

# The variation of the specific heat ratio and the speed of sound in air with temperature, pressure, humidity, and CO<sub>2</sub> concentration

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This paper describes a precise numerical calculation of the specific heat ratio and speed of sound in air as a function of temperature, pressure, humidity, and CO<sub>2</sub> concentration. The above parameters are calculated utilizing classical thermodynamic relationships and a real gas equation of state over the temperature range 0 °C–30 °C. The shortcomings of previous determinations are also discussed. For both parameters, the coefficients of an interpolating equation are given, which are suitable for use in applications requiring high precision. The overall uncertainty in the specific heat ratio is estimated to be less than 320 ppm and the uncertainty in the speed of sound is similarly estimated to be less than 300 ppm.

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## LIST OF SYMBOLS

$c_0$	speed of sound (zero frequency)
$c_\phi$	speed of sound inc. dispersion
$\gamma$	specific heat ratio ( $C_p/C_v$ )
$C_p$	specific heat at constant pressure
$C_v$	specific heat at constant volume
$C_p^0$	ideal gas specific heats
$C_p^1$	real gas specific heats
$V$	molar volume
$R$	universal gas constant
$M$	molecular mass
$p$	pressure (atmospheric)
$p_0$	standard pressure (101 325 Pa)
$\rho$	density
$T$	thermodynamic temperature
$t$	celsius temperature

$B, C$	second and third virial coefficients
$B_{aa}$	second virial coefficient for dry air
$B_{ww}$	second virial coefficient for H <sub>2</sub> O vapor
$B_{aw}$	second interaction coefficient for air/H <sub>2</sub> O
$x_c$	mole fraction of Co <sub>2</sub> in air
$x_w$	water vapor mole fraction in air
$x_a$	mole fraction for dry air
RH	relative humidity in %
$h$	relative humidity as a fraction
$\alpha_{vO}$	attenuation coefficient for O <sub>2</sub> relaxation
$\alpha_{vN}$	attenuation coefficient for N <sub>2</sub> relaxation
$f_{rO}$	relaxation frequency of O <sub>2</sub>
$f_{rN}$	relaxation frequency of N <sub>2</sub>
$p_{sv}$	saturation vapor pressure in air
$f$	enhancement factor for moist air

## INTRODUCTION

The calibration of laboratory standard microphones by the reciprocity technique requires the precise determination of various parameters for air such as the ratio of specific heats and the speed of sound in air. As these calibrations are carried out under varying environmental conditions the effects of temperature, pressure, humidity, and CO<sub>2</sub> concentration on these parameters also need to be considered. An error of 0.001 in specific heat ratio  $\gamma$  causes an error of 0.003 dB in the sensitivity of a microphone calibrated using the standard 20 cm<sup>3</sup> coupler, while a 0.15 m s<sup>-1</sup> error in the speed of sound  $c_0$  causes the final microphone sensitivity to be in error by approximately 0.005 dB for the 3 cm<sup>3</sup> or plane-wave coupler.

Recent derivations of the speed of sound in air by Wong<sup>1</sup> suggest a new value of 331.29 m s<sup>-1</sup> ± 200 ppm at standard pressure and temperature (STP: 101 325 Pa and 0 °C). This proposed new value is almost 0.2 m s<sup>-1</sup> lower

than previously accepted values of near 331.46 m s<sup>-1</sup>. Certain assumptions in this work, however, lead to errors as discussed by Greenspan in his comments on Wong's paper.<sup>2</sup> Wong's method hinges on the determination of the specific heat of air described in a previous paper by Wong and Embleton.<sup>3</sup> In this latter paper, Wong and Embleton calculate the specific heat for air at constant pressure,  $C_p$ , on a constituent basis and then calculate the specific heat at constant volume,  $C_v$ , using the following relationship:

$$C_p - C_v = R/M, \quad (1)$$

where  $R$  is the universal gas constant and  $M$  is the molecular weight. This relationship is only true for an ideal gas and the departure for a real gas, as pointed out by Greenspan, is significant. Wong's second assumption is the use of the following equation for calculating  $c_0$  which again is only accurate for an ideal gas:

$$c_0^2 = \gamma p / \rho, \quad (2)$$

where  $\rho$  is the density and  $p$  the ambient pressure.

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The aim of this paper is to extend the analysis done by Wong and Embleton by removing any ideal gas simplifications of thermodynamic relationships. The analysis also includes pressure as a variable in the formulas for calculating  $\gamma$  and  $c_0$ . The effect of pressure is of concern in the work described below because the National Metrology Laboratory in South Africa is situated approximately 1200 m above sea level at an atmospheric pressure of nominally 86 500 Pa.

## I. THEORY

The equation of state for a real gas can be written as

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots, \quad (3)$$

where  $V$  is the molar volume,  $T$  is the thermodynamic temperature, and  $B$  and  $C$  are the second and third virial coefficients of state, respectively. Changing the variable on the right-hand side from  $V$  to  $p$  and truncating the series after the second virial coefficient introduces negligible error at low gas densities. Equation (3) then becomes

$$\frac{pV}{RT} = 1 + \frac{Bp}{RT}. \quad (4)$$

Hirschfelder *et al.*,<sup>4</sup> pp. 230–232, give standard thermodynamic relationships that permit the correction of ideal gas specific heats to real gas specific heats using a real gas equation of state. The final expressions for  $C_p$ ,  $C_v$ , and  $c_0$  after substituting the above equation of state, up to the second virial coefficient, and eliminating  $V$  by substituting back  $V = RT/p$  for correction terms are

$$C_p^1 = C_p^0 - \frac{R}{M} \frac{p}{RT} \left( T^2 \frac{d^2 B}{dT^2} \right), \quad (5)$$

where  $C_p^0$  is the ideal gas specific heat and  $C_p^1$  is the real gas specific heat. Then,  $C_v^1$  can be calculated from

$$C_v^1 = C_p^1 - \frac{R}{M} \left[ 1 + \frac{2p}{RT} \left( T \frac{dB}{dT} \right) \right], \quad (6)$$

whereafter it is a simple matter to calculate  $\gamma$  as the ratio of  $C_p^1$  to  $C_v^1$  which is a function of pressure and temperature. In the above equations, the specific heats are in  $\text{kJ kg}^{-1} \text{K}^{-1}$  and  $M$  is in  $\text{g mol}^{-1}$ . The speed of sound can then be calculated from

$$c_0^2 = \gamma \left( \frac{\delta p}{\delta \rho} \right), \quad (7)$$

which by substituting the equation of state becomes

$$c_0^2 = \gamma \frac{RT}{M} \left( 1 + \frac{2pB}{RT} \right) \quad (8)$$

also as a function of pressure and temperature where  $M$  is now expressed in  $\text{kg mol}^{-1}$ . Equations (5), (6), and (8) are the same as those given by Greenspan in Ref. 2.

The speed of sound calculated from the above relationships is the zero frequency speed of sound and does not

TABLE I. Constituents of air.

Constituent	Molar mass $M_i$ ( $10^{-3} \text{ kg mol}^{-1}$ )	Mole fraction $x_i$	Contribution $x_i M_i$ ( $10^{-3} \text{ kg mol}^{-1}$ )
N <sub>2</sub>	28.0134	0.78084	21.873 983 3
O <sub>2</sub>	31.9988	0.209476	6.702 980 6
Ar	39.948	0.00934	0.373 114 3
CO <sub>2</sub>	44.009 95	0.000314	0.013 819 1
Ne	20.183	$18.18 \times 10^{-6}$	0.000 366 9
Kr	83.80	$1.14 \times 10^{-6}$	0.000 095 5
CH <sub>4</sub>	16.043 03	$2.0 \times 10^{-6}$	0.000 032 1
He	4.0026	$5.24 \times 10^{-6}$	0.000 021 0
N <sub>2</sub> O	44.0128	$0.27 \times 10^{-6}$	0.000 011 9
Xe	131.3	$0.087 \times 10^{-6}$	0.000 011 4
CO	28.01	$0.19 \times 10^{-6}$	0.000 005 3
H <sub>2</sub>	2.015 94	$0.5 \times 10^{-6}$	0.000 001 0
H <sub>2</sub> O	18.015 34	0.0	0.0

include any corrections for dispersion due to the vibrational relaxation effects of N<sub>2</sub> and O<sub>2</sub> which are functions of frequency.

## II. DATA SOURCES FOR $C_p^0$

The first step in the calculation of  $\gamma$  and  $c_0$  is to select a source of data for the specific heat at constant pressure for each constituent of air. Wong and Embleton used the data for  $C_p$  from Touloukian *et al.*<sup>5</sup> for the constituents of air to calculate  $C_p$ . They used the real gas specific heat where it was available but for several of the constituents including water vapor had to resort to ideal gas data.

Touloukian *et al.* is a compilation of specific heat data for various gases from 595 sources which have been critically evaluated. Only what were considered to be reliable results were included in the average which is presented for each gas. A tabulation for air is also given, where  $C_p^1$  is taken directly from Hilsenrath *et al.*,<sup>6</sup> while  $C_p^0$  for air is an average of data taken from Hilsenrath *et al.* as well as two other sources.

For air at STP in Touloukian *et al.*,  $C_p^1$  is 1.0057  $\text{kJ kg}^{-1} \text{K}^{-1}$  but when  $C_p^1$  is calculated on a constituent basis from the same reference a value of 1.0051  $\text{kJ kg}^{-1} \text{K}^{-1}$  is found which shows a slight inconsistency. The formulas for ideal gas data in Touloukian *et al.* are however consistent. For this reason it was decided to use the ideal gas data for each constituent from this reference to calculate  $C_p^0$  for air and then correct  $C_p^0$  to  $C_p^1$  using the virial relationship given in Eq. (5) by Hirschfelder *et al.*

## III. MODEL FOR STANDARD ATMOSPHERE

The constituents of standard atmosphere are given in ISO 2533-1975.<sup>7</sup> With the exception of CO<sub>2</sub> and H<sub>2</sub>O, the concentrations of the various constituents are assumed to be constant in this work. Table I lists the 13 most important constituents of air together with their mole fraction, molar mass, and their contribution toward the molar mass of air. Only the first five constituents and the amount of water vapor have much effect on the parameters that will be derived in this work. The constituents with low contributions to the molar mass are almost negligible but are included here for the sake of completeness.

#### IV. VIRIAL COEFFICIENTS OF STATE

In order to evaluate Eqs. (5), (6), and (8), numerical values for the second virial coefficient of air are required together with their derivatives. A recent tabulation of the second virial coefficient for a number of gases is presented in Kaye and Laby<sup>8</sup> in a useful format. The coefficients  $a$ ,  $b$ , and  $c$  for the following equation are tabulated together with a temperature range over which they are considered to be valid:

$$B(T) = a - be^{c/T}. \quad (9)$$

In the above equation,  $B(T)$  is the second virial coefficient in  $\text{cm}^3 \text{mol}^{-1}$ . The temperature range is more than wide enough in the case of most constituents with the exception of He which is limited to the range 7 K–150 K and water vapor which is only valid above 293 K (20 °C).

The American Institute of Physics Handbook<sup>9</sup> also gives a tabulation of virial coefficients for various gases. In this reference, the second virial coefficient for He is given over a wider temperature range than in Kaye and Laby. The virial coefficient for He is thus taken from the American Institute of Physics Handbook. Again in this reference, as in Kaye and Laby, the virial coefficients for water vapor are only given at higher temperatures and are therefore not of any use in this work. Fortunately, several comprehensive studies into the second virial coefficient for water vapor have been undertaken. Hyland<sup>10</sup> gives the following equation:

$$B(T) = 33.97 - \frac{55\,306}{T} 10^{72\,000/T^2} \text{ cm}^3 \text{mol}^{-1}, \quad (10)$$

which is valid over the full temperature range of interest.

The differentials of the virial coefficients for each constituent can be found by differentiating Eq. (9) or (10) with respect to  $T$ .

The question now arises of how to combine the virial coefficients for the various constituents in order to give an accurate virial coefficient for air. In calculating the virial coefficient for a mixture of two gases, an equation of the following form is commonly used:

$$B_{\text{mix}} = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}, \quad (11)$$

where  $B_{11}$  is the second virial coefficient for gas 1,  $B_{22}$  is the second virial coefficient for gas 2 and  $B_{12}$  is the second interaction virial coefficient between the two gases. In a completely rigorous treatment of the dry air mixture, it would be necessary to take into account the interaction virial coefficients for all possible interactions between the various constituents. However, since the virial coefficients for  $\text{N}_2$  and  $\text{O}_2$  are not significantly different in magnitude, it was found that the error in neglecting the interaction virial coefficient is very small. As these are the two most important constituents of dry air the interaction virial coefficients can be safely ignored in determining a second virial coefficient for dry air. A simpler form of combination can then be used:

$$B_{aa} = \sum_{i=1}^n B_i x_i \frac{M_i}{M_{\text{air}}}, \quad (12)$$

where  $B_{aa}$  is the second virial coefficient for dry air,  $x_i$  is the mole fraction of the  $i$ th constituent,  $M_i$  is the molecular mass of the  $i$ th constituent and  $M_{\text{air}}$  is molecular mass of dry air. The second virial coefficient for dry air obtained using this method of combination has a maximum deviation of only  $0.07 \text{ cm}^3 \text{mol}^{-1}$  from the virial coefficient for dry air given by Hyland.

The same is not true for the mixture of air and water vapor where neglecting the interaction virial coefficient  $B_{aw}$  introduces a significant error in the second virial coefficient for moist air. The error amounts to  $8.42 \text{ cm}^3 \text{mol}^{-1}$  at  $t=20^\circ\text{C}$ ,  $p=101325 \text{ Pa}$  and  $\text{RH}=50\%$  and is discussed more fully in Sec. VI. Equation (11) is thus used to calculate the mixture virial coefficient for moist air which becomes

$$B_{\text{mix}} = x_a^2 B_{aa} + 2x_a x_w B_{aw} + x_w^2 B_{ww}, \quad (13)$$

where  $B_{ww}$  is the second virial coefficient for water vapor and  $B_{aw}$  is the second interaction virial coefficient between the two gases. Here,  $x_a$  and  $x_w$  are the mole fractions of dry air and water vapor, respectively. The interaction coefficient  $B_{aw}$  is taken from Hyland's Eq. (9).

The calculated second virial coefficient for the moist air mixture can then be used in Eqs. (5), (6), and (8).

#### V. RESULTS

Calculations for  $\gamma$  and  $c_0$  were performed by setting up a computer spreadsheet with the data for each constituent. The effect of temperature, pressure, humidity, and  $\text{CO}_2$  concentration on the values for  $\gamma$  and  $c_0$  were then analyzed. The results are presented graphically in Fig 1. Note that although the graph of the speed of sound would seem to indicate that this parameter is independent of pressure, this is only due to the resolution of the graph. In fact the curves all have a slight positive slope with increasing pressure, which for the  $20^\circ\text{C}$  curve, is in the region of 1 ppm.

#### VI. DISCUSSION OF RESULTS

The dry air value for  $\gamma$  at STP calculated in this paper is 1.4029. This value is in good agreement with the value for  $\gamma$  at STP interpolated from the tables in Hilsenrath *et al.* of 1.4027 and the value given in the American Institute of Physics Handbook<sup>11</sup> of 1.403. US Standard Atmosphere<sup>12</sup> adopts a value for  $\gamma$  of 1.400 independent of temperature, pressure, and humidity which is obviously a simplification although this may be sufficient for the desired accuracy level in this publication. There are however substantial differences between the value calculated in this paper for dry air at STP and the theoretical value calculated by Wong and Embleton<sup>13</sup> which is 0.0031 (0.23%) lower. This deviation is due to the assumptions made by Wong and Embleton discussed in the introduction.

The difference between the values calculated for different levels of humidity in this paper and those measured

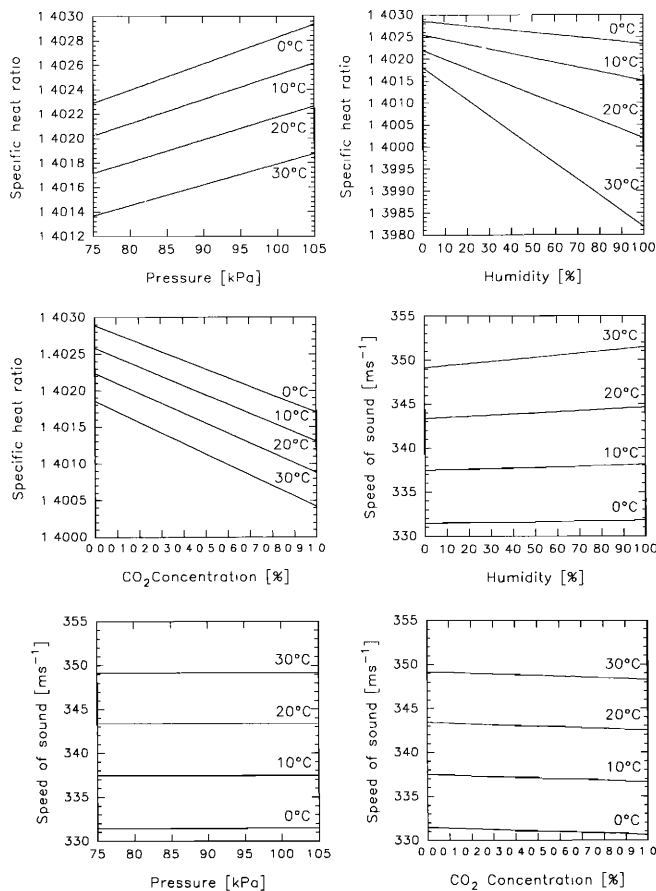


FIG. 1. Results from spreadsheet calculations for  $\gamma$  and  $c_0$ . For each graph the other variables have been held at  $x_c=314$  ppm,  $p=101\,325$  Pa,  $RH=0\%$ , and  $t=0^\circ\text{C}$ .

by Wong and Embleton<sup>14</sup> are presented graphically in Fig. 2. Wong and Embleton's theoretical values calculated in Ref. 13 are also plotted on the graph. All values have been normalized to emphasize the form of the graph and not the absolute values. The experimental values, shown as dots (250 Hz) and triangles (500 Hz), are Wong and Embleton's results for  $20^\circ\text{C}$ . The graph shows fairly good agreement between the normalized experimental results and the normalized values calculated in this paper. Similarly, there is good agreement between Wong and Embleton's theoretical and experimental results.

The value calculated in this paper for  $c_0$  in dry air at STP is  $331.46\text{ m s}^{-1}$  which is close to Greenspan's value of  $331.44\text{ m s}^{-1}$  calculated from a different source of virial coefficients ( $\text{CO}_2$ -free, dry air). The value for  $c_0$  in Table 10 of U.S. Standard Atmosphere, 1976 is  $340.294\text{ m s}^{-1}$  at  $15^\circ\text{C}$ , calculated from Eq. (2) using the assumed value for  $\gamma$  of 1.400 which will obviously not be in agreement with the value calculated in this paper of 340.44 at  $15^\circ\text{C}$  which is for a real gas.

Wong in Ref. 1 and Table II give a very useful review of speed of sound investigations dating back to 1919. From this table, one can obtain substantial experimental evidence to support a value for the speed of sound at STP of near  $331.45\text{ m s}^{-1}$ . Wong however, in the same reference, presents arguments for a speed of sound in dry air at STP

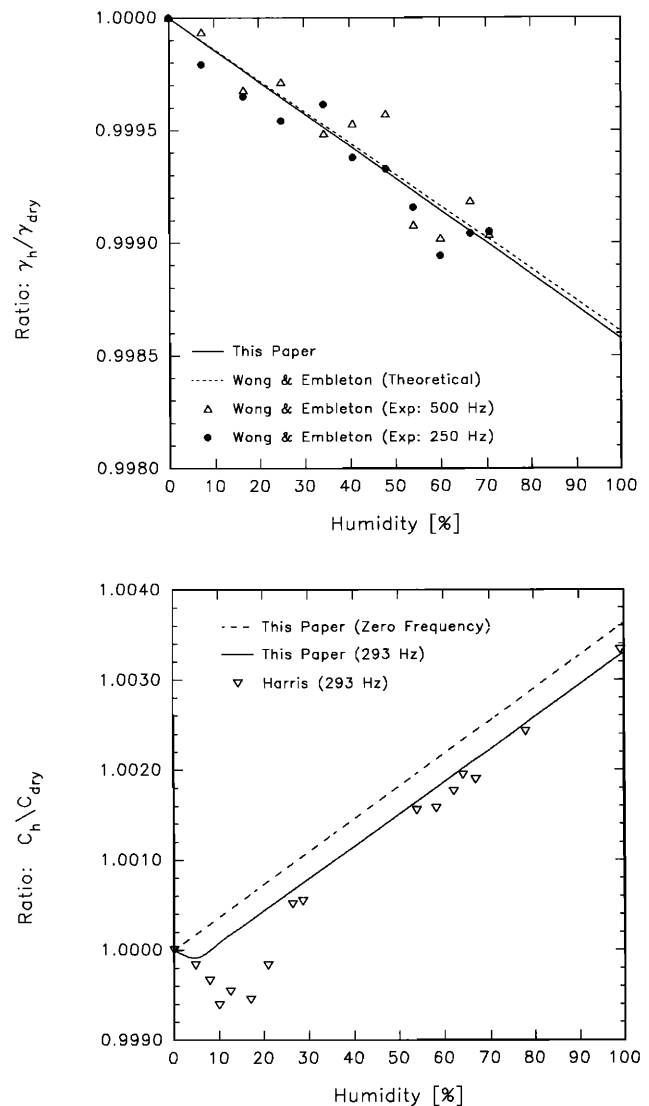


FIG. 2. Comparison of results calculated in this paper and the results of Wong and Embleton<sup>3,14</sup> and Harris<sup>18</sup> for  $t=20^\circ\text{C}$  and  $p=101\,325$  Pa.

which is substantially lower at  $331.29\text{ m s}^{-1}$ . As pointed out earlier in this paper, if the ideal gas assumptions are removed from Wong's method the value calculated for  $c_0$  is close to  $331.45\text{ m s}^{-1}$ .

It should be emphasized at this point that the differences between the values calculated in this paper and those calculated by Wong and Embleton for both  $\gamma$  and  $c_0$  do not arise from differences in the selection of the source of data for  $C_p$  or from the correction of the ideal gas specific heats to real gas specific heats. In fact the differences are almost

TABLE II. The second virial coefficients for air and water vapor at  $20^\circ\text{C}$  in  $\text{cm}^3\text{ mol}^{-1}$ .

Source of data	$B_{aa}$	$B_{ww}$	$B_{aw}$
Kaye and Laby <sup>8</sup>	-9.07	-1251.7	...
Hyland <sup>10</sup>	-9.05	-1264.7	-30.9
American Institute of Physics Handbook <sup>11</sup>	-9.04	...	...

entirely due to Wong and Embleton's use of Eqs. (1) and (2) which assume an ideal gas situation rather than Eqs. (6) and (8) which have been corrected for a real gas situation.

The differences in  $c_0$  at varying humidity levels is also presented in Fig. 2 for a number of sources. The zero frequency curve is  $c_0$  calculated in this paper. The 293-Hz curve is derived from the zero frequency curve by applying a correction for dispersion. Morfey and Howell<sup>15</sup> proposed a correction of the form

$$\frac{1}{c_0} - \frac{1}{c_\phi} = \frac{\alpha_{vN}}{2\pi f_{vN}} + \frac{\alpha_{vO}}{2\pi f_{vO}} \quad (14)$$

where  $c_\phi$  is the speed of sound including effects of dispersion,  $\alpha_{vN}$  and  $\alpha_{vO}$  are the plane-wave attenuation coefficients due to vibrational relaxation of  $N_2$  and  $O_2$ , respectively, and  $f_{vN}$  and  $f_{vO}$  are the relaxation frequencies for  $N_2$  and  $O_2$ . Morfey and Howell used the attenuation coefficients and relaxation frequencies given in ANSI S1.26-1978<sup>16</sup> to calculate  $c_\phi$ . More recent work on low-frequency absorption of sound by Zuckerwar and Meredith<sup>17</sup> has rectified the shortcomings of the ANSI standard at frequencies below 1000 Hz by making extensive measurements at frequencies between 10 and 2500 Hz. In the light of their experimental results, some modifications to the recommended formulae for  $f_{vN}$  and  $f_{vO}$ , given in the ANSI standard, are proposed by Zuckerwar and Meredith.

The differences between the values obtained by Morfey and Howell for  $c_\phi$ , using the formulas for  $\alpha$  and  $f_r$  from the ANSI standard, and calculations in this paper based on the formulae proposed by Zuckerwar and Meredith were found to be very small.

The data points on the graph (inverted triangles) taken from Harris<sup>18</sup> for 293 Hz show an unexplained difference at low humidities which was discussed in Morfey and Howell's paper. At levels of humidity above 30% however, the agreement is better although there is some systematic shift of the curves which is as yet also unexplained.

The results for  $C_p^I$  and  $C_v^I$  showed a most interesting trend. From Table II, it can be seen that the second virial coefficient for water vapor is two orders of magnitude larger than that for dry air, which leads to a much larger correction being applied  $C_p^O$  to compensate for gas imperfections. At 20 °C the ideal gas specific heat for water vapor is 1.8624 kJ kg<sup>-1</sup> K<sup>-1</sup> while the real gas specific heat, calculated via the virial coefficients, is 2.7638 kJ kg<sup>-1</sup> K<sup>-1</sup>. A similar trend is observed for  $C_v^I$ .

It would thus seem that at temperatures near 0 °C water vapor behaves as an extremely nonideal gas. Hirschfelder *et al.*, p. 221 make an observation that water molecules cluster together more than expected at lower temperatures, an effect that can be seen from experimental versus calculated virial coefficients. It is not known whether the same effect is responsible for the higher specific heats calculated for water vapor in the real gas state. The lack of experimental real gas data for  $C_p$  of water vapor at temperatures between 0 °C and 30 °C means that it is not possible to compare these corrected ideal gas values with known values.

TABLE III. Coefficients of Eq. (15).

Coefficients	Speed of sound $c_0$	Specific heat ratio $\gamma$
$a_0$	331.5024	1.400 822
$a_1$	0.603 055	$-1.75 \times 10^{-5}$
$a_2$	-0.000 528	$-1.73 \times 10^{-7}$
$a_3$	51.471 935	-0.087 362 9
$a_4$	0.149 587 4	-0.000 166 5
$a_5$	-0.000 782	$-3.26 \times 10^{-6}$
$a_6$	$-1.82 \times 10^{-7}$	$2.047 \times 10^{-8}$
$a_7$	$3.73 \times 10^{-8}$	$-1.26 \times 10^{-10}$
$a_8$	$-2.93 \times 10^{-10}$	$5.939 \times 10^{-14}$
$a_9$	-85.209 31	-0.119 971 7
$a_{10}$	-0.228 525	-0.000 869 3
$a_{11}$	$5.91 \times 10^{-5}$	$1.979 \times 10^{-6}$
$a_{12}$	-2.835 149	-0.011 04
$a_{13}$	$-2.15 \times 10^{-13}$	$-3.478 \times 10^{-16}$
$a_{14}$	29.179 762	0.045 061 6
$a_{15}$	0.000 486	$1.82 \times 10^{-6}$

The validity of the simplified Eqs. (5), (6), and (8) were also investigated. When the full equations including a third virial coefficient, were used to calculate  $\gamma$  and  $c_0$ , only small differences below 5 ppm for both  $\gamma$  and  $c_0$  were obtained. The effect of the truncation of higher virial coefficients from the equation of state is thus small enough to be neglected.

## VII. APPROXIMATE EQUATIONS

An approximate formula has been derived which can be used to calculate  $\gamma$  and  $c_0$  for any combination of environmental factors, within a given range. To simplify the curve fitting, the water vapor mole fraction and not the humidity was used as a parameter in the tables. The water vapor mole fraction was obtained by using the method given in Giacomo<sup>19</sup> to calculate the fraction of water vapor in air on a real gas basis. The formulas and constants are reproduced in the Appendix for convenience.

The coefficients of an approximate equation have been derived which can be used to calculate  $\gamma$  and  $c$ , as a function of temperature, pressure, CO<sub>2</sub> concentration, and water vapor mole fraction. The form of the equation is very similar to that used by Wong<sup>20</sup> with the exception of the pressure term:

$$f(t, p, x_w, x_c) = a_0 + a_1 t + a_2 t^2 + (a_3 + a_4 t + a_5 t^2) x_w \\ + (a_6 + a_7 t + a_8 t^2) p + (a_9 + a_{10} t + a_{11} t^2) x_c \\ + a_{12} x_w^2 + a_{13} p^2 + a_{14} x_c^2 + a_{15} x_w p x_c, \quad (15)$$

where  $t$  is the celsius temperature,  $x_w$  is the water vapor mole fraction, and  $x_c$  is the carbon dioxide mole fraction. The above equation is valid for temperatures from 0 °C to 30 °C, pressures from 75 000 Pa to 102 000 Pa, up to 0.06 H<sub>2</sub>O mole fraction and CO<sub>2</sub> concentrations up to 1%. The coefficients of Eq. (15) are given in Table III and the values of  $\gamma$  and  $c_0$  calculated using the equation are within 35 ppm for  $\gamma$ , and 60 ppm for  $C$  of the data calculated in the spreadsheet.

## VIII. UNCERTAINTIES

In practice, it is difficult to assess the uncertainty in the values for  $\gamma$  and  $c_0$  calculated in this paper. Previous estimates of the uncertainties by Wong and Embleton are 400 ppm for  $\gamma$  and 200 ppm for  $c_0$  at STP. The actual difference between their value for  $\gamma$  and the value calculated in this paper is 0.003 (over 2000 ppm). A similar situation is found for their speed of sound values.

A  $1 \text{ cm}^3 \text{ mol}^{-1}$  change in  $B_{aa}$  on the spreadsheet produced changes in the order of 40 ppm on the speed of sound but were unnoticeable in the specific heat ratio. The uncertainty in  $\gamma$  and  $c_0$  due to the truncation of the equation of state and simplifications to the thermodynamic relationships was found to be only a few ppm.

An uncertainty of better than 0.1% is estimated for the values of  $C_p^0$  from Touloukian *et al.* for  $\text{O}_2$  and  $\text{N}_2$ . The resultant uncertainty in  $\gamma$  was found to be under 300 ppm. The variation in the  $\text{N}_2$  concentration from place to place is not expected to be more than 0.2% which contributes an uncertainty of less than  $\pm 100$  ppm to  $\gamma$ . A total uncertainty in  $\gamma$  of  $\pm 318$  ppm is obtained by combining the above uncertainties quadratically (assuming independent sources of uncertainty). The uncertainties in the values for the speed of sound are similarly estimated to be in the region of  $\pm 300$  ppm.

The uncertainty in the virial coefficients is also difficult to assess in practice. Kaye and Laby<sup>8</sup> make a statement that the constants  $a$ ,  $b$ , and  $c$  for Eq. (9) are given "For Ar, Kr, Xe,  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and CO accurately, and with useful but lower accuracy for other substances." This statement is not really useful as it gives no idea of the real uncertainty in using these coefficients. The American Institute of Physics Handbook quotes discrepancies of as high as  $1.5 \text{ cm}^3 \text{ mol}^{-1}$  on the second virial coefficient and quotes the uncertainty in the virial coefficients for  $\text{O}_2$  as  $\pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$ . This would have a small effect on the accuracy of the corrections applied to the ideal gas values of the various parameters but the corrected real gas value would still be more accurate than the uncorrected value.

## IX. CONCLUSIONS

It has been shown that the speed of sound and specific heat ratio can be accurately calculated by using a real gas equation of state and standard thermodynamic relationships. The values so calculated have been found to be in close agreement with various experimental determinations. The specific heat ratio and speed of sound were also found to increase slightly with pressure.

In calibrating a microphone by the reciprocity technique, the assumptions made by Wong and Embleton could lead to an error in the determination of the sensitivity of a microphone of 0.01 dB where the total uncertainty aimed at is  $\pm 0.05$  dB or better.

Previous to the work by Wong and Embleton, the accepted value for the speed of sound in dry air at STP was in the region of 331.44 to 331.46  $\text{m s}^{-1}$ . The suggestion by Wong in Ref. 1, that a new value for the speed of sound in

air of 331.29  $\text{m s}^{-1}$  be accepted, is considered to be unwise because of the ideal gas assumptions made in his calculations.

The indirect determination of the speed of sound in this paper serves to confirm the validity of the previously accepted values for the speed of sound.

## APPENDIX

The formula given by Giacomo<sup>19</sup> for calculating the mole fraction of water vapor in air from the relative humidity is

$$x_w = hf p_{sv} / p, \quad (\text{A1})$$

where  $h$  is the relative humidity expressed as a fraction,  $f$  is the enhancement factor, and  $p_{sv}$  is the saturation vapor pressure of water vapor in air:

$$f = 1.00062 + 3.14 \times 10^{-8} p + 5.6 \times 10^{-7} t^2 \quad (\text{A2})$$

and

$$p_{sv} = \exp(1.2811805 \times 10^{-5} T^2 - 1.9509874 \times 10^{-2} T + 34.04926034 - 6.3536311 \times 10^3 / T) \text{ Pa.} \quad (\text{A3})$$

The above equations are only valid over the temperature range  $0^\circ\text{C}$  to  $30^\circ\text{C}$  (273.15 K to 303.15 K) and for the pressure range 60 000 to 110 000 Pa.

<sup>1</sup>G. S. K Wong, "Speed of sound in standard air," J. Acoust. Soc. Am. **79**, 1359–1366 (1986).

<sup>2</sup>M. Greenspan, "Comments on 'Speed of sound in standard air' [J. Acoust. Soc. Am. **79**, 1359–1366 (1986)]," J. Acoust. Soc. Am. **82**, 370–372 (1987).

<sup>3</sup>G. S. K Wong and T. F. W. Embleton, "Variation of specific heats and of specific heat ratio in air with humidity," J. Acoust. Soc. Am. **76**, 555–559 (1984).

<sup>4</sup>J. O Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964), pp. 230–232.

<sup>5</sup>Y. S. Touloukian and T. Makita, "Specific heat, nonmetallic liquids and gases," in *Thermophysical Properties of Matter* (Plenum, New York, 1970), Vol. 6.

<sup>6</sup>J. Hilsenrath, C. W. Beckett, W. S. Benedict, L. Fano, H. J. Hodge, J. F. Masi, R. J. Nuttall, Y. S. Touloukian, and H. W. Woolley, *Tables of Thermal Properties of Gases* (U.S. Dept. of Commerce, Washington, DC, 1955), National Bureau of Standards Circular 564.

<sup>7</sup>ISO 2533-1975—"Standard atmosphere" (International Organisation for Standardization, Geneva, 1975).

<sup>8</sup>G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants* (Longman, New York, 1986), 15th ed., pp. 215–218.

<sup>9</sup>J. M. H. Levelt Sengers, M. Klein, and J. S. Gallagher, "Pressure-Volume-Temperature Relationships of Gases; Virial Coefficients," in *American Institute of Physics Handbook*, edited by D. E. Grey (McGraw-Hill, New York, 1972), 3rd ed., Chap. 4i, pp. 4-204–4-221.

<sup>10</sup>R. W. Hyland, "A correlation for the second interaction virial coefficients and enhancement factors for moist air," J. Res. Natl. Bur. Stand. A. **79A** (4), 544, 559 (1975).

<sup>11</sup>L. L. Beranek, "Acoustic properties of gases," in *American Institute of Physics Handbook*, edited by D. E. Grey (McGraw-Hill, New York, 1972), 3rd ed., Chap. 3d, pp. 3–71.

- <sup>12</sup> *US Standard Atmosphere, 1976* (U.S. Govt. Printing Office, Washington, DC, 1976), pp. 4, 18, 20.
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