Prediction of Acoustic Velocities in Nonideal Gaseous Mixtures

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The speed of sound in gas mixtures is an important physical variable which is used in the petroleum industry for locating hydrate freezes and other obstructions in gas pipelines and for estimating liquid levels in gas wells by acoustic reflection. It is also needed in designing combustion chambers for rockets and jet engines, where highly nonideal gas mixtures must be considered. In this paper we apply two mixing rules, the pseudo critical method and Amagat's law, in conjunction with the generalized (three parameter) equation of state of Pitzer et al. (1955) to predict the zero frequency speed of sound in nonideal gas mixtures. The relevant compressibility factors are predicted by the method of Lee and Kessler (1975) which is based on an analytical technique that uses a modified Benedict-Webb-Rubin equation of state. One of the main advantages of this equation is that analytic differentiation replaces numerical and graphical methods, and this leads to improved accuracy. However, it is known that the three-parameter models are usually inaccurate for highly polar gases, gases which associate, and gases whose behavior is dependent on quantum effects (for example, helium and hydrogen).

Several papers have dealt with the prediction of acoustic velocities of a pure gas using generalized compressibility data. Sherwood (1962) first suggested the use of the generalized equation of state for estimating the acoustic velocity of pure components, and he developed tables of the required derivatives of the compressibility factors and heat capacity deviation factors, which are more accurate and easier to use than previously available graphs. The acoustic velocities of several pure gases at various temperatures and pressures, for which experimentally determined values were available, were compared with the predictions of the generalized compressibility method. The correlation with the available data was found to be good.

Zimmerman and Greenkorn (1969) later estimated acoustic velocities in pure component gases also using the generalized equation of state and compared their results with another set of experimental data. In this work, graphs of the compressibility factors were developed, and experimental values of the heat capacities were used whenever they were available. Good agreement between experimentally determined acoustic velocities and estimated values was also found.

Both Sherwood (1962) and Zimmerman and Greenkorn (1969) used the two parameter generalized equation of state with $Z_c = 0.27$. However, two problems arose with their method. First, not all acoustic velocity data found were in the low frequency range. In this case, extrapolations to zero frequency velocities were made where sufficient data were available. Secondly, the estimation of the heat capacities using the generalized equation of state involves the second derivative of some thermodynamic properties. To determine these derivatives, the compressibility factors were taken from graphs and graphical methods of differentiation had to be used, thereby introducing potentially large errors. Zimmerman and Greenkorn (1969) tried to use experimental heat capacity ratio data but were unable to find sufficient data which were not obtained by acoustic methods.*

PURE COMPONENT ACOUSTIC VELOCITY

If we consider infinitesimal, low frequency sound waves, the equations of motion lead to the wave equation (see Lamb, 1945)

$$\frac{\partial^2 v_x}{\partial t^2} = c^2 \frac{\partial^2 v_x}{\partial x^2} \tag{1}$$

where the speed of sound c is given by

$$c^2 = \left(\frac{\partial P}{\partial \rho} \right)_S \tag{2}$$

In obtaining Equations (1) and (2), the following assumptions are made: the medium is a continuum, the changes in pressure are small so that changes in pressure are proportional to changes in density, viscous effects are negligible, and the velocity of the medium is small compared to the velocity of sound. For finite amplitude disturbances or shock waves, other methods must be used (Hirschfelder et al., 1954).

Equation (2) is valid for all systems which obey these assumptions. It has *not* been assumed that the system contains only one pure component. Most equations of state are written in terms of molar volume, rather than density, and if the constant entropy constraint is removed, using standard methods, we obtain

$$c^2 = \frac{-v^2}{M} \left(\frac{Cp}{Cv} \right) \left(\frac{\partial P}{\partial v} \right)_T \tag{3}$$

If Equation (3) is used, the problem of calculating the acoustic velocity of a system is reduced to obtaining an equation of state and heat capacity ratio data. For a system which is a perfect gas, the acoustic velocity can be easily derived from Equation (3); that is

$$c^2 = \left(\frac{Cp}{Cv} \right) \frac{RT}{M} \tag{4}$$

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0001-1541-78-9567-0341-$00.75

* The common method of determining the heat capacity ratio is to experimentally determine the acoustic velocity of the gas and then to obtain the ratio by using P-V-T data.

TABLE 1. COMPARISON OF THEORY WITH EXPERIMENTAL DATA

(n/m²), P	(°K), T	Acoustic velocity (m/s) Experimental	Ideal gas	Pseudo critical method	Amagat's lav
† 1.013×10^5	273.16	331.5	332.3 (0.2)	331.9 (0.1)	331.9 (0.1)
* 1.013×10^5	300.16	347.9	346.8 (−0.3)	347.6 (−0.1)	347.6 (−0.1
† 1.013×10^5	973.16	621.4	613.6 (−1.3)	613.4 (−1.3)	613.4 (−1.3
* 30.40×10^5	300.16	352.2	346.8 (−1.5)	351.7 (−0.1)	351.7 (−0.1
† 60.80×10^5	273.16	336.6	332.3 (−1.3)	340.6 (1.2)	340.7 (1.2)
* 60.80×10^5	300.16	358.8	346.8 (−3.3)	358.2 (−0.2)	358.3 (−0.1
† 101.3×10^5	273.16	351.1	332.3 (−5.4)	353.3 (0.6)	353.3 (0.6)
* 101.3×10^5	300.16	370.3	346.8 (−6.3)	370.7 (0.1)	370.8 (0.1)
† 152.0×10^5	273.16	374.2	332.3 (−11.2)	376.2 (0.5)	376.3 (0.6)
† 202.7×10^5	273.16	393.4	332.3 (−15.5)	405.2 (3.0)	405.5 (3.1)

Notes:
Lee and Kesler's (1975) mixing rules were used for the pseudo critical method.
Zero enthalpy of mixing was assumed for Amagat's law.
† Experimental values from Washburn (1930).
* Experimental values from Hodge (1937). These values are not for zero frequency; however, Hodge (1937) found no variation with frequency.
Values in parentheses are percent deviation of the calculated value from the experimental value.

Since the heat capacities are functions only of temperature for an ideal gas, the acoustic velocity is seen to be only a function of temperature. However, examination of available experimental data (see Table 1) shows that the acoustic velocity is also a function of pressure.

We are primarily interested in deriving a generalized equation for the calculation of the acoustic velocity of a wide range of gases. The corresponding states principle uses a function Z which is defined as

$$Z(P_r, T_r) \equiv Pv/RT \tag{5}$$

When using the three parameter generalized equation of state of Pitzer and Curl, the factor Z will have the form

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{6}$$

When this equation of state is substituted into Equation (3), the generalized equation for the acoustic velocity of a system is given by

$$c^2 = \left(\frac{Cp}{Cv}\right)\left(\frac{ZRT}{M}\right)\left[1 - \frac{P}{ZP_c}\left(\frac{\partial Z}{\partial P_r}\right)_{T_r}\right]^{-1} \tag{7}$$

Values of Z, $Cp - Cp^*$, and $Cv - (Cp^* - R)$ have been tabulated as a function of reduced temperature and reduced pressure by Lee and Kesler (1975). We have tabulated values of $[\partial Z^{(0)}/\partial P_r]_{T_r}$ and $[\partial Z^{(1)}/\partial P_r]_{T_r}$ using their analytical equation of state.* Using these tabulated values and Equation (7), we can calculate the acoustic velocity of any system which obeys the theory of corresponding states.

ACOUSTIC VELOCITY OF A MIXTURE

To use Equation (3) for a mixture, the following quantities must be evaluated: v, Cp/Cv, and $(\partial P/\partial v)_T$. Two sets of mixing rules using the generalized equation of state are described below which can be used to evaluate the above quantities for gaseous mixtures.

Pseudo Critical Method

The simplest approach is the pseudo critical method. In this method, a pseudo critical temperature, pseudo critical pressure, and pseudo accentric factor are determined for a mixture which, when used with the tabulated compressibility factors for pure components, accurately represent the equation of state of the mixture. The simplest set of rules for determining pseudo critical constants of a mixture are those of Kay (1936). A more complex and reportedly more accurate set of rules was devised by Lee and Kesler (1975), and these have been used in this paper. Thus

$$v_c = \frac{1}{8} \sum_{j=1}^{n} \sum_{k=1}^{n} y_j y_k (v_{cj}^{1/3} + v_{ck}^{1/3})^3 \tag{8}$$

$$v_{ci} = (0.2905 - 0.085\omega_i) RT_{ci}/P_{ci} \tag{9}$$

$$T_c = \frac{1}{8v_c} \sum_{j=1}^{n} \sum_{k=1}^{n} y_j y_k (v_{cj}^{1/3} + v_{ck}^{1/3})^3 \sqrt{T_{cj} T_{ck}} \tag{10}$$

$$\omega = \sum_{j=1}^{n} y_j \omega_j \tag{11}$$

$$P_c = (0.2905 - 0.085\omega) RT_c/v_c \tag{12}$$

In the range of temperatures, pressures, and compositions, where the pseudo critical method is accurate, the quantities of interest are evaluated as follows: $v = Z_m RT/P$ with $Z_m = Z(P_{rm}, T_{rm})$, Cp and Cv are calculated from the tabulated values of Lee and Kesler (1975, or they may be obtained analytically, using standard methods, from an equation of state and the low pressure heat capacities of the mixture, and $(\partial P/\partial v)_T = -P/v\,[1 - (P/Z_m P_c)(\partial Z_m/\partial P_r)_{T_r}]^{-1}$. Smith and Van Ness (1959) report that the pseudo critical method is fairly accurate within the pressure range of 50 to 300 atm. Several calculations using this method are presented later.

Amagat's Law

At pressures above approximately 300 atm (see Smith and Van Ness, 1959), Amagat's law of additive volumes is likely to hold fairly well. Amagat's law states that the sum of the volumes which each pure component would occupy at the same temperature and total pressure as that of the mixture is equal to the total volume of that mixture; that is

$$v_m = \sum_{i=1}^{n} y_i v_i \tag{13}$$

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* Supplementary material has been deposited as Document No. 03194 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N.Y. 10016, and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

where v_i is defined as the molar volume of the pure component i at the total pressure and temperature of the mixture. If it is assumed that the generalized equation of state is valid for each pure component, then

$$Z_m = \sum_{i=1}^{n} y_i Z_i \tag{14}$$

where Z_i is calculated for the total pressure of the mixture.

The quantities of interest are evaluated as follows:

1. $v = Z_m RT/P$.

2. It can be shown (see Whiting, 1976) that if Amagat's law *and* the ideal solution law hold, then there is zero heat of mixing. This leads to the following equations:

$$Cp_m \equiv \left(\frac{\partial H_m}{\partial T}\right)_P = \sum_{i=1}^{n} \left(\frac{\partial h_i}{\partial T}\right)_P = \sum_{i=1}^{n} y_i Cp_i \tag{15}$$

$$Cv_m \equiv \left(\frac{\partial U_m}{\partial T}\right)_v = \sum_{i=1}^{n} \left(\frac{\partial u_i}{\partial T}\right)_v = \sum_{i=1}^{n} y_i Cv_i \tag{16}$$

It should be apparent that one cannot compute the heat capacity ratio Cp/Cv of the mixture from the heat capacity ratios of the pure components.

3. The required differential is given by

$$\left(\frac{\partial P}{\partial v}\right)_T = \frac{-P}{v}\left[1 - \frac{P}{Z_m} \sum_{i=1}^{n} y_i \left(\frac{1}{P_{ci}}\right)\left(\frac{\partial Z_i}{\partial P_r}\right)_T\right]^{-1} \tag{17}$$

Several calculations using this method are presented in the next section.

COMPARISON OF THEORY WITH EXPERIMENTAL DATA

A literature search revealed very little acoustic velocity data for gaseous mixtures at temperatures and/or pressures where the mixtures are nonideal. Data were found only for air at high pressures and high temperatures (Washburn, 1930; Hodge, 1937). As discussed before, the acoustic velocity of an ideal gas is a function of temperature only. As can be seen from Table 1, large deviations from this assumption are apparent at high pressures. A comparison of air data and calculated values of this acoustic velocity, using the pseudo critical method and Amagat's law, is also shown in Table 1. The agreement is seen to be quite good. However, if these methods are to be tested as to their accuracy, it is important to acquire much more experimental data for a variety of mixtures at various compositions, temperatures, and pressures.

In conclusion, a very limited amount of experimental data was available to test the various methods of predicting the acoustic velocity of gaseous mixtures in nonideal situations. Both the pseudo critical method and Amagat's law are compatible with computer computation using an analytical form of the generalized equation of state. For ease of use, the pseudo critical method is recommended. However, we believe that more experimental acoustic velocity data for gaseous mixtures must be collected to meaningfully test these methods.

ACKNOWLEDGMENT

Robert C. Ackerberg was partially supported by National Science Foundation Grant No. ENG 75-16606 during the course of this work.

NOTATION

c = zero frequency acoustic velocity
Cp = isobaric molar heat capacity
Cp^* = low pressure Cp
Cv = isochoric molar heat capacity
h_i = pure component molar enthalpy of substance i
H = molar enthalpy
M = molecular weight
n = number of pure components in a mixture
P = absolute pressure
P_c = critical pressure
P_r = P/P_c
R = gas constant
S = entropy
t = time
T = absolute temperature
T_c = critical temperature
T_r = T/T_c
u_i = pure component molar internal energy of substance i
U = molar internal energy
v = molar volume
v_c = critical molar volume
v_x = velocity in x direction
x = distance in x direction
y_i = mole fraction of component i
Z = compressibility factor
Z_c = critical compressibility factor
ρ = mass density
ω = accentric factor

Subscripts

i = value of parameter for i component of mixture
m = value of parameter for mixture

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Manuscript received August 3, and accepted August 9, 1977.