



Speed of sound measurements in (carbon monoxide + ethane) and (carbon monoxide + propane) gas mixtures at $T = (260 \text{ to } 350) \text{ K}$ and up to 12 MPa

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ABSTRACT

Speed of sound data are reported for (carbon monoxide + ethane) and (carbon monoxide + propane) mixtures in the gas region at mole fractions of carbon monoxide of 0.25, 0.5 and 0.75 in the temperature range from 273.15 K to 350 K for mixtures containing ethane, and compositions $x_{\text{CO}} = 0.5$ and 0.75 at $T = (260 \text{ to } 350) \text{ K}$ for mixtures with propane. Measurements are performed by means of a spherical acoustic resonator with an expanded relative uncertainty ($k = 2$) better than 250 parts in 10^6 . Experimental data are fitted to a virial type equation, obtaining standard deviations within the uncertainty of the measurements, and the adiabatic coefficient as perfect gas is derived from this fitting. Finally, all these data are compared to GERG-2008 and AGA92-DC equations of state, which are used as reference in the gas industry.

1. Introduction

The European Commission is implementing its REPowerEU Plan [1], which means accelerating the green transition by promoting renewable energies, among other measures. In the case of biomethane, the purpose is to increase the production and use of sustainable biomethane and to facilitate its integration into the EU internal gas market by providing incentives for biogas upgrading.

Biogas is produced by the anaerobic digestion of organic matter in an oxygen-free environment. The organic matter can come from crop residues, animal manure, municipal solid waste, or wastewater sludge. Its composition depends on the production pathway and the kind of feedstock, although, the main components are methane (45 % to 75 %) and CO_2 . After purification and refining – when it reaches sufficient quality to be injected into the network – it is called referred to as “biomethane” and this is when it can replace natural gas. Biomethane is also obtained by thermal gasification of solid biomass followed by methanation.

In the European Union, combined biogas and biomethane production in 2021 amounted to 196 TWh or 18.4 bcm of energy, with an increase of 20 % in biomethane production compared to 2020 [2]. The REPowerEU Plan target is to reach 35 bcm of biomethane by 2030.

The deployment of biomethane requires harmonizing quality standards in order to meet the requirements for trade, and for the safety of

equipment. The different biogas production processes also affect the content of minor polluting compounds. The objective of this work is to advance current knowledge of mixtures related to biogas that include non-majority gases. This is important because their presence not only modifies the composition of the mixture but also its properties. In addition, reference equations used for these transactions – such as GERG-2008 [3] – show high deviations in the estimated properties having a significant economic impact. In order to improve this equation, specific measurements of binary mixtures are required [4]. There are scarce accurate data related to speed of sound measurements in gas phase for binary mixtures related to energy gases, in Table 1 is summarized a literature review.

This study aims to provide new accurate experimental data of speed of sound for (carbon monoxide + ethane) and (carbon monoxide + propane) mixtures in the gas phase. To the best of our knowledge, no sound speed data are reported in the literature and a limited number of data – in the gas region – have been found for carbon monoxide [20], ethane [21] and propane [22,23]. Additionally, for the two mixtures studied, we only found vapour liquid equilibrium data measured by Trust and Kurata [24] at four isotherms between 233.15 K and 273.15 K for (carbon monoxide + ethane) mixtures, whereas VLE for (carbon monoxide + propane) mixtures were measured at eight isotherms between 148.15 K and 323.15 K.

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Table 1
Literature review of the speed of sound data for relevant binary gas mixtures.

Mixture	Temperature range	Pressure range	Reference
CH ₄ + C ₂ H ₆	200 K – 375 K	0.03 MPa – 13 MPa	[5]
CH ₄ + C ₃ H ₈	225 K – 375 K	0.05 MPa – 1.4 MPa	[6]
CH ₄ + n-C ₄ H ₁₀	311 K	2 MPa – 17 MPa	[7]
CH ₄ + CO ₂	200 K – 450 K	0.4 MPa – 17 MPa	[8]
CH ₄ + H ₂	273 K – 375 K	0.5 MPa – 20 MPa	[9]
CH ₄ + He	273 K – 375 K	0.5 MPa – 20 MPa	[10]
CH ₄ + N ₂	170 K – 400 K	20 MPa – 30 MPa	[11]
	298 K – 473 K	50 MPa – 400 MPa	[12]
C ₂ H ₆ + CO ₂	220 K – 450 K	0.05 MPa – 1.3 MPa	[13]
C ₃ H ₈ + CO ₂	248 K – 373 K	7.9 MPa – 200 MPa	[14]
	273 K – 325 K	0.1 MPa – 2.2 MPa	[15]
CO + N ₂	273 K – 325 K	0.01 MPa – 10 MPa	[16]
CO ₂ + He	313 K – 353 K	500 MPa – 5000 MPa	[17]
H ₂ + N ₂	260 K – 350 K	0.5 MPa – 20 MPa	[18]
He + N ₂	157 K – 298 K	200 MPa – 1000 MPa	[19]

Table 2
Information of the pure components used for the mixtures under study.

	Supplier	Purity / mol fraction ^{a,b}	CAS number	<i>M</i> / g·mol ⁻¹
Carbon Monoxide	Praxair	≥ 0.99998	630-08-0	28.010
Ethane	Air Liquide	≥ 0.99995	74-84-0	30.069
Propane	Air Liquide	≥ 0.99950	74-98-6	44.096

^a Data supplied by CEM.

^b No additional purification was done for the studied gases.

Table 3
Molar composition, x_1 , and standard uncertainty ($k = 1$) for the mixtures under study prepared at CEM.

	x_1 ^a	$u(x_1)$ ^a	x_2 ^a	$u(x_2)$ ^a
CO (x_1) + C ₂ H ₆ (x_2)	0.25075	0.00004	0.74925	0.00006
CO (x_1) + C ₂ H ₆ (x_2)	0.50047	0.00011	0.49953	0.00007
CO (x_1) + C ₂ H ₆ (x_2)	0.74931	0.00002	0.25070	0.00004
CO (x_1) + C ₃ H ₈ (x_2)	0.50078	0.00028	0.49922	0.00013
CO (x_1) + C ₃ H ₈ (x_2)	0.75094	0.00014	0.24910	0.00007

^a Data supplied by CEM.

Carbon monoxide is more relevant for thermo-chemical production of biomethane, and the presence of hydrocarbons such as ethane and especially propane should be taken into account to avoid their condensation. In this work, the speeds of sound for mixtures with ethane, and nominal compositions of $x_{\text{CO}} = 0.25, 0.5$ and 0.75 , were measured at temperatures from 273.15 K to 350 K and pressures up to 12 MPa. In addition, for mixtures with propane and nominal compositions for $x_{\text{CO}} = 0.5$ and 0.75 , speeds of sound were determined at temperatures from 260 K to 350 K and pressures up to 4.5 MPa.

2. Experimental

2.1. Materials

The Spanish Institute of Metrology (CEM) prepared the five binary mixtures under study, following the standard gravimetric procedures given in ISO 6142-1 [25]. The amount fraction of the components in the mixture and its uncertainty were also calculated according to that standard. The uncertainty of the amount fraction for each component depends, among other factors, on the environmental condition the weighing is performed, the piece of masses used in the weighing cycle for each component, the purity of the mother gas...etc. This can lead to different uncertainty of the amount fraction. Table 2 and Table 3 report

the purity of the pure components and the composition of the mixtures including their standard uncertainties, respectively.

The mixtures are homogenized before loading them into the equipment by rolling the cylinders which contain them, and composition uncertainty is taken into account for the overall uncertainty calculations.

2.2. Experimental technique

Speed of sound is obtained using a spherical resonator which has been amply described in previous papers [9,10,15,16,18] and the main features of the technique are explained in this section. The resonator is a spherical cavity of a nominal internal radius of 40 mm made of grade 321 austenitic stainless steel. It consists of two aligned hemispheres welded by electron beam as designed by Prof. J.P.M. Trusler at the Imperial College in London. There are two transducers located in the north hemisphere forming an angle of 90°, which play the roles of source and detector. These transducers are capacitors made of two conductive surfaces (steel and a gold layer) separated by a dielectric polyimide membrane. When the electrical signal is supplied to one of these transducers, using a wave generator, the membrane is induced to vibrate. The acoustic pressure vibrations impact the membrane of the detector transducer and the electrical signal produced is pre-amplified and supplied to a lock-in. The relative standard uncertainty of frequency measurement is below one part in 10⁶.

The temperature on the resonator is measured by means of two capsule-type platinum resistance thermometers, calibrated in our laboratory facilities and traceable to national standards, whose standard uncertainties are $u(T) = 2$ mK.

Two resonant quartz-crystal manometers for pressure ranges (0 to 2) MPa and (1 to 20) MPa provide accurate pressure measurements. The manometers were also calibrated in our laboratory with relative standard uncertainties of $(4 \cdot 10^{-4} p/\text{MPa} + 1 \cdot 10^{-4})$, and are traceable to national standards.

The measurement procedure involves isothermal measurements, with the resonator being kept at a constant temperature by means of a system with different stages and three temperature control loops. Initially, the resonator is charged with the gas mixture at the highest pressure, and resonance frequencies are recorded when the system is stabilized. The pressure is then reduced by venting the equipment in order to carry out the next measurement point.

3. Results and discussion

As described below, the experimental technique provides resonance frequency measurements which are related to the speed of sound (w) by equation (1):

$$w = 2\pi a(f_{lm} - \Delta f_{lm})/\nu_{lm} \quad (1)$$

where a is the radius of the cavity, f_{lm} is the frequency of resonance of acoustic mode (l,m), Δf_{lm} is a correction term which takes into account the effect of the thermal boundary layer, the coupling of gas and shell motion and the presence of ducts in the cavity and, finally, ν_{lm} is the eigenvalue of acoustic mode (l,m).

The radius of the cavity as a function of pressure and temperature was determined by acoustic measurements in argon [16], due to the accurate knowledge of the speed of sound derived from its equation of state [26].

In our measurements, the first five acoustic radial modes were recorded: (0, 2), (0, 3), (0, 4), (0, 5), (0,6) which corresponds to a frequency range from 4560 Hz to 25520 Hz. However, modes (0,3) and (0,6) were discarded since the excess relative resonance halfwidths (the difference between the experimental and the acoustic model halfwidths divided by the experimental resonance frequencies) were larger than those obtained for the other modes. Therefore, the final experimental

Table 4

Experimental speed of sound^a $w_{\text{exp}}(p,T)$ for the (carbon monoxide + ethane) gaseous mixtures and relative deviations $\Delta w_{\text{EoS}} = (w_{\text{exp}} - w_{\text{EoS}})/w_{\text{EoS}}$ from the values predicted by the AGA8-DC92 and GERG-2008 equations of state.

CO (0.25) + C ₂ H ₆ (0.75) ^b				CO (0.5) + C ₂ H ₆ (0.5) ^b			
p / MPa	$w_{\text{exp}} / \text{m}\cdot\text{s}^{-1}$	$10^2\cdot\Delta w_{\text{AGA}}$	$10^2\cdot\Delta w_{\text{GERG}}$	p / MPa	$w_{\text{exp}} / \text{m}\cdot\text{s}^{-1}$	$10^2\cdot\Delta w_{\text{AGA}}$	$10^2\cdot\Delta w_{\text{GERG}}$
$T = 273.15 \text{ K}$				$T = 300.00 \text{ K}$			
0.27645	303.848	0.0049	0.0121	0.25134	317.821	0.0027	0.0023
0.50146	300.832	0.0090	0.0214	0.50149	315.276	0.0098	0.0105
0.76259	297.422	0.0681	0.0860	0.99986	310.138	0.0218	0.0211
1.00207	294.065	0.0691	0.0914	1.99802	299.733	0.0797	0.0600
1.49803	286.869	0.0669	0.0959	3.00095	288.934	0.0784	0.0102
2.00115	279.193	0.0551	0.0862	4.01116	278.110	0.0437	-0.1209
2.50725	271.026	0.0276	0.0518	4.99268	268.279	-0.0225	-0.3640
				6.05671	259.803	-0.1536	-0.8995
				7.02605	256.700	-0.2794	-1.8994
$T = 325.00 \text{ K}$				$T = 350.00 \text{ K}$			
0.25477	329.793	0.0269	0.0235	0.25135	341.090	0.0123	0.0067
0.49969	327.812	0.0249	0.0212	0.25094	341.104	0.0157	0.0101
1.00253	323.812	0.0401	0.0328	0.50075	339.526	0.0188	0.0122
1.99737	316.043	0.0983	0.0681	0.49911	339.548	0.0224	0.0159
2.99028	308.380	0.1195	0.0413	1.00115	336.419	0.0315	0.0200
4.00411	300.986	0.1332	-0.0304	1.98446	330.551	0.0775	0.0428
5.01110	294.407	0.1321	-0.1704	2.99417	324.773	0.0976	0.0172
5.86960	289.786	0.1258	-0.3595	3.99718	319.513	0.1122	-0.0417
				5.00187	314.924	0.1209	-0.1434
				5.77757	312.003	0.1264	-0.2559
$T = 273.15 \text{ K}$				$T = 300.00 \text{ K}$			
0.25133	313.101	-0.0047	-0.0075	0.25097	327.014	0.0011	-0.0067
0.50095	311.330	0.0027	-0.0056	0.49973	325.755	0.0135	-0.0020
0.99987	307.801	0.0133	-0.0133	0.99608	323.271	0.0298	-0.0078
2.00080	300.929	0.0464	-0.0479	2.00031	318.542	0.0724	-0.0387
3.98797	288.295	-0.0630	-0.4435	3.50482	312.245	0.0852	-0.2131
6.01048	279.674	-0.3896	-1.4161	5.01074	307.519	0.0607	-0.5351
8.01766	280.287	-0.8958	-3.4315	6.50979	305.139	0.0108	-1.0242
9.05084	285.826	-1.1712	-5.0283	7.99546	305.913	-0.0280	-1.6839
9.86490	293.075	-1.3251	-6.4053	10.0557	313.393	-0.0348	-2.8880
				10.9327	319.005	-0.0357	-3.4792
$T = 325.00 \text{ K}$				$T = 350.00 \text{ K}$			
0.25014	339.204	0.0104	0.0002	0.26334	350.730	0.0163	0.0039
0.49995	338.272	0.0188	0.0003	0.51332	350.057	0.0224	0.0014
0.99933	336.461	0.0327	-0.0082	0.99666	348.781	0.0247	-0.0179
2.00296	333.133	0.0688	-0.0417	1.99725	346.491	0.0530	-0.0546
3.39607	329.197	0.0894	-0.1730	3.99477	343.109	0.0781	-0.2401
5.01783	326.033	0.0939	-0.4314	6.00194	341.788	0.0847	-0.5534
6.52171	324.859	0.0851	-0.7762	8.00568	343.035	0.0853	-0.9799
8.02239	325.783	0.0807	-1.2137	8.95931	344.652	0.0895	-1.2150
9.61259	329.380	0.0877	-1.7727				
$T = 273.15 \text{ K}$				$T = 300.00 \text{ K}$			
0.25133	323.610	0.0004	-0.0084	0.18379	338.301	-0.0062	-0.0089
0.50080	323.010	0.0074	-0.0129	0.49723	337.894	0.0018	-0.0147
0.98822	321.901	0.0177	-0.0324	0.99783	337.307	0.0105	-0.0348
1.99115	319.955	0.0366	-0.1032	1.98925	336.422	0.0212	-0.1037
3.50041	317.940	0.0288	-0.3073	3.49830	335.862	0.0214	-0.2718
5.02172	317.324	-0.0110	-0.6059	5.01442	336.402	0.0071	-0.4986
6.54837	318.455	-0.0718	-0.9807	6.50228	338.141	-0.0163	-0.7621
7.94124	321.257	-0.1295	-1.3715	8.00760	341.231	-0.0426	-1.0557
9.08868	324.946	-0.1713	-1.7203	9.01139	344.077	-0.0575	-1.2597
10.47053	331.102	-0.2112	-2.1618	10.0224	347.581	-0.0722	-1.4713
$T = 325.00 \text{ K}$				$T = 350.00 \text{ K}$			
0.25072	351.034	0.0062	-0.0068	0.25045	363.167	-0.0034	-0.0176
0.49852	350.900	0.0104	-0.0140	0.49990	363.175	-0.0003	-0.0258
0.99784	350.690	0.0186	-0.0338	1.00600	363.243	0.0043	-0.0482
1.99795	350.511	0.0282	-0.0984	2.00264	363.588	0.0087	-0.1115
3.49391	350.893	0.0289	-0.2449	3.49033	364.653	0.0059	-0.2430
5.00268	352.154	0.0192	-0.4348	4.81181	366.187	-0.0019	-0.3852
6.30161	353.997	0.0054	-0.6211	6.30809	368.621	-0.0151	-0.5652
8.00587	357.538	-0.0158	-0.8843	8.00488	372.302	-0.0331	-0.7830
9.00123	360.214	-0.0278	-1.0427	9.00601	374.940	-0.0438	-0.9141
10.07454	363.596	-0.0425	-1.2176	10.2064	378.564	-0.0543	-1.0695

^a Expanded uncertainties ($k = 2$): $U(p) = 7.5 \cdot 10^{-5} (p/\text{Pa}) + 200 \text{ Pa}$; $U(T) = 4 \text{ mK}$; $U_r(w) = 2.5 \cdot 10^{-4}$.

^b The exact mixture compositions and their uncertainties are provided in Table 3.

Table 5

Experimental speed of sound^a $w_{\text{exp}}(p,T)$ for the (carbon monoxide + propane) gaseous mixtures and relative deviations $\Delta w_{\text{EoS}} = (w_{\text{exp}} - w_{\text{EoS}})/w_{\text{EoS}}$ from the values predicted by the AGA8-DC92 and GERG-2008 equations of state.

CO (0.5) + C ₃ H ₈ (0.5) ^b							
p / MPa	$w_{\text{exp}} / \text{m}\cdot\text{s}^{-1}$	$10^2 \cdot \Delta w_{\text{AGA}}$	$10^2 \cdot \Delta w_{\text{GERG}}$	p / MPa	$w_{\text{exp}} / \text{m}\cdot\text{s}^{-1}$	$10^2 \cdot \Delta w_{\text{AGA}}$	$10^2 \cdot \Delta w_{\text{GERG}}$
$T = 260.00 \text{ K}$				$T = 260.00 \text{ K}$			
0.20078	266.471	-0.0136	-0.0568	0.39460	263.391	-0.0493	-0.1128
0.30158	264.882	-0.0298	-0.0837	0.50252	261.633	-0.0764	-0.1505
$T = 273.15 \text{ K}$				$T = 300.00 \text{ K}$			
0.19386	272.982	0.0169	-0.0386	0.29223	284.331	0.0367	-0.0339
0.28800	271.702	0.0166	-0.0557	0.54301	281.740	0.0560	-0.0584
0.38724	270.337		-0.0761	0.77731	279.297	0.0724	-0.0863
0.49345	268.861		-0.1000	0.99181	277.042	0.0868	-0.1154
0.59325	267.456		-0.1251	1.19159	274.927	0.0986	-0.1462
0.69901	265.952		-0.1539	1.38268	272.893	0.1090	-0.1785
0.81350	264.302		-0.1883	1.60105	270.553	0.1185	-0.2199
				1.78488	268.583	0.1285	-0.2543
$T = 325.00 \text{ K}$				$T = 350.00 \text{ K}$			
0.28005	295.484	0.0348	-0.0233	0.29434	305.829	0.0230	-0.0280
0.47502	293.933	0.0526	-0.0301	0.48542	304.649	0.0392	-0.0293
0.69132	292.217	0.0738	-0.0383	0.69113	303.380	0.0541	-0.0346
0.89187	290.623	0.0914	-0.0497	0.87667	302.250	0.0699	-0.0384
1.08734	289.070	0.1077	-0.0634	1.08671	300.982	0.0878	-0.0439
1.29269	287.446	0.1256	-0.0784	1.28255	299.811	0.1045	-0.0503
1.48963	285.893	0.1419	-0.0951	1.46308	298.738	0.1184	-0.0584
1.69379	284.292	0.1591	-0.1133	1.69671	297.372	0.1383	-0.0682
1.88217	282.824	0.1745	-0.1316	1.90481	296.165	0.1532	-0.0808
CO (0.75) + C ₃ H ₈ (0.25) ^b							
p / MPa	$w_{\text{exp}} / \text{m}\cdot\text{s}^{-1}$	$10^2 \cdot \Delta w_{\text{AGA}}$	$10^2 \cdot \Delta w_{\text{GERG}}$	p / MPa	$w_{\text{exp}} / \text{m}\cdot\text{s}^{-1}$	$10^2 \cdot \Delta w_{\text{AGA}}$	$10^2 \cdot \Delta w_{\text{GERG}}$
$T = 260.00 \text{ K}$				$T = 260.00 \text{ K}$			
0.19907	292.461	0.0021	-0.0194	0.76008	289.280		-0.0577
0.39191	291.362		-0.0294	0.99878	287.948		-0.0811
0.59922	290.182		-0.0454	1.21055	286.780		-0.1054
$T = 273.15 \text{ K}$				$T = 300.00 \text{ K}$			
0.20949	299.290	0.0158	-0.0153	0.50171	311.723	0.0354	-0.0235
0.35384	298.609	0.0204	-0.0201	0.99613	310.242	0.0614	-0.0419
0.58825	297.513	0.0255	-0.0314	1.48726	308.873	0.0849	-0.0678
0.76654	296.692	0.0282	-0.0419	1.92604	307.744	0.1030	-0.0971
0.97447	295.747		-0.0563	2.51201	306.391	0.1241	-0.1420
1.18620	294.801		-0.0738	3.02432	305.365	0.1376	-0.1871
1.39222	293.896		-0.0933	3.52398	304.518	0.1457	-0.2355
1.58925	293.050		-0.1131	4.02074	303.844	0.1505	-0.2853
1.86162	291.912		-0.1426	4.58790	303.295	0.1510	-0.3441
$T = 325.00 \text{ K}$				$T = 350.00 \text{ K}$			
0.49971	323.766	0.0311	-0.0254	0.49176	335.168	0.0213	-0.0316
1.02457	322.770	0.0623	-0.0359	0.96989	334.633	0.0441	-0.0414
1.50657	321.938	0.0856	-0.0560	1.47005	334.161	0.0673	-0.0567
1.91836	321.308	0.1056	-0.0759	1.96728	333.788	0.0906	-0.0751
2.51748	320.525	0.1315	-0.1115	2.49347	333.488	0.1109	-0.1017
3.02317	320.000	0.1520	-0.1449	2.99966	333.308	0.1301	-0.1295
3.51513	319.612	0.1695	-0.1806	3.48092	333.234	0.1464	-0.1589
3.90240	319.398	0.1819	-0.2101	4.00733	333.276	0.1652	-0.1904
4.41713	319.245	0.1973	-0.2498	4.41329	333.389	0.1774	-0.2170

^a Expanded uncertainties ($k = 2$): $U(p) = 7.5 \cdot 10^{-5} (p/\text{Pa}) + 200 \text{ Pa}$; $U(T) = 4 \text{ mK}$; $U_r(w) = 2.5 \cdot 10^{-4}$.

^b The exact mixture compositions and their uncertainties are provided in Table 3.

speed of sound is the average of modes (0, 2), (0, 4) and (0, 5). Additionally, the values obtained using GERG-2008 [3] and AGA8-DC92 [27] equations of state were calculated using Refprop software [28]. The experimental speed of sound and the relative deviations from reference equations are reported in Table 4 for (carbon monoxide + ethane) mixtures and, in Table 5, for (carbon monoxide + propane) mixtures.

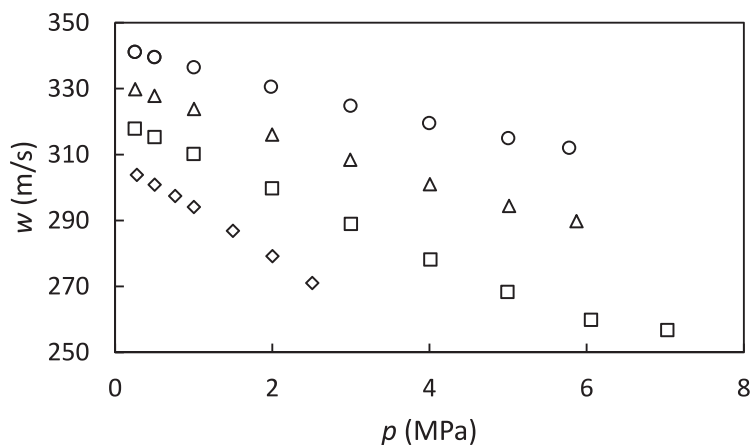
Fig. 1 shows graphically the speed of sound values as a function of pressure for the different isotherms of the three mixtures containing carbon monoxide and ethane. As can be seen, the higher the temperature, the greater the speed of sound. Moreover, the speed of sound decreases with pressure for the $x_{\text{ethane}} = 0.75$ mixture. However, it presents a minimum with pressure for the equimolar mixture, and the minimum is displaced to lower pressures for the $x_{\text{ethane}} = 0.25$ mixture and, at $T = 350 \text{ K}$, an increase with pressure is observed in the measurement range.

The behaviour of the reference models in terms of deviations of speed of sound from experimental values is also depicted in Fig. 2. The results show that the deviations from the AGA8-DC92 equation are much lower

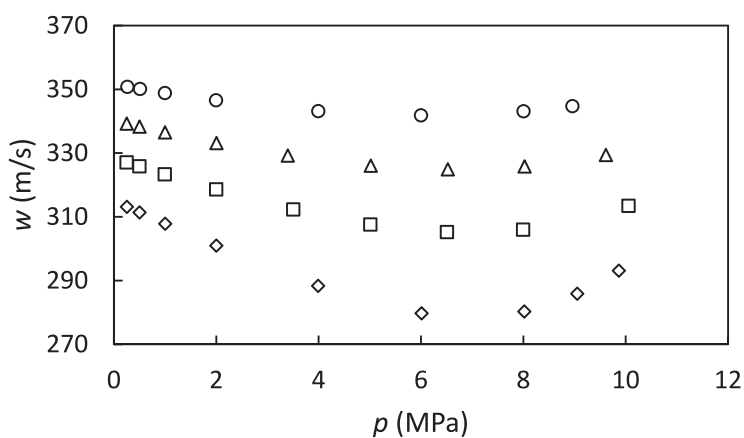
than those from GERG-2008 for the carbon monoxide + ethane mixtures.

In the case of the AGA8-DC92 equation, average absolute deviation ranges from 0.017 % (for the mixture of composition $x_{\text{CO}} = 0.75$ at $T = 350 \text{ K}$) to 0.43 % (for $x_{\text{CO}} = 0.5$ mixture and $T = 273.15 \text{ K}$). Deviations are mainly positive at compositions $x_{\text{CO}} = 0.25$ and 0.50, although they are negative above 6 MPa for the $x_{\text{CO}} = 0.75$ mixture. Furthermore, most deviations are within the uncertainty of this equation for the speed of sound which is stated as 0.2 %.

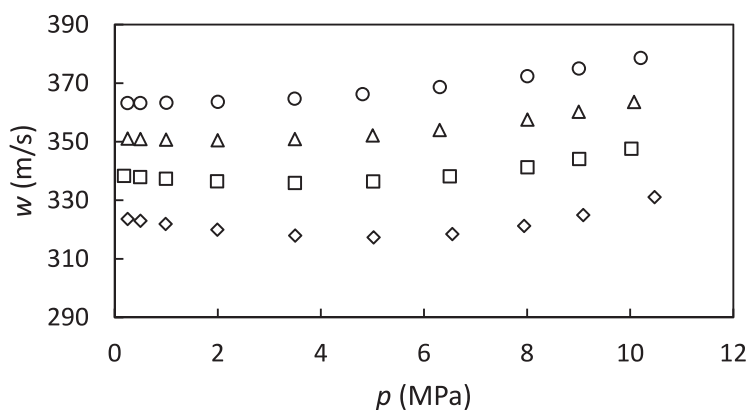
In contrast, the average absolute deviations of the GERG-2008 equation range from 0.057 % to 1.87 %, at $T = 350 \text{ K}$ for the $x_{\text{CO}} = 0.25$ mixture and $T = 273.15 \text{ K}$ for the $x_{\text{CO}} = 0.5$ mixture, respectively. These deviations are negative and rise with increasing pressure in the whole range for the $x_{\text{CO}} = (0.5 \text{ and } 0.75)$ mixtures, whereas the $x_{\text{CO}} = 0.25$ mixture initially exhibits small positive deviations up to 3 MPa before then changing to larger negative deviations above 4 MPa. Moreover, most deviations are greater than 0.1 %, which is the stated



(a)



(b)



(c)

Fig. 1. Speed of sound for the (carbon monoxide + ethane) mixtures (a) $x_1 = 0.25$; (b) $x_1 = 0.5$; (c) $x_1 = 0.75$ as a function of pressure at different isotherms (\diamond) 273.15 K; (\square) 300 K; (Δ) 325 K; (\circ) 350 K.

uncertainty of speed of sound for this equation of state.

As regards (carbon monoxide + propane) mixtures, measurements were taken in a narrow pressure range to ensure the superheated condition for the mixture. However, AGA8-DC92 calculations predict the presence of two phases at low temperatures and these deviations were not calculated (no data appear in Table 5).

The comparison between the experimental data and those predicted by the GERG-2008 and AGA8-DC92 equations of state are also depicted in Fig. 3.

This plot shows that the relative deviations of experimental speeds of sound from the values calculated with the GERG-2008 equation are always negative and these deviations increase at higher pressure. Values range from -0.023% up to -0.25% , with average values being -0.089% for the equimolar mixture and -0.11% for the $x_{\text{CO}} = 0.75$ mixture. Nevertheless, the equimolar mixture was measured up to 2 MPa, whereas the measurements for the enriched CO mixture were performed up to 4.4 MPa. Again, deviations above the uncertainty of the GERG-2008 equation were found at high pressures, although they are lower

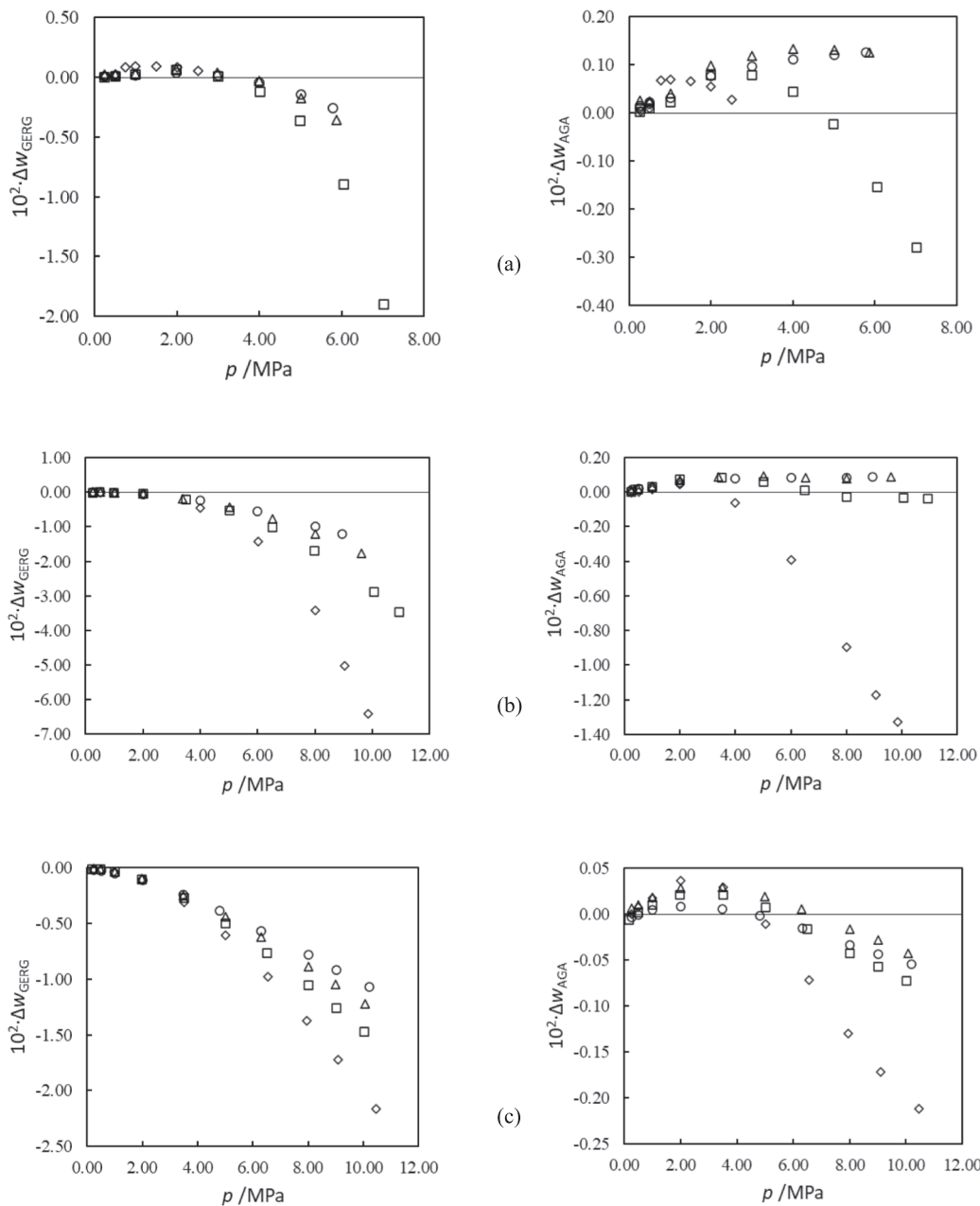


Fig. 2. Relative deviation of speed of sound ($\Delta w_{EoS} = (w_{exp} - w_{EoS})/w_{EoS}$), for the mixture $[\text{CO}(x_1) + \text{C}_2\text{H}_6(1-x_1)]$ (a) $x_1 = 0.25$, (b) $x_1 = 0.5$, (c) $x_1 = 0.75$, from the GERG-2008 [3] equation of state (left) and the AGA8-DC92 [27] equation of state (right) as a function of pressure at different temperatures: (\diamond) 273.15 K; (\square) 300 K; (Δ) 325 K; (\circ) 350 K.

than those obtained for the mixtures with ethane.

Deviations from the AGA8-DC92 equation are positive with an increasing trend with higher pressures, except for the equimolar mixture at 260 K whose deviations are negative. Their values range between -0.076% and 0.20% , and the average deviations are 0.083% , and 0.099% , for the $x_{\text{CO}} = 0.5$ and $x_{\text{CO}} = 0.75$ mixtures, respectively, with most deviations being within the equation uncertainty.

Despite the need for them—as pointed out by the authors of the GERG-2008 model—it is worth highlighting the lack of accurate speed of sound measurements. In fact, no data have been found for either of the mixtures in the literature.

The squared experimental speeds of sound are also fitted to a virial type function of pressure, equation (2):

$$w^2(p, T) = A_0 + A_1 p + A_2 p^2 + A_3 p^3 + \dots \quad (2)$$

where the coefficients A_i depend on temperature, and the first acoustic virial parameter A_0 is related to the adiabatic coefficient γ^{ps} as a perfect gas through equation (3), with R being the ideal gas constant and M the molar mass.

$$A_0 = \gamma^{ps} RT/M \quad (3)$$

The results of the adjustment to equation (2) are shown in Table 6 and Table 7, for the (carbon monoxide + ethane) and (carbon monoxide + propane) mixtures, respectively. Both tables contain the fitting parameters and the root mean square deviation (RMSD) obtained for the different mixtures. The significant figures of these parameters are

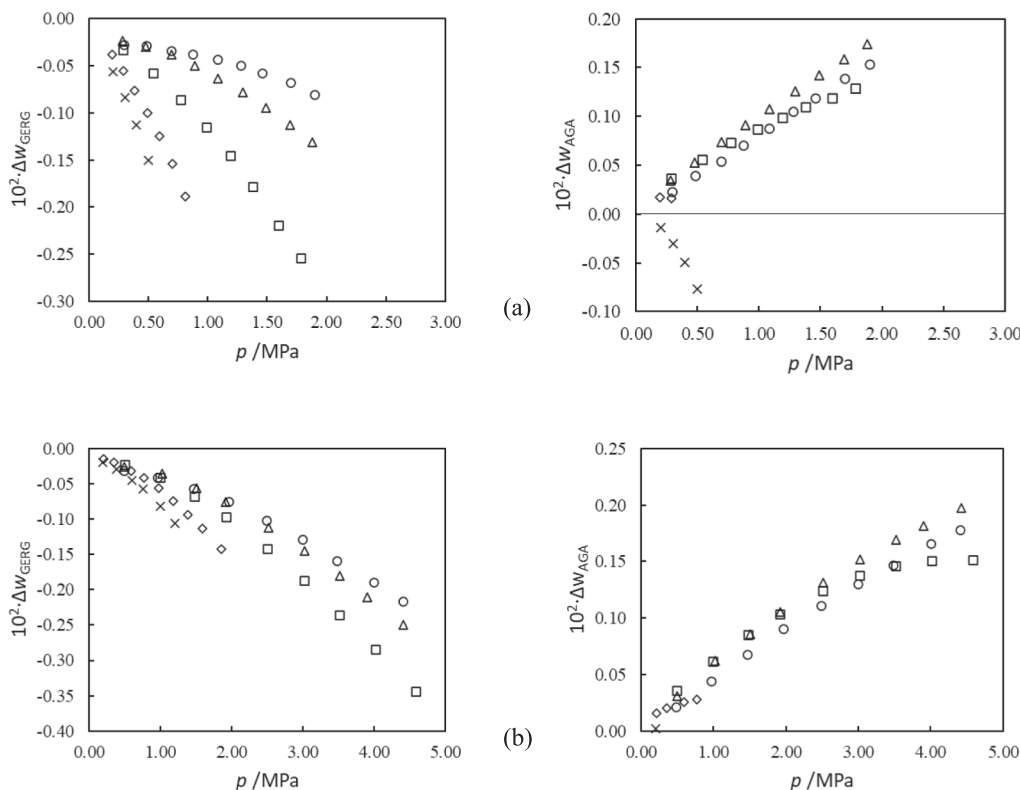


Fig. 3. Relative deviation of speed of sound ($\Delta w_{\text{EoS}} = (w_{\text{exp}} - w_{\text{EoS}})/w_{\text{EoS}}$), for the mixture $[\text{CO} (x_1) + \text{C}_3\text{H}_8 (1-x_1)]$ (a) $x_1 = 0.5$, (b) $x_1 = 0.75$, from the GERG-2008 [3] equation of state (left) and AGA8-DC92 [27] equation of state (right) as a function of pressure at different temperatures: (×) 260 K; (◇) 273.15 K; (□) 300 K; (Δ) 325 K; (○) 350 K.

Table 6

The fitting coefficients (A_i) of squared speeds of sound (Eq. (2)) and the root mean square deviation (RMSD) obtained from the experimental data of the (carbon monoxide + ethane) mixtures, for the different isotherms measured.

T (K)	A_0 (m^2/s^2)	A_1 ($\text{m}^2/\text{s}^2\text{MPa}$)	A_2 ($\text{m}^2/\text{s}^2\text{MPa}^2$)	A_3 ($\text{m}^2/\text{s}^2\text{MPa}^3$)	A_4 ($\text{m}^2/\text{s}^2\text{MPa}^4$)	RMSD• 10^6
CO (0.25) + C ₂ H ₆ (0.75)						
273.15	94,440	-7610	-370	30		98
300	102,710	-6770	310	-100	10	171
325	110,040	-5110	-50	30		121
350	117,400	-4250	40	20		52
CO (0.5) + C ₂ H ₆ (0.5)						
273.15	99,100	-4330	-10	20	2	143
300	107,720	-3220	10	20		103
325	115,690	-2560	80	10		28
350	123,520	-1970	110	10		28
CO (0.75) + C ₂ H ₆ (0.25)						
273.15	105,130	-1640	110	9		35
300.00	114,630	-980	120	5		22
325.00	123,340	-470	110	3		18
350.00	131,900	-60	100	2		9

consistent with their uncertainties which were calculated using a Monte-Carlo method [29].

As can be seen from the root mean square values, they are below the uncertainty of the measurements for all the mixtures under study. In the case of the ethane mixtures $x_{\text{C}_2\text{H}_6} = 0.75$ at $T = 300$ K and $x_{\text{C}_2\text{H}_6} = 0.5$ at $T = 273.15$ K– a fifth parameter is required to obtain RMSD values below uncertainty.

Additionally, the calculated values of the adiabatic coefficient and the isobaric heat capacity as a perfect gas using equation (3) are reported in Tables 8 and 9, for the mixtures under study. These tables also contain

Table 7

The fitting coefficients (A_i) of squared speeds of sounds (Eq. (2)) and the root mean square deviation (RMSD) obtained from the experimental data of the (carbon monoxide + propane) mixtures, for the different isotherms measured.

T (K)	A_0 (m^2/s^2)	A_1 ($\text{m}^2/\text{s}^2\text{MPa}$)	A_2 ($\text{m}^2/\text{s}^2\text{MPa}^2$)	A_3 ($\text{m}^2/\text{s}^2\text{MPa}^3$)	RMSD• 10^6
CO (0.5) + C ₃ H ₈ (0.5)					
260.00	72,660	-8150	-450		1
273.15	75,940	-7300	-220		1
300.00	82,560	-5880	20		13
325.00	88,640	-4770	90		14
350.00	94,670	-3880	120		6
CO (0.75) + C ₃ H ₈ (0.25)					
260.00	86,210	-3400	100		5
273.15	90,180	-2920	130		11
300.00	98,170	-2040	110	9	13
325.00	105,500	-1410	110	6	5
350.00	112,760	-910	110	4	6

the deviations of these derived properties, from those obtained by the AGA8-DC92 and GERG-2008 equations of state. The estimated uncertainty of the adiabatic coefficient is the same as that of the coefficient A_0 , whose uncertainty values are less than 0.2 %.

The results summarized in Tables 8 and 9 allow us to conclude that the predictions of heat capacity ratios and isobaric heat capacities as perfect gas are similar for both equations of state and that the deviations between our data derived from equation (3) and those calculated by the models are below the uncertainty of these models, which state a relative uncertainty of 1 % in heat capacity.

Table 8

Perfect gas heat capacity ratios (γ^{PG}) and perfect gas molar heat capacities at constant pressure ($C_{p,m}^{\text{PG}}$) obtained for (carbon monoxide + ethane) mixtures. Relative deviations thereof, from the predicted values $\Delta X_{\text{EoS}} = (X_{\text{exp}} - X_{\text{EoS}})/X_{\text{EoS}}$ obtained by the AGA8-DC92 and GERG-2008 equations of state.

T / K	γ^{PG}	$10^2 \cdot \Delta \gamma_{\text{AGA}}^{\text{PG}}$	$10^2 \cdot \Delta \gamma_{\text{GERG}}^{\text{PG}}$	$C_{p,m}^{\text{PG}} / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$10^2 \cdot \Delta C_{p,m}^{\text{PG}}_{\text{AGA}}$	$10^2 \cdot \Delta C_{p,m}^{\text{PG}}_{\text{GERG}}$
CO (0.25) + C ₂ H ₆ (0.75)						
273.15	1.2289	-0.1106	-0.1081	44.634	0.4833	0.4721
300.00	1.2169	0.0702	0.0671	46.646	-0.3236	-0.3093
325.00	1.2034	-0.0241	-0.0308	49.187	0.1184	0.1512
350.00	1.1923	-0.0094	-0.0185	51.557	0.0490	0.0960
CO (0.5) + C ₂ H ₆ (0.5)						
273.15	1.2671	-0.0854	-0.0835	39.447	0.3197	0.3128
300.00	1.2540	-0.0810	-0.0843	41.044	0.3187	0.3318
325.00	1.2432	-0.0152	-0.0219	42.503	0.0624	0.0899
350.00	1.2325	0.0124	0.0034	44.069	-0.0534	-0.0146
CO (0.75) + C ₂ H ₆ (0.25)						
273.15	1.3205	-0.0157	-0.0155	34.259	0.0490	0.0485
300.00	1.3109	-0.0120	-0.0070	35.054	0.0385	0.0226
325.00	1.3021	0.0077	0.0015	35.840	-0.0255	-0.0050
350.00	1.2930	-0.0095	-0.0176	36.692	0.0324	0.0599

Table 9

Perfect gas heat capacity ratios (γ^{PG}) and perfect gas molar heat capacities at constant pressure ($C_{p,m}^{\text{PG}}$) obtained for (carbon monoxide + propane) mixtures. Relative deviations thereof, from the predicted values $\Delta X_{\text{EoS}} = (X_{\text{exp}} - X_{\text{EoS}})/X_{\text{EoS}}$ obtained by the AGA8-DC92 and GERG-2008 equations of state.

T / K	γ^{PG}	$10^2 \cdot \Delta \gamma_{\text{AGA}}^{\text{PG}}$	$10^2 \cdot \Delta \gamma_{\text{GERG}}^{\text{PG}}$	$C_{p,m}^{\text{PG}} / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$10^2 \cdot \Delta C_{p,m}^{\text{PG}}_{\text{AGA}}$	$10^2 \cdot \Delta C_{p,m}^{\text{PG}}_{\text{GERG}}$
CO (0.5) + C ₃ H ₈ (0.5)						
260.00	1.2114	0.0099	-0.0298	47.646	-0.0468	0.1411
273.15	1.2052	0.0244	-0.0183	48.843	-0.1188	0.0894
300.00	1.1929	0.0372	-0.0103	51.412	-0.1930	0.0536
325.00	1.1823	0.0286	-0.0220	53.935	-0.1570	0.1206
350.00	1.1724	0.0062	-0.0459	56.543	-0.0362	0.2662
CO (0.75) + C ₃ H ₈ (0.25)						
260.00	1.2768	0.0176	-0.0154	38.350	-0.0635	0.0555
273.15	1.2714	0.0288	-0.0073	38.951	-0.1062	0.0270
300.00	1.2601	0.0135	-0.0283	40.283	-0.0519	0.1088
325.00	1.2501	0.0050	-0.0409	41.561	-0.0201	0.1636
350.00	1.2406	-0.0062	-0.0549	42.870	0.0256	0.2282

4. Conclusions

Accurate speed of sound data of different binary mixtures of carbon monoxide with ethane or propane, in the gas region, are reported in this paper. The comparison between the experimental data and the values predicted by the AGA8-DC92 equation of state gives an absolute average deviation of 0.081 % (bias -0.017 %) for mixtures with ethane, and an absolute average deviation of 0.091 % (bias 0.085 %) for mixtures with propane. Although these values are much larger than the uncertainty of the measurements, they are within the 0.2 % uncertainty of the equation of state. As regards the predictions obtained with the GERG-2008 equation of state, the absolute average deviation is 0.55 % (bias -0.54 %) for mixtures with ethane and 0.10 % (bias -0.10 %) for mixtures with propane. These values are at the limit of the uncertainty for this equation of state (0.1 %) in the case of mixtures containing propane but are five times higher than the uncertainty for mixtures with ethane. In both equations of state, it is observed that the deviations are greater as the pressure increases.

Finally, the fitting of the squared speed of sound to a virial type equation was performed for each isotherm and the root mean square deviation (RMSD) of the speed of sound ranges between nine parts in 10^6 (at $x_{\text{C}_2\text{H}_6} = 0.25$ and $T = 350$ K) and 171 parts in 10^6 (at $x_{\text{C}_2\text{H}_6} = 0.75$ and $T = 350$ K) for mixtures with ethane, and between one part in 10^6 (at $x_{\text{C}_3\text{H}_8} = 0.5$ and $T = 260$ K and 273.15 K) and 14 parts in 10^6 (at $x_{\text{C}_2\text{H}_6} = 0.5$ and $T = 325$ K) for mixtures with propane, which were measured in a smaller pressure range. The heat capacity ratio as perfect gas was calculated from this adjustment and these values were consistent with those given by both reference equations of state (AGA8-DC92 and GERG-2008).

CRediT authorship contribution statement

José J. Segovia: Writing – review & editing, Writing – original draft, Supervision, Methodology, Formal analysis, Conceptualization. **M. Carmen Martín:** Formal analysis, Writing – review & editing, Funding acquisition, Project administration. **Xavier Paredes:** Investigation, Formal analysis. **Andrés Rojo:** Resources. **Fredy Vélez:** Investigation, Formal analysis. **David Vega-Maza:** Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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