

Heat capacities and acoustic virial coefficients for a synthetic coal mine methane mixture by speed of sound measurements at $T = (273.16 \text{ and } 250.00) \text{ K}$.

Fernando J. Pérez-Sanz^a, M. Carmen Martín^a, César R. Chamorro^a, Teresa Fernández-Vicente^b, José J. Segovia^{a,*}

^aResearch Group TERMOCAL. University of Valladolid, Paseo del Cauce 59, 47011 Valladolid. Spain

^bCentro Español de Metrología, Alfar 2, 28760 Tres Cantos, Madrid, Spain

* To whom correspondence should be addressed. E-mail: jose.segovia@eii.uva.es

This is an author-created, un-copyedited version of an article accepted for publication in The Journal of Chemical Thermodynamics (Volume 97, 2016, Pages 137–141). Elsevier is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The definitive publisher-authenticated version is available online at <http://dx.doi.org/10.1016/j.jct.2016.01.020>

© 2015. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Abstract

Measurements of speed of sound for a synthetic coal mine methane mixture of ten components are reported. Data were obtained using a spherical resonator for two isotherms $T = (273.16 \text{ and } 250.00) \text{ K}$ and pressures up to 8 MPa. The uncertainty study is detailed and the total uncertainty of the speed of sound is no worse than 0.01%. Heat capacities and acoustic virial coefficients were obtained through said measurements. Results are compared with the GERG-2008 equation of state.

1. Introduction

Coal mine methane (CMM) and other kind of coal seam gases are by-products of coal mining. These gases are a safety issue inside mines since they might prove explosive if mixed with air in a certain proportion. In fact, many fatalities have occurred in recent years because of these gases [1]. Therefore coalbed methane, like CMM, must be removed from mines, yet it becomes an environmental issue if released into the atmosphere, since it contains high levels of methane whose global warming potential is over 25 times higher than CO_2 [2]. Coal mine methane needs to be processed before being released into the atmosphere. The process applied is combustion, where methane burns and becomes water and carbon dioxide which contributes much less to global warming.

CMM must be extracted to avoid hazardous situations, and burned so as to reduce environmental impact. These two issues are dealt with when CMM is used as an energy source. Furthermore, it will enhance mine productivity [3] thanks to the energy produced.

In recent years, increased energy demand and the high price of conventional energy sources such as coal and oil have sparked greater interest in new energy sources. In addition, public environmental awareness has furthered this interest in securing less polluting and more

renewable sources. This has also led to the idea of using energy sources that were not previously taken into account. Such is the case of coal mine methane and other coal seam gases, although others, like exhaust gases from coal ovens, are also a good example.

Coal mine methane and other gas mixtures originating in coal seams, such as virgin coalbed methane, abandoned mine methane or ventilation air methane are more often used as an energy source. Yet, in order to improve performance and achieve greater efficiency, accurate thermodynamic properties and equations of state are required. Unfortunately, there is a lack of these gas mixture properties. Some equations of state as GERG-2008 [4] were developed to predict natural gas like mixtures. GERG-2008 was developed thanks to the extended data base of experimental measurements of gases and mixtures alike. However, coal mine methane composition is significantly different and, therefore experimental measurements are necessary to compare reliability of the equation of state and theoretical properties which is the main purpose of this study.

The present study focuses on providing accurate measurements of speed of sound in a synthetic coal mine methane mixture in order to calculate certain thermodynamic properties such as isobaric and isochoric heat capacities, adiabatic coefficient as a perfect gas and acoustic virial coefficients. A spherical resonator was used for the measurements and this technique provides reliable data of equation of state and heat capacities, information which is required to predict gas behaviour in common gas processes such as transport, compression or storage. The present work also includes a comparison with previous research [5] where experimental densities for a similar mixture were taken at several pressures and temperatures by means of a single-sinker densimeter and compared to GERG-2008. The research forms part of various projects linked to describing of energy gases. Due to the limited quantity of sample, only two isotherms could be measured with $T = (250.00 \text{ and } 273.16) \text{ K}$ being chosen, since higher deviations from GERG-2008 were found in the previous study [5].

2. Experimental

2.1 CMM preparation

Bundesanstalt für Materialforschung und -prüfung (BAM) prepared two synthetic coal mine methane mixtures gravimetrically as described by Hernández-Gómez, R., et al. [5]. One was used to study densities at several pressures and temperature [5], the other whose composition is detailed in Table 1 was used in this study to determine the thermodynamic properties and acoustic equation of state.

As will be seen later, composition and composition uncertainty are extremely important parameters when heat capacities are calculated and its uncertainty therefore contributes significantly to overall uncertainty.

2.2 Acoustic model

Speed of sound in gases is an important thermodynamic parameter from which it is possible to obtain many other properties. It is related to equation of state as it can be seen in equation (1):

$$u^2 = \left(\frac{\partial p}{\partial \rho} \right)_S \quad (1)$$

where u is the speed of sound, p is pressure, ρ is gas density and S is entropy.

Speed of sound provides useful information when presented as a virial function. This equation might be expressed as function of density, equation (2) truncated at the third coefficient, or pressure, equation (3).

$$u^2 = A_0 \left(1 + \beta_a \rho + \gamma_a \rho^2 \right) \quad (2)$$

$$u^2 = A_0 + A_1 p + A_2 p^2 + A_3 p^3 \quad (3)$$

A_0 is equal in both cases and it contains more thermodynamic information, β_a is the first acoustic virial coefficient, γ_a is the second acoustic coefficient, A_1 and A_2 are the second and

third acoustic virial parameters when presented as a function of pressure. They are related to ordinary acoustic virial coefficients as is explained later.

The first acoustic virial parameter A_0 is very important, since, according to kinetic theory, it is related to thermodynamic temperature T , adiabatic coefficient γ^{pg} as a perfect gas and the molar mass M , as detailed in equation (4).

$$A_0 = \frac{\gamma^{pg} R \cdot T}{M} \quad (4)$$

R is the ideal gas constant, the adiabatic coefficient as a perfect gas (γ^{pg}) drives the molar isochoric and isobaric heat capacities (C_v and C_p , respectively) thanks to Mayer's relation, as seen in equations (5) and (6).

$$C_p = \gamma^{pg} C_v \quad (5)$$

$$R = C_v (\gamma^{pg} - 1) \quad (6)$$

This study thus uses equation (3) to calculate acoustic virial coefficients β_a and γ_a , which are related to the parameters of equation (3) by the following expressions:

$$\beta_a = \frac{A_1}{A_0} RT \quad (7)$$

$$\gamma_a = \frac{A_2}{A_0} (RT)^2 \quad (8)$$

As stated at the beginning of this section, measurements of speed of sound may provide a great deal of useful thermodynamic information. Equations (1) to (8) in this case offer information about heat capacities and density as a function of pressure or speed of sound, in other words information about equation of state.

2.3 Experimental procedure

A spherical resonator was used for speed of sound measurements for the CMM mixture. The experimental set-up is described in a previous work [6]. It is equipped with two capsule-type platinum resistance thermometers whose calibration standard uncertainties are ± 2 mK at $T = 273.16$ K and ± 5 mK at $T = 250.00$ K. Pressure is measured by means of two resonant quartz-crystal manometers for pressure ranges (0 to 2) MPa and (1 to 20) MPa with a relative standard uncertainty of $\pm 1 \cdot 10^{-4}$ Pa/Pa.

Two isotherms were measured in this study, at $T = 250.00$ K and at $T = 273.16$ K. The resonator is filled with the gas mixture at maximum pressure and is then discharged to decrease the pressure whilst maintaining a constant temperature. The initial pressure of measurements depends on the pressure of the mixture in the container which was around 6 MPa for the first isotherm ($T = 250$ K). Using a manual cylinder and piston device, initial measurements started at $p = 8$ MPa and pressure was decreased by 1MPa steps, with the final measurement being taken at $p = 0.1$ MPa.

The other isotherm ($T = 273.16$ K) started at $p = 5.5$ MPa. Due to depleting bottle mixture, a higher pressure could not be reached. In order to obtain enough reliable data, pressure was decreased by 0.5 MPa pressure steps rather than 1MPa, as was done with the previous isotherm, the lowest pressure being $p = 0.5$ MPa.

Acoustic resonance measurements are carried out inside a spherical cavity whose internal radius must be known in order to calculate speed of sound from the acoustic frequency of resonance. However, internal radius changes with pressure and was measured by acoustic resonance using argon as a reference gas, whose speed of sound is accurately calculated using its equation of state [7]. Equation (9) gives the relation between speed of sound u , and acoustic resonance frequencies:

$$u = \frac{2\pi a(f_{lm} + \Delta f_{lm})}{V_{lm}} \quad (9)$$

where a is the mean radius, f_{lm} is the frequency of resonance for acoustic resonance mode (l,m) , Δf_{lm} is a correction term, and ν_{lm} is the eigenvalue for acoustic mode (l,m) .

The correction term is a sum of different corrections which take into account the effect of the thermal boundary layer, the coupling of gas and shell motion and the presence of ducts. Details may be found in a previous work where this technique was used to determine the Boltzmann constant [8].

The values of the radius were obtained at different temperatures and pressures and were fitted as a function of pressure at each isotherm. This study was carried out previously [9] and radius behaviour can be described by equations (10) and (11) at $T = 250$ K and $T = 273.16$ K, respectively.

$$(a / \text{mm}) = 40.1496 + 7.7618 \cdot 10^{-5} \cdot (p / \text{MPa}) + 5.6348 \cdot 10^{-5} \cdot (p / \text{MPa})^2 \quad (10)$$

$$(a / \text{mm}) = 40.1628 - 12.7619 \cdot 10^{-5} \cdot (p / \text{MPa}) + 7.1290 \cdot 10^{-5} \cdot (p / \text{MPa})^2 \quad (11)$$

3. Results

Speed of sound is not measured directly. Four radial modes of resonance were determined, from $(0, 2)$ to $(0, 5)$, and their frequency of resonance and peak half-widths were measured and used to calculate speed of sound through equation (9). The frequency range for these measurements was $f = (5600-20100)$ Hz. The quality of the data was checked for all the modes. By way of an example, excess half-widths at $T = 273.16$ K are shown in Figure 1. These results imply that all modes can be used for the calculation and the excess half-widths values are taken into account for the uncertainty calculations. Moreover, these excess half-widths tend to increase at low pressure since signal detection is worse, and this is the reason why it is not possible to measure accurately enough at lower pressures.

The corrected values of the speed of sound, obtained from the experimental frequencies of resonance were calculated as the average of the four modes, as shown in Table 1, using equation

(9). These data have been compared with those obtained from the GERG-2008 equation of state as is used for this type of mixture [4, 10].

Speed of sound uncertainties were calculated following the “Guide to the expression of uncertainty in measurements” [11]. Standard uncertainty in speed of sound measurements is calculated using equation (12):

$$u(u) = \left[u^2(u)_{\text{disp}} + \left(\frac{\partial u}{\partial a} \right)^2 u^2(a) + \left(\frac{\partial u}{\partial f} \right)^2 u^2(f) \right]^{1/2} \quad (12)$$

where $u(u)_{\text{disp}}$ is the contribution due to the dispersion of the four acoustic modes measured, calculated as the standard deviation of the mean of the four measurements. The other contributions are radius calculation (a) and frequency measurements $u(f)$.

All of these results are reported in Tables 2 and 3 for the isotherms at 250 K and 273.16 K respectively.

In order to obtain the thermodynamic parameters: adiabatic coefficient, heat capacities and acoustic virial parameters through equations (4) to (8), it is necessary to correlate the square speed of sound experimental measurements with pressure for both isotherms using equation (3).

As an example of the fitting, Figure 2 shows the residuals of speed of sound as a function of pressure for both isotherms.

The fitted parameters of equation (3) and their uncertainties, calculated using the Monte Carlo method, are given in Table 4. This also includes the standard deviation of the mean defined by the following equation:

$$\sigma = \left[\left(\sum (u_{\text{exp}}^2 - u_{\text{calc}}^2) / (n-1) \right) / n \right]^{1/2} \quad (13)$$

Once the experimental data have been fitted to equation (3), heat capacities and, virial acoustic coefficients are calculated through equations (4) to (8). The standard uncertainties of these quantities have been evaluated according to the following equations:

$$u_c(\gamma^{pg}) = \left[\left(\frac{\partial \gamma^{pg}}{\partial A_0} \right)^2 u^2(A_0) + \left(\frac{\partial \gamma^{pg}}{\partial R} \right)^2 u^2(R) + \left(\frac{\partial \gamma^{pg}}{\partial T} \right)^2 u^2(T) + \left(\frac{\partial \gamma^{pg}}{\partial M} \right)^2 u^2(M) \right]^{1/2} \quad (14)$$

$$u_c(C_v) = \left[\left(\frac{\partial C_v}{\partial \gamma^{pg}} \right)^2 u^2(\gamma^{pg}) + \left(\frac{\partial C_v}{\partial R} \right)^2 u^2(R) \right]^{1/2} \quad (15)$$

$$u_c(C_p) = \left[\left(\frac{\partial C_p}{\partial \gamma^{pg}} \right)^2 u^2(\gamma^{pg}) + \left(\frac{\partial C_p}{\partial C_v} \right)^2 u^2(C_v) \right]^{1/2} \quad (16)$$

$$u_c(\beta_a) = \left[\left(\frac{\partial \beta_a}{\partial A_0} \right)^2 u^2(A_0) + \left(\frac{\partial \beta_a}{\partial A_1} \right)^2 u^2(A_1) + \left(\frac{\partial \beta_a}{\partial R} \right)^2 u^2(R) + \left(\frac{\partial \beta_a}{\partial T} \right)^2 u^2(T) \right]^{1/2} \quad (17)$$

$$u_c(\gamma_a) = \left[\left(\frac{\partial \gamma_a}{\partial A_0} \right)^2 u^2(A_0) + \left(\frac{\partial \gamma_a}{\partial A_1} \right)^2 u^2(A_1) + \left(\frac{\partial \gamma_a}{\partial R} \right)^2 u^2(R) + \left(\frac{\partial \gamma_a}{\partial T} \right)^2 u^2(T) \right]^{1/2} \quad (18)$$

Uncertainty in R was obtained from the bibliography [12], and overall uncertainty of mixture molar mass was calculated using data from Table 1. Values for $k=1$ are:

$$M = 0.0228921 \pm 1.2 \cdot 10^{-6} \text{ kg} \cdot \text{mol}^{-1}$$

$$R = 8.3144621 \pm 7.5 \cdot 10^{-6} \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

Table 5 reports the thermodynamic properties: adiabatic coefficient, isobaric and isochoric heat capacities as a perfect gas and acoustic virial coefficient values as well as their uncertainties at two different temperatures.

Experimental results of adiabatic coefficient, heat capacities and acoustic virial coefficients were compared to the values obtained according to the GERG-2008 equation of state. Tables 6 and 7 show this comparison at $T = 250$ K and $T = 273.16$ K, respectively.

4. Discussion

The speed of sound of a synthetic coal mine methane was measured with relative standard uncertainties below 0.011 % ($k=1$) at two different temperatures $T = 250$ K and $T = 273.16$ K in a pressure range up to 8 MPa. The squares of the sound speeds were fitted to a polynomial equation (3) and the standard deviations of the mean were 42 and 25 $\text{m}^2 \cdot \text{s}^{-2}$, respectively.

These values of speed of sound and those obtained by the GERG-2008 equation of state, deviations are always lower than 0.11%, deviation which even decreases at lower pressures.

These results are in good agreement with the density deviations obtained by Hernández et al. [5] in a similar mixture. Average density deviation at $T = 250$ K is about 0.33 % and at $T = 275$ K is 0.16%. Experimental values of speed of sound were used to obtain the virial acoustic equation of state as well as adiabatic coefficient and heat capacities as a perfect gas. The relative expanded uncertainties of second acoustic virial coefficients are below 2% at $T = 273.16$ K and below 1% at $T = 250.00$ K, for $k = 2$. Adiabatic coefficient relative expanded uncertainty is always below 0.06%, and heat capacity uncertainties range from 0.19 % to 0.24 %.

The experimental value of those parameters was compared to the GERG-2008 equation of state. Adiabatic coefficient, and heat capacities at $T = 250$ K have a disagreement below 0.24 %, while at $T = 273.16$ K deviations are below 0.11 %. Speed of sound at zero pressure according to the GERG-2008 equation of state deviates from the experimental one by less than 0.05% at both temperatures. Second virial acoustic coefficient deviations are above 7.2%. This high disagreement was observed in a previous work [9] and could be attributed to software.

Finally, the coherence between density [5] and speed of sound data was checked, despite the studied mixtures were slightly different. Speeds of sound were calculated using the acoustic

virial coefficients and the experimental densities through equation (2). For example, the relative deviation of the speed of sound at 1 MPa and 250 K was 0.05%.

Acknowledgements

Support for this work came from of the Spanish Ministry of Economy and Competitiveness, project ENE2013-47812- R, from Regional Government of Castilla y León, project VA391A12-1, and from the research project ENG54, “Metrology for Biogas” of the European Metrology Research Programme.

References

1. C.O. Karacan, F.A.Ruiz, M.Cotèc, S. Phipps, *Int. J. Coal Geology* 86 (2011) 121-156.
2. L.D. Danny Harvey, *Energy Policy* 21 (1993) 24-34.
3. R. Sander, L.D. Connell, *Int. J. Greenhouse Gas Control* 8 (2012) 34-44.
4. O. Kunz, W. Wagner, *J. Chem. Eng. Data* 57(2012) 3032-3091.
5. R. Hernández-Gómez, D. Tuma, M.A. Villamañán, M.E. Mondéjar, C.R. Chamorro, J. *Chem. Thermodyn.* 68 (2014) 253-259.
6. J. Segovia, D. Vega-Maza, M.C. Martín, E. Gómez, C. Tabacaru, D.del Campo, *Int. J. Thermophys.* 31 (2010) 1294-1309.
7. C.S.R. Tegeler, W. Wagner, *J. Phys. Chem. Ref. Data* 28 (1999) 71.
8. F.J. Pérez-Sanz, J.J. Segovia, M.C. Martín, M.A. Villamañán, D. del Campo, C. García, *Metrologia* 52 (2015) S257–S262.
9. F.J. Pérez-Sanz, J.J. Segovia, M.C. Martín, D. del Campo, M.A. Villamañán, *J. Chem. Thermodyn.* 79 (2014) 224–229.
10. E. W. Lemmon, M.O.McLinden, M. L. Huber (2002) NIST Reference Fluid Thermodynamic and transport Properties - REFPROP. NIST Standard Reference Database 23 (Version 9.0).

11. JCGM 100:2008, J. (2008) (GUM 1995 with minor corrections). Evaluation of measurement data - Guide to the expression of uncertainty in measurement.
12. NIST. (2010) NIST Database. [cited 2014 03/27/2014]; Available from:
<http://physics.nist.gov/cuu/Constants/index.html>

Table 1. Synthetic coal mine methane molar composition and expanded relative uncertainties (cover factor $k=2$)^a.

Component	x_i	$U_r(x_i)/\%$
Nitrogen	0.16427766	0.011
Oxygen	0.00484217	0.026
Propane	0.00076146	0.052
i-Butane	0.00010392	0.052
n-Butane	0.00059180	0.052
Ethane	0.00852310	0.052
Carbon dioxide	0.16656170	0.010
n-Pentane	0.00000736	0.20
i-Pentane	0.00001701	0.20
Methane	0.65484644	0.008

^a Data from the supplier (BAM).

Table 2. Experimental values of speed of sound at $T = 250.000$ K for each pressure with their standard uncertainties and a comparison with the GERG-2008 equation of state for the synthetic mixture of coal mine methane^a.

p/MPa	T/K	$u_{\text{exp}}/(\text{m}\cdot\text{s}^{-1})$	$u_{\text{GERG}}/(\text{m}\cdot\text{s}^{-1})$	$10^6\cdot(u_{\text{exp}}-u_{\text{GERG}})/u_{\text{GERG}}$	$u(u_{\text{exp}})/(\text{m}\cdot\text{s}^{-1})$
7.934	249.887	319.541	319.155	1240	0.035
6.949	249.928	319.214	318.800	1350	0.034
6.045	249.923	320.459	320.031	1390	0.034
4.885	249.973	323.723	323.339	1230	0.034
3.935	249.989	327.365	327.018	1100	0.034
2.925	250.011	331.905	331.618	920	0.034
1.975	249.996	336.616	336.363	780	0.035
0.978	250.011	341.901	341.689	650	0.035
0.101	250.002	346.600	346.533	220	0.035

^a Standard uncertainties ($k=1$): $u_r(P) = 1\cdot 10^{-4}$ Pa/Pa; $u(T) = 5$ mK.

Table 3. Experimental values of speed of sound at $T = 273.16$ K for each pressure with their uncertainties and a comparison with the GERG-2008 equation of state for the synthetic mixture of coal mine methane^a.

p/MPa	T/K	$u_{\text{exp}}/(\text{m}\cdot\text{s}^{-1})$	$u_{\text{GERG}}/(\text{m}\cdot\text{s}^{-1})$	$10^6 \cdot (u_{\text{exp}} - u_{\text{GERG}})/u_{\text{GERG}}$	$u(u_{\text{exp}})/(\text{m}\cdot\text{s}^{-1})$
5.506	273.157	345.694	345.322	1080	0.037
4.993	273.161	346.520	346.151	1070	0.037
4.514	273.169	347.462	347.102	1040	0.037
4.005	273.162	348.609	348.267	980	0.037
3.491	273.172	349.927	349.616	890	0.037
2.997	273.154	351.335	351.023	890	0.037
2.491	273.162	352.890	352.608	800	0.038
2.005	273.145	354.474	354.216	730	0.038
1.485	273.169	356.432	356.066	1030	0.038
0.999	273.155	358.183	357.853	920	0.038
0.499	273.171	360.015	359.785	640	0.038

^a Standard uncertainties ($k=1$): $u_r(P) = 1 \cdot 10^{-4}$ Pa/Pa; $u(T) = 2$ mK.

Table 4. Parameters of equation (3) and their expanded uncertainties ($k = 2$) at two different temperatures and standard deviation of the mean (σ), for the synthetic CMM mixture.

	$T = 250.00 \text{ K}$	$T = 273.16 \text{ K}$
$A_0/(\text{m}^2 \cdot \text{s}^{-2})$	120474	131002
$A_1/(\text{m}^2 \cdot \text{s}^{-2} \cdot \text{MPa}^{-1})$	-3608	-2851
$A_2/(\text{m}^2 \cdot \text{s}^{-2} \cdot \text{MPa}^{-2})$	-51.45	74.01
$A_3/(\text{m}^2 \cdot \text{s}^{-2} \cdot \text{MPa}^{-3})$	-51.45	10.76
$U(A_0)/(\text{m}^2 \cdot \text{s}^{-2})$	48	30
$U(A_1)/(\text{m}^2 \cdot \text{s}^{-2} \cdot \text{MPa}^{-1})$	52	22
$U(A_2)/(\text{m}^2 \cdot \text{s}^{-2} \cdot \text{MPa}^{-2})$	15	3.7
$U(A_3)/(\text{m}^2 \cdot \text{s}^{-2} \cdot \text{MPa}^{-3})$	1.2	1.0
$\sigma/(\text{m}^2 \cdot \text{s}^{-2})$	42	25

Table 5. Thermodynamic properties: adiabatic coefficient as a perfect gas, γ^{pg} ; isocoric heat capacity, C_v and isobaric heat capacity, C_p , as a perfect gas; second virial acoustic coefficient β_a ; third virial acoustic coefficient γ_a , and their corresponding expanded uncertainties (for a covering factor $k=2$) at two different temperatures for the CMM mixture.

	$T = 250.000 \text{ K}$		$T = 273.160 \text{ K}$	
	Value	$U (k=2)$	Value	$U (k=2)$
T/K	250.000	0.010	273.160	0.004
γ^{pg}	1.32720	$7.6 \cdot 10^{-4}$	1.32064	$6.2 \cdot 10^{-4}$
$C_v^{pg}/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	25.411	0.059	25.931	0.050
$C_p^{pg}/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	33.726	0.081	34.245	0.068
$\beta_a/(\text{m}^3 \cdot \text{mol}^{-1})$	$-6.232 \cdot 10^{-5}$	$6.0 \cdot 10^{-7}$	$-4.944 \cdot 10^{-5}$	$7.9 \cdot 10^{-7}$
$\gamma_a/(\text{m}^3 \cdot \text{mol}^{-1})^2$	$-1.93 \cdot 10^{-9}$	$1.3 \cdot 10^{-10}$	$2.91 \cdot 10^{-9}$	$2.9 \cdot 10^{-10}$

Table 6. Comparison between calculated values of the isochoric and isobaric heat capacities (C_v^{pg} and C_p^{pg}) and the adiabatic coefficient (γ^{pg}) at zero pressure and the acoustic virial coefficients (β_a, γ_a) obtained from equations (7) and (8) and, those calculated using the GERG-2008 EoS for the synthetic CMM mixture at $T = 250$ K.

	Experimental	GERG-2008	$10^2 (\text{Exp} - \text{GERG})/\text{GERG}$
γ^{pg}	1.32720	1.32801	0.061
$C_v^{pg}/(\text{J}\cdot\text{mol}^{-1}\text{K}^{-1})$	25.411	25.349	0.24
$C_p^{pg}/(\text{J}\cdot\text{mol}^{-1}\text{K}^{-1})$	33.726	33.663	0.19
$\beta_a/(\text{m}^3\cdot\text{mol}^{-1})$	$-6.232\cdot 10^{-5}$	$-6.716\cdot 10^{-5}$	7.2
$\gamma_a/(\text{m}^6\cdot\text{mol}^{-2})$	$-1.93\cdot 10^{-9}$	$1.13\cdot 10^{-1}$	
$u_0 /(\text{m}\cdot\text{s}^{-1})$	347.094	347.097	$8.6\cdot 10^{-4}$

Table 7. Comparison between calculated values of the isochoric and isobaric heat capacities (C_v^{pg} and C_p^{pg}) and the adiabatic coefficient (γ^{pg}) at zero pressure and the acoustic virial coefficients (β_a, γ_a) obtained from equations (7) and (8) and those calculated using the GERG-2008 EoS for the synthetic CMM mixture at $T = 273.16$ K.

	Experimental	GERG-2008	$10^2 \cdot (\text{Exp-GERG})/\text{GERG}$
γ^{pg}	1.32064	1.32077	0.028
$C_v^{pg}/(\text{J} \cdot \text{mol}^{-1} \text{K}^{-1})$	25.931	25.961	0.11
$C_p^{pg}/(\text{J} \cdot \text{mol}^{-1} \text{K}^{-1})$	34.245	34.276	0.09
$\beta_a/(\text{m}^3 \cdot \text{mol}^{-1})$	$-4.944 \cdot 10^{-5}$	$-5.060 \cdot 10^{-5}$	2.3
$\gamma_a/(\text{m}^6 \cdot \text{mol}^{-2})$	$2.91 \cdot 10^{-9}$	$7.73 \cdot 10^{-2}$	
$u_0/(\text{m} \cdot \text{s}^{-1})$	361.941	361.760	0.05

Figure Captions:

Figure 1. Excess half-width of resonance peaks for acoustic modes Δ (0,2), \diamond (0,3), \square (0,4) and \times (0,5) at $T = 273.16$ K in the pressure range $p = (1.0 \text{ to } 5.5)$ MPa, for the synthetic CMM mixture.

Figure 2. Residual analysis of measured speeds of sound and the values fitted by equation (3) and expanded uncertainty is shown as a dotted line, at $T = 250.00$ K (Δ) and $T = 273.16$ K (\times) for the synthetic CMM mixture.

Figure 1. Excess half-width of resonance peaks for acoustic modes Δ (0,2), \diamond (0,3), \square (0,4) and \times (0,5) at $T = 273.16$ K in the pressure range from $p = 1.0$ MPa up to $p = 5.5$ MPa, for the synthetic CMM mixture.

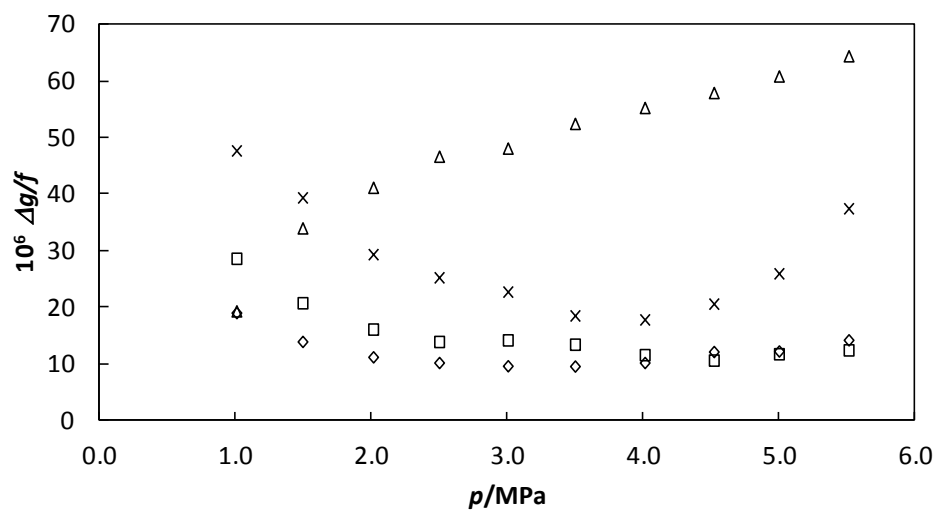


Figure 2. Residual analysis of measured speeds of sound and the values fitted by equation (3) and expanded uncertainty is shown as a dotted line, at $T = 250.00\text{ K}$ (Δ) and $T = 273.16\text{ K}$ (\times) for the synthetic CMM mixture.

