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Sound Speed Measurements on Gas Mixtures of Natural Gas Components Using a Cylindrical Resonator

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A description of a fixed-path length acoustic resonator which uses electrostatic transducers for sound generation and detection is given. Also, a summary of the measurements on 13 binary and 4 multicomponent gas mixtures of natural gas components is given. Data were obtained at pressures to 10 MPa for five isotherms at 25 K increments from 250 to 350 K. The binary mixtures are primarily methane-rich, with either ethane, nitrogen, carbon dioxide, or propane as the second constituent. The multicomponent mixture compositions represent four naturally occurring natural gas mixtures.

KEY WORDS: binary mixtures; carbon dioxide; cylindrical resonator; electrostatic transducers; ethane; gas; isotherm; methane; mixtures; multicomponent mixtures; natural gas; nitrogen; propane; sound speed.

1. INTRODUCTION

Orifice plates and turbine meters are widely used to determine the mass flow rate of natural gas, and they play a vital role in custody transfer of this valuable commodity. Calibration of a flow meter can be accomplished by measuring the mass flow rate with a sonic nozzle placed in series with the meter. The sonic nozzle is operated at maximum flow rate which is the sound speed. We can compute the mass flow rate [1, 2] using

$$m = A\rho WC \tag{1}$$

where m is the mass flow rate, A is the cross-sectional area of the nozzle at the throat, ρ is the density, W is the sound speed, and C is a calibration

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constant for the nozzle and depends on geometrical imperfections and energy losses of the nozzle. The ideal value for C is unity, for a lossless system. In practice C is usually within a few tenths of a percent of the ideal value. The temperature, pressure, and composition are used to compute the density and sound speed from an equation of state.

In the present study, sound speed data have been obtained, for mixtures of natural gas components. The study is part of a program to provide the natural gas industry with a mathematical model that can be used to calculate the sound speed, W, of a natural gas mixture within 0.1 %, given its pressure, P, temperature, T, and mole fractions, X_i:

$$W = W(P, T, X_i) \tag{2}$$

Pure-fluid and binary-mixture sound speed data are used in the development of the model. Data have been obtained for 13 binary mixtures; these are primarily methane-rich with either ethane, propane, carbon dioxide, or nitrogen as the second component. The data on four multicomponent mixtures, Gulf Coast, Amarillo, Statoil dry gas, and Statoil Statvordgass, have been taken to test the predictions of the model. All of these mixtures were prepared gravimetrically using a high-precision balance. Measurements were taken on five isotherms, at 250, 275, 300, 325, and 350 K, at pressures to 10 MPa. These ranges for temperature and pressure encompass the region involved in custody transfer.

Sound speed in gases is generally measured with an acoustic cavity or resonator. These devices can be grouped into types that operate at low frequencies, below 200 kHz [3–11], or high frequencies, usually in the megahertz range [12–19], and with fixed path length [3–13] or with variable path length [14–19]. Usually with high-frequency devices the path length is varied, and with low-frequency devices, the frequency is varied to achieve a resonance condition. In some of the early work both path length and frequency were kept fixed, and the resonances were found by changing pressure [12, 13] or temperature [13].

An example of the variable path system is the interferometer of Gammon [14]. Variable-path length devices incur difficulties associated with the rod which moves the reflector. The rod must be brought out through shaft seals, its position must be adjusted for effects of temperature gradients along its length, and it must not disturb the alignment of the reflector. The fixed-path length systems have no moving parts. Resonance is achieved by varying the frequency. The relative merits of fixed- and variable-path systems have been discussed in papers by Colclough [3] and Quinn et al. [4].

Most of these systems are cylindrical resonators. Cylindrical cavities require a significant correction for viscous drag at the walls, whereas the

radial modes of a spherical cavity do not have this loss and consequently have more sharply defined resonances [7, 8]. In the present work, the selection of a cylindrical cavity with a fixed path length was motivated by a desire for a system which was both simple to construct and to operate. The resonator's small size allowed the use of an existing pressure cell and cryostat.

2. THEORY

The sound speed, far removed from walls, is given by the relation between the frequency f and the wavelength λ as

$$W = f\lambda \tag{3}$$

At resonance, the cavity length L is an integral multiple of half-wavelengths,

$$L = N\lambda/2 \qquad \text{where} \quad N = 1, 2, 3, \ldots. \tag{4}$$

The value of N can be deduced by measuring successive resonances. From this and a known value of L, the wavelength can be computed from Eq. (4), and if f is known, an experimental value of sound speed W', can be calculated from Eq. (3). W' must then be corrected for the effects of wall losses. An attenuation coefficient α for this effect is [20]

$$\alpha = \frac{1}{rW'}\left\{\left(\frac{\eta}{\rho}\right)^{1/2} + (\gamma - 1)\left(\frac{k}{eC_p}\right)^{1/2}\right\}(\pi f)^{1/2} \tag{5}$$

Here η is viscosity, γ is the ratio of the heat capacities C_p/C_v, k is the thermal conductivity, ρ is the density, and r is the cylinder radius.

The correction for the energy loss, β, on reflection at the end surfaces, is given by [21]

$$\beta = \frac{1}{LW'}(\gamma - 1)\left(\frac{k}{eC_p}\right)^{1/2}(\pi f)^{1/2} \tag{6}$$

Values for viscosity and thermal conductivity were computed using the transport properties program TRAPP of Ely and Hanley [22]. Ideal-gas values of the specific heats were used for C_p and C_v. This approximation is adequate since the total correction to sound speed from these dissipative effects is between 0.02 and 0.1%.

The total attenuation coefficient Γ is the sum

$$\Gamma = \alpha + \beta \tag{7}$$

which is used to correct the measured sound speed W' to the thermodynamic sound speed W according to

$$W = W'/\{1 - \Gamma W'/(2\pi f)\} \tag{8}$$

3. EXPERIMENTAL

3.1. Determination of the Frequency for Cavity Resonance

The condition of resonance of the sonic cavity was detected electronically. The signal from the drive oscillator (see Fig. 1) was manually set to an approximate resonant frequency, typically in the range of 40 to 70 kHz. As shown in Fig. 1, the drive oscillator is frequency modulated by the modulating oscillator, which was a 100-Hz crystal oscillator. This modulation is enough to cause the drive frequency to sweep through the resonant frequency of the cavity. When the frequency modulation is small, the response of the cavity is amplitude modulated. The amplitude of the modulation is proportional to the slope of the resonance response of the cavity. The phase of this amplitude modulation changes sign as the drive oscillator frequency passes through the cavity resonance. This amplitude modulation component is detected and sent to a phase-sensitive detector (lock-in amplifier), where it is compared with the original 100-Hz signal. Since the output of the phase-sensitive detector goes through zero at the cavity resonance, it is used to lock the drive oscillator to the cavity's resonance. Suitable filtering of the tuning voltage from the phase-sensitive detector served to minimize short-term noise. The output of the drive oscillator was sent to a frequency counter which averages the frequency for 1 s. The computer records the frequency reading provided by the counter. The effect of the modulation frequency on the drive frequency is averaged out since the counter reading time greatly exceeds the modulation period of 0.01 s. Each frequency reading was an average of the drive oscillator output for 1 s. Five of these 1-s readings were averaged, and a root-mean-square (rms) deviation from this average was computed. The deviation was usually less than 5 ppm of the averaged frequency. A sound speed was

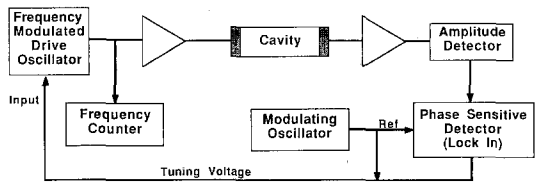

Fig. 1. Resonant cavity measurement system.

computed for four or more such averages, each one for a separate mode number, N. These mode numbers were generally between 15 and 21. The rms deviation of the sound speed from these measurements was usually 0.01 % or less.

3.2. Sonic Cavity

The sonic cavity is a tube of high-nickel steel with a length of 67 mm, an internal diameter of 10 mm, and a wall thickness of 1 mm. Electrostatic transducers are the end surfaces of the cavity. The inner cylindrical surface was ground and polished to a smooth finish. The ends of the cylinder were ground and polished to have plane, parallel surfaces within 0.003 mm over the cylinder's diameter. A small hole, of 0.3-mm diameter, was drilled into the cylindrical shell to allow the sample gas to enter and exit the cavity. We observed the change in resonance frequencies in air when a steel plug was placed in the hole. The effect of the hole on the cavity resonances was found to be negligible. Cavity dimensions were corrected for thermal expansion and the effects of hydrostatic compression.

3.3. Transducers

In earlier work on nitrogen gas [23], we developed transducers using an electrostatically driven thin plastic film as the source of sound. In the current work we found it necessary to modify our transducers to produce more intensity for the higher pressures.

Our transducers now use polyimide [24] plastic films, 0.013 mm thick, coated on one side with a thin layer of gold and lightly stretched over copper backing plates at the end faces of the cavity. This film is the mechanically active part of the transducer and is the only moving part of the system. The source transducer was driven electrostatically with a signal of about 50 V and with a bias from 100 to 200 V, and the receiving transducer was biased with 90 V. Higher voltages were needed at the higher pressures to maintain signal strength. The signal amplitude decreases by a factor of 10 to 20 when the pressure is increased from 0.1 to 5 MPa. A similar decrease in sensitivity with increasing pressure was noted in a manual for a commercially available microphone [25].

Electrostatically driven thin films have very small mass and produce negligible mechanical vibration through the cavity wall. Polyimide film was chosen because of its resistance to electrical breakdown and for its mechanical stability up to our maximum temperature of 350 K [26]. Higher sound intensities are produced with a small amount of surface roughness in the copper backing plate. Good results were produced with

three concentric circular grooves, about 0.5 mm wide and 0.5 mm deep, cut into its surface. The film was tensioned lightly to establish a flat surface so as to define the length of the cavity.

The signal developed at the receiving transducer was amplified with a very low-noise, current-sensitive amplifier. A voltage-sensitive amplifier would be adverselly affected by the capacitive loading of the 1.5-m-long coaxial cable, which connects the receiving transducer to the amplifier located on top of the cryostat. The electrical leads for the transducers were brought through the pressure cell closure with high pressure electrical feedthroughs [28]. The feedthroughs are modification of a high-pressure 1.6-mm capillary tube fitting. A 1.6-mm solid stainless steel or brass rod replaces the 1.6-mm tube, and the tube ferrule is replaced with a PPMI [24] ferrule which provides electrical isolation from ground.

3.4. Temperature and Pressure Measurement

The temperature measurement and control for the sample cell and the isothermal shield have been reported previously [28, 29]. The temperature was measured with a 25-Ω platinum resistance thermometer mounted in the wall of the pressure cell. This thermometer was calibrated on the IPTS-1968 temperature scale at the National Institute of Science and Technology, Gaithersburg, Md. The sample temperature was regulated within 1 to 3 mK of the desired temperature as measured with a six-dial potentiometer with a resolution of 0.1 μV. The total uncertainty in temperature is approximately 0.02 K at 250 K and 0.03 K at 350 K. A stable constant-current source supplied the thermometer current of 2 mA. The temperature gradients along the cell length and between the cell and its surrounding isothermal shield were monitored with copper–constantan thermocouples. The shield temperature was maintained at the cell temperature with an automatic control.

Pressure measurements were made using a 10-MPa quartz pressure gauge, calibrated with a deadweight gauge. The uncertainty in pressure is estimated to be 0.001 MPa.

3.5. Pressure Cell and Cryostat

The thermal evironment was provided by a metal cryostat, as seen in Fig. 2. The cryostat is capable of operating at low temperatures when using liquid nitrogen as a refrigerant. It is similar to the one described by Goodwin [28] . The resonator was placed in a copper pressure cell with an internal volume of 65 cm^3, a 30-mm internal diameter, a 90-mm length, and walls 23 mm thick. An isothermal shield surrounded the pressure cell

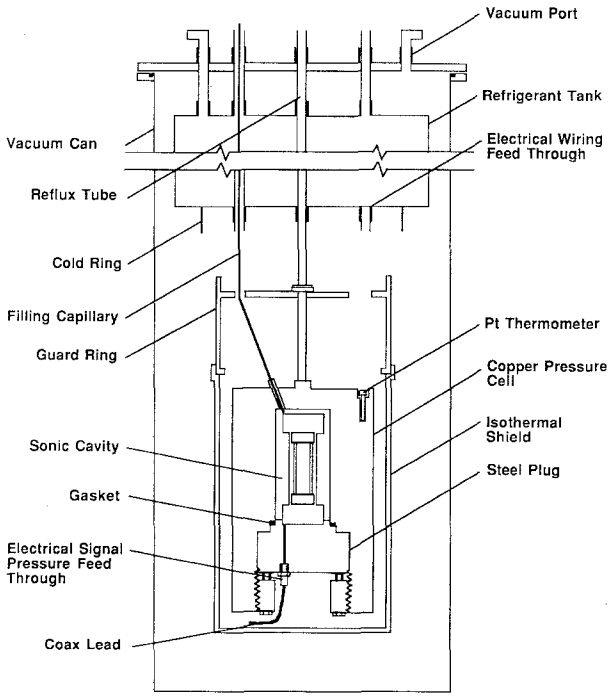

Fig. 2. Cryostat with pressure cell and resonant cavity.

and was maintained at the temperature of the pressure cell. Heat carried by the electrical leads from outside the cryostat was intercepted by two heat sinks. The wires were wound on a cold ring atached to the refrigerant tank and then wound on a guard ring which is the top of the isothermal shield. Cooling needed for temperature control of the sample cell came from radiation to the refrigerant tank and from a small amount of heat carried away from the sample cell by the electrical leads. Additional cooling could be provided by the reflux tube. Rapid cooling of about $20\,\mathrm{K}\cdot\mathrm{h}^{-1}$ was obtained when a pressure of 0.1 MPa of nitrogen gas was used in the tube. The liquid, which forms inside the reflux tube in the region of the refrigerant tank, will flash intro vapor when it reaches the the sample cell.

3.6. Sample Preparation

Mixtures were prepared in clean aluminum cylinders. The cylinders were heated and pumped to a vacuum of approximately $10\,\mu\mathrm{Pa}$. The mixtures were prepared using a 25-kg, high-precision, double pan balance. The precision for successive weighings was, under best conditions,

± 0.5 mg, but in practice, the basic uncertainty of a weight could approach 5 mg. All of the mixtures except the Gulf Coast mixture were prepared using this gravimetric system. The Gulf Coast mixture was suplied from a commercial source but conformed to the accuracies for the other mixtures reported here. Maximum uncertainty in mole fraction is estimated to be 0.006%.

The sample cylinders and the entire filling manifold were heated to approximately 330 K while the sample was transferred to the sound speed cell. Heating prevents composition changes in the filling manifold and cell, especialy for mixtures containing heavy components such as pentane and hexane.

4. SUMMARY OF RESULTS

Data were obtained for 13 binary and 4 multicomponent mixtures on 250, 275, 300, 325, and 350 K isotherms. The maximum pressure was approximately 10 MPa (1450 psia). Compositions of the mixtures are given in Tables I and II. The sound speed data, consisting of over 1000 points, will be reported in an NIST Technical Note [30]. Only selected data are presented here in graphical form to facilitate comparison with predictive models.

Figure 3 shows the sound speed data for the binary mixture 69% methane–31% ethane, and Fig. 4 shows the data for the Gulf Coast multicomponent mixture. Figure 5 and 6 show the deviations of these measurements from the predicted values of Starling et al. [31], which is a

Table I. Compositions in Mole Percentage of the Binary Mixtures

94.985 methane– 5.015 ethane
84.992 methane–15.008 ethane
68.526 methane–31.474 ethane
50.217 methane–49.783 ethane
34.524 methane–65.476 ethane
90.016 methane– 9.984 propane
95.114 methane– 4.886 nitrogen
71.373 methane–28.627 nitrogen
85.130 methane–14.870 nitrogen
94.979 methane– 5.021 carbon dioxide
85.026 methane–14.974 carbon dioxide
69.944 methane–30.056 carbon dioxide
49.593 nitrogen–50.407 carbon dioxide

Table II. Compositions in Mole Percentage of the Multicomponent Mixtures

Gulf Coast	
	96.561 methane
	1.829 ethane
	0.410 propane
	0.098 normal butane
	0.098 isobutane
	0.032 normal pentane
	0.046 isopentane
	0.067 normal hnexane
	0.262 nitrogen
	0.597 carbon dioxide
Amarillo	
	90.708 methane
	4.491 ethane
	0.815 propane
	0.141 normal butane
	0.106 isobutane
	0.065 normal pentane
	0.027 isopentane
	0.034 normal hexane
	3.113 nitrogen
	0.500 carbon dioxide
Statoil—dry gas	
	83.980 methane
	13.475 ethane
	0.943 propane
	0.067 normal butane
	0.040 isobutane
	0.008 normal pentane
	0.013 isopentane
	0.718 nitrogen
	0.756 carbon dioxide
Statoil—statvordgass	
	74.348 methane
	12.005 ethane
	8.251 propane
	3.026 normal butane
	0.575 normal pentane
	0.230 normal hexane
	0.537 nitrogen
	1.027 carbon dioxide

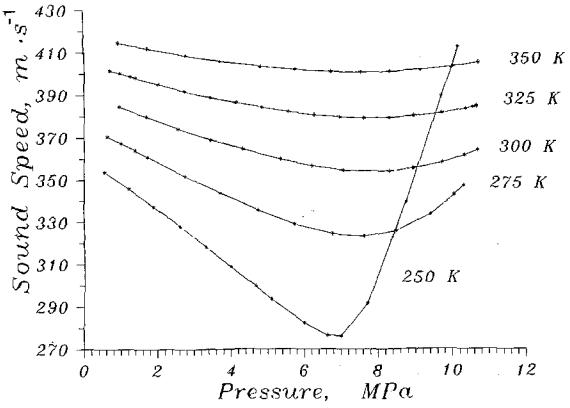

Fig. 3. Sound speed data for the binary mixture: 65% methane–ethane.

program known as SUPERZ. The largest deviations occur on the 250 K isotherm, which is showing some effects of being near the critical point of the mixture, as seen in Fig. 5. The deviations seen in Fig. 6 are illustrative of the deviations that the new formulation will attempt to improve, which is directed toward the natural gas mixtures. Generally the predictions of SUPERZ were excellent for temperatures at 300 K and above.

We compared our data for the 250 K isotherm of the Gulf Coast mixture, as seen in Fig. 7, with Goodwin's 255 K data [32]. His mixture

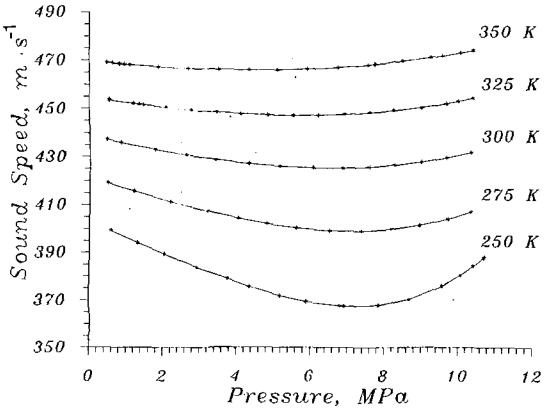

Fig. 4. Sound speed data for the Gulf Coast multicomponent mixture.

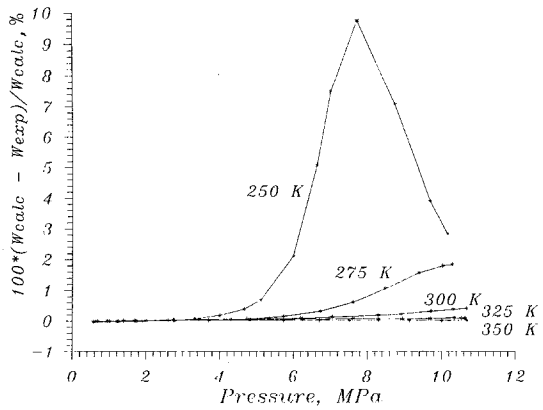

Fig. 5. Deviation of the sound speed data for the binary mixture 69% methane–31% ethane from calculations according to SUPERZ [31].

has a composition that is very close to the Gulf Coast sample but with about 2.5% less methane and 2% more ethane. Agreement of the two sets of data is better than 0.1%.

To assess further the accuracy of our data, sound speed was measured in methane at 273.15 K to 10 MPa and compared to Gammon's data [33]. The rms deviation of the 17 experimental data points from an equation of state fitted to Gammon's data was 0.012%.

For purposes of comparison and to demonstrate the capabilities of the

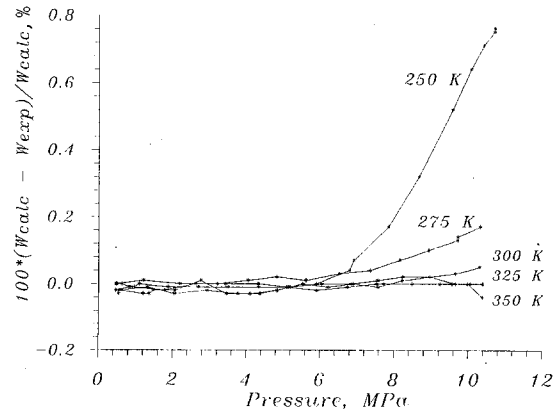

Fig. 6. Deviation of the sound speed data for the Gulf Coast mixture from calculations according to SUPERZ [31].

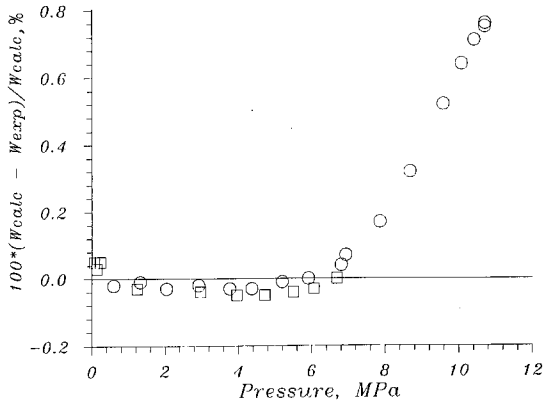

Fig. 7. Deviations of sound speed for the Gulf Coast mixture at 250 K from Ref. 31 (○) and the corresponding deviations of the 225 K isotherm of Goodwin [32] (□). These mixtures have very similar compositions.

spherical resonator technique, Moldover [34] measured the sound speed for the 69% methane–31% ethane mixture for three isotherms at 300, 325, and 350 K and at pressures to 3.4 MPa. These measurements were performed at this laboratory, using the same techniques for temperature and pressure measurements as in the above work. The spherical resonator was housed in a stainless-steel pressure vessel, which was placed in a thermostated and stirred oil bath. This system has the ability to measure sound speed with an uncertainty in the range 0.01 to 0.001%. Agreement with the

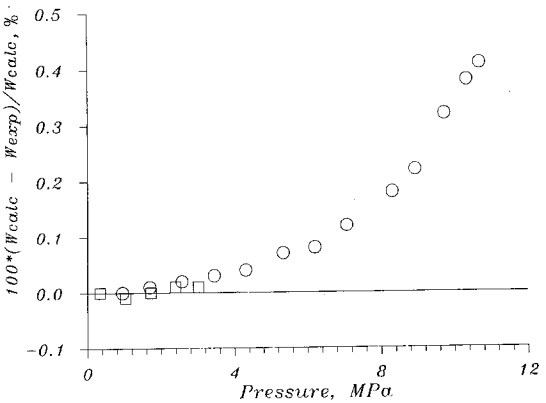

Fig. 8. Deviations of sound speed from Ref. 31 for the 69% methane–31% ethane mixture at 300 K, for the cylindrical resonator (○) and the spherical resonator (□).

measurements of this work, using the cylindrical cavity, was within 0.03% (see Fig. 8), which shows deviations at 300 K for the two sets of data from the SUPERZ model.

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