value

$$\overline{C_p^1} = \sum C_{p(i)}^1 x'_i M_i / M \quad (4)$$

For a real gas at the standard pressure, the value of $C_p - C_v$ is not greatly different from the gas constant R , and one may use the approximate equation:

$$C_p - C_v = R \quad (5)$$

It is important to point out that, for dry air, an approximation can also be derived for real-gas application by modifying the right-hand side of Eq. (5) with virial coefficients. However, the virial coefficients for water vapor over the temperature range of interest (0~30°C) are not available, and since this investigation includes water vapor as one of the constituents, the above method with virial coefficients is not used.

By substituting real-gas C_p^1 into Eq. (5), one is able to obtain a relatively comprehensive uncertainty audit with the data given by Touloukian and Makita¹⁸⁾ (Also see Ref. 6), Table III). The specific heats in Eq. (5) are molar heat capacities (units in J kmol⁻¹ K⁻¹). By dividing Eq. (5) with the molar mass M , the specific heats become specific heat capacity per unit mass (units in kJ kg⁻¹ K⁻¹); and substituting C_p^1 for C_p in Eq. (5), one can deduce the constant volume specific heat at 1 atmosphere:

$$C_v^1 = \overline{C_p^1} - R/M \quad (6)$$

Table 1 Composition of standard dry air.

Con- stituent	Molar mass M_i (10 ⁻³ kg mol ⁻¹)	Mole fraction x_i	Contribution $x_i \cdot M_i$ (10 ⁻³ kg mol ⁻¹)
N ₂	28.0134	0.78084	21.873983
O ₂	31.9988	0.209476	6.702981
Ar	39.948	0.00934	0.373114
CO ₂	44.00995	0.000314	0.013819
Ne	20.183	18.18 × 10 ⁻⁶	0.000367
Kr	83.80	1.14 × 10 ⁻⁶	0.000096
CH ₄	16.04303	2 × 10 ⁻⁶	0.000032
He	4.0026	5.24 × 10 ⁻⁶	0.000021
N ₂ O	44.0128	0.27 × 10 ⁻⁶	0.000012
Xe	131.30	0.087 × 10 ⁻⁶	0.000011
CO	28.01	0.19 × 10 ⁻⁶	0.000006
H ₂	2.01594	0.5 × 10 ⁻⁶	0.000001
H ₂ O	18.01534	0	0

From Eq. (5) and Eq. (6), the ratio of specific heats of air for real-gas application is

$$\gamma = \overline{C}_p^1 / C_v^1 \quad (7)$$

The speed of sound according to Laplace's adiabatic assumption for an ideal gas, is given by

$$c = (\gamma_i P / \rho)^{1/2} \quad (8)$$

where γ_i , P and ρ are the ideal specific heat ratio, pressure, and density of the medium, respectively.

Based on the ideal-gas equation resulting from Boyle's law, and substituting γ for real-gas application into Eq. (8), an approximate equation for the sound speed is

$$c = (RT\gamma/M)^{1/2} \quad (9)$$

Similar to Eq. (5), a relatively comprehensive uncertainty audit can be obtained for Eq. (9). It must be noted that if the ideal-gas specific heat ratio γ_i were utilized in Eq. (9), an approximate equation for real-gas sound speed may be obtained by modifying the right-hand side of Eq. (9) with

virial coefficients. Again, as pointed out earlier, the virial coefficients of interest for water vapor are not available.

The characteristic impedance ρc is derived from the product of Eq. (3) and Eq. (9), and is given by

$$\rho c = (P/Z)[\gamma M / (RT)]^{1/2} \quad (10)$$

where Z is the compressibility factor.

In a previous investigation, this author presented a ρc equation (Ref. 5), Eq. 1) which does not include the compressibility factor. That approach is consistent with the density equation given in Ref. 14), Eq. (42). In view of the need to develop equations for real-gas applications, the compressibility factor Z is included in this investigation as shown in Eq. (3) and Eq. (10). However, the difference between the numerical value (428.11 rays) for $(\rho c)_0$ given in Ref. 7), Eq. (3), and the value of $(\rho c)_0 = 428.37$ (See Table 2), is 0.06%. It is important to note that in both investigations, the sound speed c_0 remains the same (symbols with subscript zero denote ref-

Fig. 1 The variation of sound speed with humidity, carbon dioxide content and temperature.

Table 2 Reference values (symbols with subscript zero) of normalized data for dry standard air at 0°C, and at a barometric pressure of 101.325 kPa.

Functions	Numerical values	Units
c_0	331.29	m s^{-1}
$(\rho c)_0$	428.37	$\text{kg m}^{-2} \text{s}^{-1}$
$(\overline{C}_p^1)_0$	1.0051	$\text{kJ kg}^{-1} \text{K}^{-1}$
$(C_v^1)_0$	0.7181	$\text{kJ kg}^{-1} \text{K}^{-1}$
γ_0	1.3998	dimensionless
ρ_0	1.2930	kg m^{-3}
M_0	28.9644	$10^{-3} \text{kg mol}^{-1}$

reference values for dry standard air at 0°C, see Table 2).

3. DATA PRESENTATION

For standard dry air (with 314 ppm carbon dioxide) at 0°C and at a pressure of 101.325 kPa,

the numerical values for the reference parameters c_0 , $(\rho c)_0$, $(\overline{C}_p^1)_0$, $(C_v^1)_0$, γ_0 , ρ_0 , and M_0 are listed in Table 2. Over the temperature range from 0~30°C, in steps of 10°C, the variation of the normalized data for the above parameters with relative humidity h from 0 to 1, and with CO₂ content from 0 to 10 percent, are shown in Fig. 1 to Fig. 7.

In general, the normalized values $(\overline{C}_p^1)/(\overline{C}_p^1)_0$, $(C_v^1)/(C_v^1)_0$, and c/c_0 become larger with the inclusion of humidity and rising temperature; and they also vary inversely to the CO₂ content. Similarly, ρ/ρ_0 , $(\rho c)/(\rho c)_0$ and M/M_0 vary directly with the CO₂ content, but inversely with humidity and temperature. However, the normalized value γ/γ_0 becomes smaller with the increase of humidity, temperature and CO₂ content.

The curves shown in Fig. 1 to Fig. 7 deviate from a straight line by amounts ranging from approximately 15 ppm to 300 ppm; and for dry air, one can observe from Fig. 7 that the variation of M/M_0 with CO₂ content is unaffected by temperature variations.

Fig. 2 The variation of characteristic impedance with humidity, carbon dioxide content and temperature.

Fig. 3 The variation of constant pressure specific heat with humidity, carbon dioxide content and temperature.

There are experimental and theoretical data which support some of the predictions shown above:

The variation of the specific heat ratio in standard air with humidity has been verified experimentally by Wong and Embleton.⁷⁾ The experimental data was within 100~250 ppm from the theoretical prediction which is identical to the approximate method used in this investigation (see Ref. 7), Figs. 3 and 4).

The slope of the experimental data curve provided by Harris³⁾ on the variation of sound speed in air with humidity from 0.3 to 1, at 20°C is practically the same as the slope of the theoretical curve given by Wong and Embleton (Ref. 7), Fig. 2). The maximum deviation between Harris' experimental data and the theoretical prediction by Wong and Embleton,⁷⁾ is approximately 400 ppm. Morfey and

Howell⁴⁾ gave theoretical sound speed predictions which were in good agreements with the measurements obtained by Harris³⁾ (see Ref. 4), Fig. 1).

4. APPROXIMATE EQUATIONS

With the above computed data, one can deduce approximate empirical equations to facilitate numerical calculations for the variations of the above physical properties of standard air with humidity, carbon dioxide content and temperature. The general empirical equation for the function $F(hCt)$ which enables one to calculate the variation of the normalized physical parameters c/c_0 , $\rho c/(\rho c)_0$, $\bar{C}_p/(\bar{C}_p)_0$, $C_v/(\bar{C}_v)_0$, γ/γ_0 , ρ/ρ_0 , and M/M_0 with relative humidity h , carbon dioxide content C and temperature t , is given by

Fig. 4 The variation of constant volume specific heat with humidity, carbon dioxide content and temperature.

Fig. 5 The variation of specific heat ratio with humidity, carbon dioxide content and temperature.

Fig. 6 The variation of density with humidity, carbon dioxide content and temperature.

$$\begin{aligned}
 F(hCt) = & a_0 + a_1t + a_2t^2 + a_3t^3 + a_4C + a_5Ct + a_6Ct^2 \\
 & + a_7Ct^3 + a_8h + a_9ht + a_{10}ht^2 + a_{11}ht^3 \\
 & + a_{12}C^2 + a_{13}h^2 + a_{14}hCt
 \end{aligned} \quad (11)$$

where a_0 to a_{14} are coefficient constants, C is carbon dioxide content in percent and t is the temperature in degrees Celsius.

The coefficients for the computation of the above normalized physical parameters are listed in Table 3. With Eq. (11), the physical properties of air can be deduced by multiplying $F(hCt)$ with the corresponding reference parameters shown in Table 2.

Over the range for relative humidity from 0 to 1.0, carbon dioxide content from 0 to 10 percent, temperature from 0 to 30 degrees Celsius, and at a barometric pressure of 101.325 kPa, the maximum differences between the numerical values obtained with Eq. (11), and the corresponding predicted values obtained with the computation procedure¹⁵⁾ (such as

those data shown in Fig. 1 to Fig. 7) are less than those listed in Table 4. It can be seen from the latter that the maximum deviations range from 14 ppm for ρ/ρ_0 and M/M_0 to 90 ppm for $C_v/(C_v)_0$.

5. UNCERTAINTIES

To provide a detailed error analysis for the theoretical results presented here is very difficult. It is realistic to give an estimation of their uncertainties with the information supplied by Touloukian and Makita.¹⁸⁾ Their recommended mean and maximum deviations, summarized in Ref. 6), Table III, are dependent on their judgement of the original experimental and theoretical data.

From the molar mass contributions of each constituent (Table 1), one can see that the predominant constituents are nitrogen and oxygen; and it is reasonable to weight their mean and maximum deviations (Ref. 6), Table III) with their correspond-

Fig. 7 The variation of the molar mass with humidity, carbon dioxide content and temperature.

ing fractional molar mass contributions: $x_i M_i / (\sum x_i M_i)$. For dry air, the weighted mean and maximum deviations for the above major constituents are as follows:

	Deviations, ppm	
	Mean	Max.
N ₂	300	1,900
O ₂	200	900

For humid air, the uncertainty due to water vapor concentration alone is relatively small. It can be shown that for a relative humidity of 0.95 at 20°C, the weighted mean and maximum deviations contributed by water vapor are only 4 ppm and 10 ppm, respectively. From the above, by taking the rms values of the deviations, one may assume that the

effects of humid air on the mean deviation of the uncertainties for C_p , C_v , and γ are approximately 360 ppm. The percentage deviations shown in Ref. 6), Table III, apply to a relatively wide temperature range. For example, the maximum deviation of 2,500 ppm for N₂ applies to temperatures between 250 K and 780 K. By examining the graphical data presented in Ref. 18), and in view of the relatively limited temperature range (0~30°C) of this investigation, with consideration given to the good correlation between experimental and theoretical data discussed earlier, it may be reasonable to assume that the overall uncertainty of the computed data for C_p , C_v and γ due to humidity is of the order of 400 ppm.

Similarly, the deviations for CO₂, (Ref. 6), Table III), apply to a relatively wide temperature range between 220 K and 540 K. The weighted mean

Table 3 Numerical values of the coefficients for the computation of some normalized physical parameters with Eq. (11).

Coefficient constants	$F(hCt)$						
	c/c_0	$\rho c/(\rho c)_0$	$\overline{C_p^1}/(\overline{C_p^1})_0$	$C_v^1/(C_v^1)_0$	γ/γ_0	ρ/ρ_0	M/M_0
a_0	1.000100	0.999965	1.000102	1.000055	1.000034	0.999838	0.999837
a_1	1.8286×10^{-3}	-1.84466×10^{-3}	1.2694×10^{-3}	6.9050×10^{-6}	-2.8100×10^{-5}	-3.67222×10^{-3}	0.0000
a_2	-1.6925×10^{-6}	4.5935×10^{-6}	3.2570×10^{-7}	7.7000×10^{-7}	-2.1210×10^{-7}	1.33797×10^{-5}	0.0000
a_3	0.0000	0.0000	0.0000	0.0000	0.0000	-4.1309×10^{-8}	0.0000
a_4	-3.1066×10^{-3}	2.0947×10^{-3}	-2.6824×10^{-3}	-1.6660×10^{-3}	-1.01223×10^{-3}	5.19609×10^{-3}	5.19593×10^{-3}
a_5	-7.9762×10^{-6}	-6.54469×10^{-6}	1.3121×10^{-5}	2.0937×10^{-5}	-5.2500×10^{-6}	-1.90785×10^{-5}	8.5000×10^{-9}
a_6	3.4000×10^{-9}	2.0328×10^{-8}	-1.1500×10^{-8}	-1.1150×10^{-7}	1.1290×10^{-8}	6.8333×10^{-8}	0.0000
a_7	0.0000	0.0000	0.0000	3.9300×10^{-10}	0.0000	-1.7900×10^{-10}	0.0000
a_8	8.9180×10^{-4}	-1.3378×10^{-3}	3.0228×10^{-3}	3.3256×10^{-3}	-3.4920×10^{-4}	-2.26848×10^{-3}	-2.2770×10^{-3}
a_9	7.7893×10^{-5}	-9.7953×10^{-5}	2.5940×10^{-4}	2.8100×10^{-4}	-2.8560×10^{-5}	-1.63756×10^{-4}	-1.7760×10^{-4}
a_{10}	1.3795×10^{-6}	-2.0400×10^{-6}	4.4158×10^{-6}	5.0900×10^{-6}	-5.9000×10^{-7}	-3.53537×10^{-6}	-3.5247×10^{-6}
a_{11}	9.5330×10^{-8}	-9.4700×10^{-8}	2.8680×10^{-7}	3.3000×10^{-7}	-2.9710×10^{-8}	-1.4170×10^{-7}	-1.89396×10^{-7}
a_{12}	1.2990×10^{-6}	-2.82134×10^{-6}	1.2253×10^{-5}	6.1838×10^{-6}	4.23427×10^{-6}	0.0000	0.0000
a_{13}	4.8016×10^{-5}	3.0000×10^{-5}	1.0630×10^{-4}	1.8000×10^{-4}	8.0000×10^{-7}	0.0000	0.0000
a_{14}	-1.4660×10^{-6}	8.5700×10^{-7}	-4.1370×10^{-6}	-4.5300×10^{-6}	5.1000×10^{-7}	2.0900×10^{-3}	-3.0000×10^{-9}

Table 4 The maximum deviations between the numerical values for the normalized physical parameters obtained with Eq. (11) by applying the coefficient constants listed in Table 3, and the corresponding predicted values, are less than those shown here.

$F(hCt)$	Maximum deviation (ppm)
c/c_0	± 48
$\rho c/(\rho c)_0$	± 35
$\overline{C_p^1}/(\overline{C_p^1})_0$	± 80
$C_v^1/(C_v^1)_0$	± 90
γ/γ_0	± 17
ρ/ρ_0	± 14
M/M_0	± 14

deviations for the uncertainty due to 1% and 10% CO₂ concentration are 24 ppm and 240 ppm, respectively. By taking the rms values of the mean deviations, including 400 ppm humidity contribution, the overall uncertainties for C_p , C_v , and γ due to the combined effects of humidity and CO₂ are each 401 ppm and 466 ppm for 1% and 10% CO₂ concentration, respectively.

For the variation of the speed of sound in air with humidity, it has been shown²⁾ that the uncertainty is about 400 ppm. Hence, the overall uncertainty due to the combined effects of humidity and CO₂ concentration is also 401 ppm and 466 ppm for 1% and 10% CO₂ concentration, respectively.

The uncertainty in air density due to the equation itself has been shown to be ranging from 40 ppm to 130 ppm (Ref. 8), p. 39). Based on 130 ppm, the combined effects of humidity and CO₂ concentration on the uncertainty of ρ are approximately 132 ppm and 273 ppm for 1% and 10% CO₂ concentration, respectively.

The molar mass M for air (see Eq. (2)), is the sum of the products of the mole fraction x_i of the constituents and the corresponding molar mass M_i , which is based upon the carbon-12 isotope. The molar mass values, listed in Table 1, are accepted internationally. However, the mole fraction x_i depends on the location at which measurements have been taken, and the uncertainty in M is relatively difficult to determine precisely. One may assume that the uncertainty in M is much less than

that for the air density ρ which is a function of the gas constant R , the compressibility factor Z and the molar mass M .

Based on the above uncertainties on the air density ρ and on the speed of sound c , the combined effects of humidity and CO₂ concentration on the uncertainty of the characteristic impedance ρc can be shown to be less than 533 ppm and 739 ppm for 1% and 10% CO₂ concentration, respectively.

The reference value of 331.29 ms⁻¹ for the speed of sound c_0 in standard air (at 0°C), shown in Table 2, has an uncertainty of approximately 200 ppm (Ref. 1), p. 1360). It may be interesting to point out that the sound speed at sea level at 15°C, has been quoted as 340.294 ms⁻¹ in two references: (a) U.S. Standard Atmosphere (Ref. 14), p. 20, table 10) and (b) ISO 2533: Standard Atmosphere (Ref. 13), table 6). The sea level sound speed quoted above may be reduced to a corresponding value at 0°C, $c_0 = 331.318$ ms⁻¹ which is 85 ppm higher than the reference value shown in Table 2. However, both of these references did not provide any estimate of uncertainty or detailed description of the computation method used.

6. CONCLUSION

A comprehensive description on the computation of the variations in some acoustical and thermodynamic properties of air with humidity and carbon dioxide content is presented. The computation is based on standard air over a temperature range of 0~30°C and at a barometric pressure of 101.325 kPa. With information available, estimations on the uncertainties of the numerical method are formulated. The uncertainties of the computed data for c_0 , C_p , C_v , and γ , are each 401 ppm and 466 ppm for 1% and 10% CO₂ concentration, respectively. The uncertainty for the air density ρ is between 132 ppm and 273 ppm, and for the characteristic impedance ρc , the uncertainty increases to 533 ppm and 739 ppm for 1% and 10% CO₂ concentration, respectively.

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G. S. K. WONG: ACOUSTICAL AND THERMODYNAMIC PROPERTIES OF AIR

Dr. George S. K. Wong obtained his Ph. D. and M. Sc. Tech. degrees from the University of Manchester Institute of Science and Technology, University of Manchester, England, for his research work on precision measurements and automatic correction of alignment errors in machine tools. In 1966 he joined the Division of Physics of the National Research Council Canada in Ottawa, and he became a senior research officer in 1979. His field of

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