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Second and Third Interaction Virial Coefficients of the (Methane + Propane) System Determined from the Speed of Sound[1]

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The speed of sound has been measured in the binary gaseous mixture $(0.85CH_4 + 0.15C_3H_8)$ along seven isotherms at temperatures between 225 and 375 K and at pressures up to 1.4 MPa. From the measurements, second and third acoustic virial coefficients of the mixture were obtained. These results were analyzed together with values of the second and third acoustic virial coefficients of the two pure components to obtain a set of model intermolecular potential-energy functions for the methane–propane system. Nonpairwise additivity of the intermolecular forces was included in this analysis. Ordinary second and third interaction virial coefficients calculated from the model are reported, as are the second and third virial coefficients of the pure components. Gas densities calculated by means of these virial coefficients for the mixture $(0.9298CH_4 + 0.0702C_3H_8)$ were found to agree with experimental values at temperatures between 280 and 330 K to within 0.02% at pressures up to 3 MPa and to within 0.08% at 4MPa.

KEY WORDS: intermolecular potentials; methane; mixtures; propane; speed of sound; virial coefficients.

1. INTRODUCTION

There is a currently considerable interest in the development of accurate wide-ranging equations of state for natural gas systems from which all the thermodynamic properties may be obtained. Several equations [1–3] have been developed over recent years based largely on the available (p, ρ, T) data, of which they give a good account, but not to any great extent on other

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properties such as the speed of sound or the isobaric heat capacity. Consequently, the accurancy with which these other properties may be predicted is not as good as might be desired. It is probable that improved equations of state can be devised but that new measurements of heat capacity and/or the speed of sound will be required first.

In order to facilitate such developments, we have embarked on a program of highly accurate sound speed measurements on a number of methane-rich gas mixtures. Results for pure methane, (methane + ethane), and (methane + propane) at high pressures have all been reported recently [4–6]. In this paper, we report new measurements of the speed of sound in the binary mixture $(0.85\ CH_4 + 0.15\ C_3H_8)$ made at pressures below 1.4 MPa and at temperatures between 225 and 375 K; these results complement our previous work on this mixture at higher pressures [6].

By far the most important interaction terms in an equation of state for methane-rich gas mixtures are those equivalent to the second and third interaction virial coefficients between methane and the other components. In the present work we have determined these interaction virial coefficients for the methane–propane system by invoking a set of model intermolecular potential-energy functions, the parameters of which were fitted to acoustic virial coefficients of the mixture and each of the pure components.

2. EXPERIMENTS

The speed of sound was measured using the spherical acoustic resonator and associated apparatus described previously [4]. A single-mixture composition was studied in this work and sufficient material for all the measurements was prepared, mixed and stored in a 0.5-dm^3 stainless-steel cylinder ready for use. The precise composition was not determined at the time of mixture preparation, rather it was determined for the gas actually used for each isotherm from the value of the speed of sound extrapolated to the limit of zero density.

Measurements were made on seven isotherms at 225, 250, 275, 300, 325, 350, and 375 K. The greatest pressure on each isotherm was generally about 1.4 MPa but, at the lowest temperature, a lesser value was used so as to remain well below the dew pressure. The resonator was filled at the start of each isotherm with fresh gas taken from the sample cylinder. In order to ensure that the gas mixture was entirely homogeneous, it was then remixed in the apparatus by means of convection currents obtained by imposing a large temperature gradient on the resonator.

Measurements were made using the (0,2) to (0,5) radial modes of the spherical resonator at typically 10 pressures on each isotherm, starting at the highest pressure and proceeding downwards in even decrements. Speeds

Table I. Speeds of Sound in $\{(1-x)\ CH_4 + xC_3H_8\}$ at Temperatures T and Pressures p

T (K)	p (kPa)	u ($m \cdot s^{-1}$)	p (kPa)	u ($m \cdot s^{-1}$)	p (kPa)	u ($m \cdot s^{-1}$)	p (kPa)	u ($m \cdot s^{-1}$)
225.000	448.12	337.7642	400.24	338.5015	349.26	339.2825	300.65	340.0230
	249.96	340.7912	199.76	341.5478	149.54	342.3026	99.81	343.0414
	49.33	343.7866						
250.000	1364.30	346.3807	1200.87	348.2635	1002.44	350.5338	801.06	352.8212
	651.14	354.5127	500.73	356.1995	345.88	357.8798	200.59	359.5325
	99.84	360.6411	49.49	361.1903				
275.000	1365.53	366.5639	1201.23	367.9067	1003.46	369.5266	800.50	371.1944
	650.67	372.4273	500.57	373.6637	350.35	374.9012	200.17	376.1383
	99.79	376.9639	49.77	377.3722				
300.000	1402.75	384.2685	1200.09	385.4689	999.64	386.6682	800.94	387.8688
	650.19	388.7860	499.06	389.7112	350.10	390.6278	199.81	391.5557
	99.53	392.1753	49.40	392.4818				
325.000	1414.36	400.5680	1200.53	401.4912	1000.47	402.3698	800.11	403.2625
	649.98	403.9396	500.13	404.6212	349.80	405.3113	199.75	406.0068
	99.96	406.4704						
350.000	1399.56	415.7214	1200.61	416.3423	999.92	416.9825	800.52	417.6322
	650.26	418.1297	500.23	418.6336	350.44	419.1434	199.67	419.6617
	100.03	420.0058	50.11	420.1765				
375.000	1363.17	429.9377	1200.93	430.2954	1001.06	430.7483	800.39	431.2160
	650.54	431.5733	499.77	431.5733	349.62	432.3079	200.29	432.6818
	99.89	432.9364	48.37	433.0637				

of sound u were obtained from the resonance frequencies as described previously [4, 6], and those from the four radial modes always agreed to better than $8 \times 10^{-6}\,u$. Temperatures were measured with an estimated uncertainty of ± 3 mK using a pair of platinium resistance thermometers calibrated on ITS-90. Pressures were measured with an estimated uncertainty of ± 0.14 kPa using a quartz-crystal manometer with a full-scale range of 1.4 MPa. The results are given in Table I.

3. ANALYSIS OF THE SPEEDS OF SOUND

The results on each isotherm were analyzed in terms of the series expansion

$$u^2 = A_0\{1 + \beta_a \rho_n + \gamma_a \rho_n^2 + \cdots\} \tag{1}$$

to obtain values of the second β_a and third γ_a acoustic virial coefficients and also of the quantity $A_0 = \mathrm{Lim}_{\rho_n \to 0}\, u^2$. The results of the regressions are given in Table II. Values of the amount-of-substance density ρ_n required for this analysis were calculated at the experimental temperatures and

Table II. Results of the Regression Analyses for $\{(1-x)\,CH_4 + xC_3H_8\}$

T (K)	A_0 ($m^2 \cdot s^{-2}$)	β_a ($cm^3 \cdot mol^{-1}$)	γ_a ($cm^6 \cdot mol^{-2}$)	x
225	118,690 ± 1	− 159.49 ± 0.17	10,100 ± 600	0.14900
250	130,852 ± 1	− 125.76 ± 0.05	11,290 ± 70	0.14918
275	142,722 ± 1	−99.68 ± 0.06	10,520 ± 90	0.14906
300	154,286 ± 1	−79.03 ± 0.08	9,560 ± 125	0.14910
325	165,600 ± 1	−62.45 ± 0.03	8,890 ± 50	0.14909
350	176,699 ± 1	−48.62 ± 0.07	8,140 ± 130	0.14909
375	187,655 ± 1	−37.07 ± 0.06	7,600 ± 120	0.14904

pressures from the equation of state of Starling et al. [1] Errors in the calculated densities are expected to influence the values obtained for the third acoustic virial coefficient (but not the second). However, an alternative analysis with densities calculated from the Lee–Kesler equation of state [7] gave values of γ_a that did not differ from those given in Table II by more than the estimated uncertainties and we therefore concluded that the method adopted did not introduce significant errors.

The precise composition of the gas used on each isotherm was calculated from the corresponding A_0 by means of the relation

$$A_0 = \frac{RT\{(1-x)\,C^{pg}_{p,1} + xC^{pg}_{p,2}\}}{\{(1-x)\,C^{pg}_{p,1} + xC^{pg}_{p,2} - R\}\,\{(1-x)\,M_1 + xM_2\}} \tag{2}$$

in which M_i and $C^{pg}_{p,i}$ are the molar mass and isobaric perfect-gas heat capacity of component i and x is the mole fraction of component 2. Values of perfect-gas heat capacities required for this purpose were those determined previously [4,8]. The mole fractions x of propane obtained in this way are given in Table III. We note that there appears to be some variation in the actual composition obtained on each filling of the apparatus, but in no case does x differ from the mean value of 0.14908 by more than 10^{-4}.

4. INTERACTION VIRIAL COEFFICIENTS

The acoustic virial coefficients of Eq. (1) are each related to the corresponding coefficient (and all the lower-order coefficients) in the virial equation of the state by second-order differential equations. Thus β_a is related to the second virial coefficient B and its first two temperature derivatives, while γ_a is related to both B and C and their first two temperature derivatives [9]. In this work, we have exploited the relationships which exist between each of these quantities and the intermolecular potential-energy functions of the system in an analysis that led ultimately to the pure-component and interaction terms of B and C. Model intermolecular potentials have been used for this purpose, the parameters of which were optimized to fit the second and third acoustic virial coefficients of the mixture and of both of the pure components.

The model used throughout this work to represent the intermolecular pair potential $U(r)$ was the Maitland–Smith function [10] in which

$$U(r) = \{\varepsilon/(n-6)\}\{6(r_m/r)^n - n(r_m/r)^6\} \tag{3}$$

Here ε is the depth of the intermolecular potential well, r_m is the intermolecular separation at the minimum of $U(r)$, and n is an exponent which varies with the separation r through the linear relationship

$$n = m + \nu\{(r/r_m) - 1\} \tag{4}$$

Here m and ν are adjustable parameters. We further assumed that the non-pairwise-additive contribution ΔU to the intermolecular potential energy of a cluster of three molecules was represented adequately by the Axilrod–Teller triple–dipole term. This term is given by

$$\Delta U = \upsilon_{123}(r_{12}r_{13}r_{23})^{-3}(1 + 3\cos\theta_1\cos\theta_2\cos\theta_3) \tag{5}$$

where r_{ij} is the distance between molecules i and j, θ_i are the interior angles of the triangle formed by three molecules, and υ_{123} is the three-body dispersion coefficient. In the case of the pure gases, υ_{123} was estimated from the Midzuno–Kihara formula

$$\upsilon_{123} = \tfrac{3}{4}C_6\alpha \tag{6}$$

using the leading two-body dispersion coefficient C_6 and the mean polarizability α. C_6 was set equal to the coefficient of $-r^{-6}$ in Eq. (3) evaluated at $r = r_m$, while the mean polarizability was calculated from literature values of the refractive index [11]. The validity of this approximation was checked independently for argon using the known pair potential together with Eq. (5); calculated values of both γ_a and C were found to be in good agreement with experiment [8].

Measurements and analysis of the pure component acoustic virial coefficients have been reported elsewhere [8]. For methane, the parameters of Eqs. (3) and (4) which simultaneously fitted both β_a and γ_a were $r_m = 0.3953$ nm, $\varepsilon/k = 204.50$ K, $m = 19$, and $\nu = 0$. In the case of propane, a similar analysis gave $r_m = 0.4832$ nm, $\varepsilon/k = 569.51$ K, $m = 71$, and $\nu = 10$.

Table III. Second and Third Virial Coefficients of the Methane (1)–Propane (2) System

T (K)	B_{11} ($cm^3 \cdot mol^{-1}$)	B_{12} ($cm^3 \cdot mol^{-1}$)	B_{22} ($cm^3 \cdot mol^{-1}$)	C_{111} ($cm^6 \cdot mol^{-2}$)	C_{112} ($cm^6 \cdot mol^{-2}$)	C_{122} ($cm^6 \cdot mol^{-2}$)	C_{222} ($cm^6 \cdot mol^{-2}$)
225	−82.01	−228.1	−721.7	3,240	6,190	5,940	−108,400
250	−65.35	−185.4	−570.0	2,840	5,780	9,740	−22,200
275	−52.38	−152.7	−463.4	2,530	5,250	10,290	7,500
300	−42.00	−127.0	−384.7	2,290	4,760	9,810	17,600
325	−33.51	−106.3	−324.4	2,100	4,340	9,040	20,200
350	−26.45	−89.2	−276.7	1,960	4,000	8,270	20,100
375	−20.49	−74.8	−238.2	1,840	3,730	7,570	18,900

These models were used in this work to calculate all of the pure component terms which contribute to β_a and γ_a for the mixture. We found that while the methane terms made a large contribution to the mixture acoustic virial coefficients, those for propane were, because of the relatively small mole fraction of that component, of only minor importance.

The terms which remained in β_a and γ_a after elimination of the pure component terms were then used to obtain the parameters of Eqs. (3) and (4) for the case of the unlike intermolecular potential energy function. In these calculations, the three-body dispersion coefficients ν_{123} for methane–methane–propane and methane–propane–propane were obtained from a sum rule based on the values of C_6 and α for the pure components [12]. Altough as we have noted, the direct contribution of the propane intermolecular potential to the mixture acoustic virial coefficients was small, the value of C_6 for propane had a large effect on ν_{123} and thence on the nonadditive contributions to γ_a. It was found that a good representation of γ_a for the mixture could be obtained only if the value of C_6 for propane used in the estimation of ν_{123} was permitted to vary from that given by the model pair potential.

The results of the analysis were found to be quite insensitive to the value of the parameter ν in Eq. (4), which was therefore constrained arbitrarily to the value 10. The remaining four parameters (r_m, ε, m, and the value of C_6 for propane used in the calculation of ν_{123}) were then optimised in the fit, with the results $r_m = 0.4699$ nm, $\varepsilon/k = 276.29$ K, $m = 20$, and $C_6/k = 3.26$ K.nm^6. The value of C_6 for propane is approximately half that obtained from the model pair potential. It was found that the model offered a rather good representation of the mixture acoustic virial coefficients; the standard deviation of β_a from the fit was 0.2 $cm^3 \cdot mol^{-1}$, while that of γ_a was about 150 $cm^6 \cdot mol^{-2}$.

Values of the pure component and interaction virial coefficients calculated from the model potentials are given in Table III. In order to test

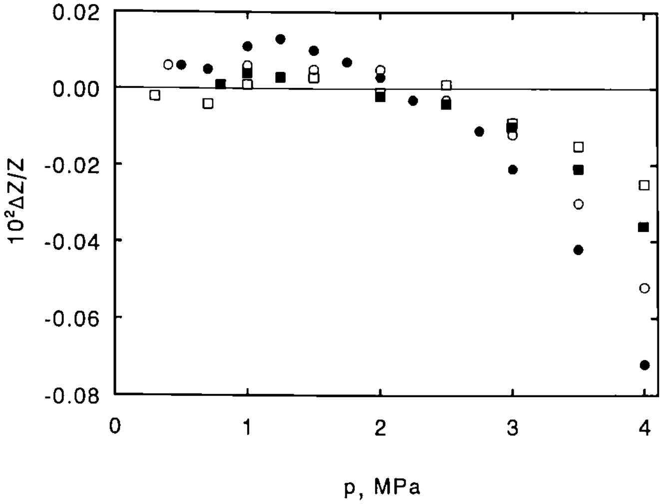

Fig. 1. Deviations $\Delta Z = Z(\text{calc}) - Z(\text{exp})$ between calculated $Z(\text{calc})$ and experimental $Z(\text{exp})$ values of the compression factors for the mixture ($0.9298\ CH_4 + 0.0702\ C_3H_8$). Experimental results from Ref. 13. (●) 280 K; (○) 290 K; (■) 310 K; (□) 330 K.

the usefulness of these results, we have made calculations of gas density for the mixture ($0.9298\ CH_4 + 0.0702\ C_3H_8$) along the isotherms at 280, 290, 310, and 330 K. The results, expressed in terms of the compression factor Z are compared with the experimental values of Jaeschke and Humphreys [13] at pressures up to 4 MPa in Fig. 1. In this entire range, the deviations from the experimental data do not exceed the estimated uncertainty in the latter of ±0.08%, and at pressures up to 3 MPa the agreement is within 0.02%. We conclude that the methodology adopted in this paper leads to values of the second and third virial coefficients from which gas densities may be obtained with excellent accuracy in the experimental pressure range. Furthermore, a considerable extrapolation to higher pressures is possible before significant inaccurancy is found.

5. DISCUSSION

The analysis used here is one method by which the equation of state of a gas may be obtained from measurements of the speed of sound without recourse to any other thermodynamic measurements. As shown above, the results are of excellent accurracy and we expect that the same analysis could be applied in the future over a rather wider range of experimental pressures.

The technique is self-consistent in the sense that the same pair potential-energy function is used in the calculation of both the second and the third virial coefficients and their acoustic counterparts. The inclusion of nonpairwise-additive intermolecular forces was an essential step in achieving this. Although the intermolecular potential-energy function obtained for the methane–propane interaction is only a simple model, we expect that application of similar methodology with angular-dependent potential models could lead to useful information about real intermolecular potentials.

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