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Note

Sound Velocity of Equimolar Dense Noble-Gas Mixtures

D. Vidal,[1] P. Malbrunot,[1] and J. Vermesse[1]

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The sound velocity in argon–helium, argon–neon, argon–krypton, and argon–xenon equimolar dense mixtures has been measured with a pulse-echoes overlap method at room temperature, 298.15 K, and at pressures up to 800 MPa. The accuracy of these results is 0.2%. Furthermore, the validity of the one-fluid compared with these experimental data is examined.

KEY WORDS: argon mixtures; high pressure; one-fluid model; sound velocity.

1. INTRODUCTION

Our previous high-pressure measurements on mixtures referred to density and dielectric-constant properties [1–3]. They are now completed with sound-velocity measurements performed on four quasi-equimolar mixtures, namely, argon–helium, argon–neon, argon–krypton, and argon–xenon, by means of the pulse-echoes overlap method. A good accuracy, 0.1–0.2%, is the main interest of such experimental sound-velocity data, because this physical quantity is one of the most phenomenologically sophisticated thermodynamic properties of gases depending on fundamental quantities such as density, diabatic compressibility, and specific heat ratio. Knowledge of the sound velocity is thus important for thermodynamic calculations. Furthermore, the present results on mixtures of gases are useful as a test of the validity of the "one-fluid model."

[1] Laboratoire d'Ingénièrie des Matériaux et des Hautes Pressions, CNRS, Centre Universitaire Paris-Nord, 93430 Villetaneuse, France.

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2. RESULTS

Our experimental device has been used previously for pure dense gases [4]. The sound velocity results from two measurements: distance L and time t. The acoustical path $2L$ is twice the distance between two parallel ends of a hollow cylinder: one of them is a plane quartz transducer, the other a polished reflector the backface of which has a conical shape to ensure absorption of the transmitted wave. The length L is measured within 0.02% with a micrometer. The pressure correction to the value of L is calculated from the compressibility factor of the cylinder material. The time t is obtained with an accuracy of 0.01% from the echoes-overlap technique of Papadakis [5] using a "Matec" equipment. A correction on this travel time t due to the diffraction effect can be evaluated from computation data of Papadakis [5]; in the present case it corresponds to a maximum decrease of velocity of 0.004% and has thus been neglected. The pressure of the gas sample is measured with a manganine gauge calibrated with a pressure balance with a maximum error of 0.1%. Finally, we estimate that our sound-velocity results have an accuracy of about 0.2%. The exact argon percentages of the mixtures are 49.94, 49.90, 50.95, and 50.16, respectively, as evaluated from density measurements at atmospheric pressure [1, 2].

Table I gives for each mixture the density ρ and the sound velocity V

Table I. The Density ρ ($kg \cdot m^{-3}$) and the Sound Velocity V ($m \cdot s^{-1}$) as a Function of the Pressure P (MPa) for the Equimolar Mixtures

	Argon–helium		Argon–neon		Argon–krypton		Argon–xenon	
P (MPa)	ρ ($kg \cdot m^{-3}$)	V ($m \cdot s^{-1}$)	ρ ($kg \cdot m^{-3}$)	V ($m \cdot s^{-1}$)	ρ ($kg \cdot m^{-3}$)	V ($m \cdot s^{-1}$)	ρ ($kg \cdot m^{-3}$)	V ($m \cdot s^{-1}$)
80	0.48318	682.91	0.66105	619.74				
100	0.55214	741.79	0.75176	679.92	1.4614	660.58	1.9208	653.92
150	0.68469	872.31	0.91383	811.37	1.6450	790.03	2.1067	769.42
200	0.77873	983.69	1.0268	921.28	1.7711	889.90	2.2382	857.90
250	0.85285	1080.4	1.1155	1015.37	1.8657	972.06	2.3435	930.55
300	0.91501	1166.1	1.1881	1098.21	1.9470	1042.7	2.4308	993.38
350	0.96798	1243.3	1.2484	1172.35	2.0174	1105.4	2.5065	1048.6
400	1.0145	1313.6	1.3000	1239.67	2.0788	1161.5	2.5723	1098.5
450	1.0551	1378.4	1.3493	1301.56	2.1331	1213.0	2.6320	1144.0
500	1.0932	1438.7	1.3924	1358.80	2.1819	1260.4	2.6856	1186.0
600	1.1558	1547.7	1.4665	1462.50	2.2674	1345.7	2.7828	1261.3
700	1.2107	1644.5	1.5270	1554.36	2.3424	1421.1	2.8670	1328.4
800	1.2594	1732.5	1.5820	1638.04	2.4097	1489.6	2.9428	1389.2

Table II. Deviations (%) Between Hanayama's Sound-Velocity Values [3] and Ours (Table I) for the Equimolar Argon–Helium Mixture at $T = 298.15$ K

P (MPa)	$\Delta V/V$ (%)
200	−1.7
300	−1.8
400	−1.1
500	−0.7
600	+0.2
700	−0.1
800	−0.4

as a function of the pressure P. Table II shows a comparison of these results with those of Hanayama [6] for an equimolar argon–helium mixture, the only mixture for which literature data are available. We note that the deviations which vary from -1.8 to $+0.2$% are included in the 3% measurement uncertainty claimed by Hanayama. This relatively large error is due mainly to a lack of accuracy of the pressure measurements because, having only one calibration point, the coefficient of their manganin gauge was assumed to be constant [7].

3. THE ONE-FLUID LENNARD–JONES MODEL

Several recent papers treat mixtures with a simple theory called the "one-fluid model" (OFM) [8–10]. It predicts that the properties of a mixture are the same as those of a pure fluid characterized by an intermolecular potential containing two specific parameters: the hard core σ_m and the depth of the potential well (ε_m/k). The aim of these papers is to study different simple mixing rules for obtaining these two potential parameters for the mixture from those of the two pure gases. Two standard mixing rules are used. The first, from the Van der Waals theory of mixtures, is given by the following two expressions:

$$\sigma_m^3 = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \sigma_{ij}^3, \quad \varepsilon_m = (1/\sigma_m^3) \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \sigma_{ij}^3 \varepsilon_{ij} \tag{1}$$

Here σ_{11} and ε_{11}, and σ_{22} and ε_{22}, are the LJ parameters of the pure fluids, while σ_{12} and ε_{12} are from the Lorentz–Berthelot rules:

$$\sigma_{12} = 0.5(\sigma_{11} + \sigma_{22}), \qquad \varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2} \tag{2}$$

According to the second mixing rule, from the Lennard–Jones mixture theory, σ_m and ε_m are defined by solving the following expressions:

$$\sigma_m^3 = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \sigma_{ij}^3 [B_{ij}^*(\varepsilon_{ij})/B_m^*(\varepsilon_m)],$$

$$\sigma_m^6 = \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{k=1}^{2} x_i x_j x_k (C_{ijk}/C_m^*) \tag{3}$$

which involve the second and the third virial coefficients of the equation of state of a LJ system [11].

Table III gives the different mixture molecular parameters σ_m and ε_m/k for the VDW and LJ models, and also their respective ratios $R_\sigma = [\sigma_m(\text{VDW})/\sigma_m(\text{LJ})]$ and $R_\varepsilon = [\varepsilon_m(\text{VDW})/\varepsilon_m(\text{LJ})]$. The differences between the VDW and the LJ parameters are signifiant for the two mixtures with noticeably different atoms. Table IV shows the deviations between our present experimental velocity data and those obtained with OFM based on pure gas values of Ref. 4. In this table, densities, velocity, and temperature are expressed in reduced quantities: for the mixture $\rho^* = \rho\,\sigma_m^3$, $V^* = V(N\varepsilon_m/M)^{1/2}$, and $T^* = kT/\varepsilon_m$, and for the pure gas $\rho^* = \rho\,\sigma^3$, $V^* = V(N\varepsilon/M)^{1/2}$, and $T^* = kT/\varepsilon$, σ and ε being the LJ molecular parameters of pure gases.

The Ar–Kr and Ar–Xe mixtures are very well represented by this model, but this is not the case for the mixtures of argon with the light gases. In fact the discrepancies between the potential parameters in Table III reappear. Furthermore, the LJ model is obviously revealed as inadapted, and this, whatever molecular parameter values σ_m and ε_m. The

Table III. σ_m (10^{-10} m) and ε_m/k (K) from the VDW and the LJ Model Using the LB rules and the Ratios $R_\sigma = \sigma_m(\text{VDW})/\sigma_m(\text{LJ})$ and $R_\varepsilon = \varepsilon_m(\text{VDW})/\varepsilon_m(\text{LJ})$

Mixture	σ_m, VDW LJ	ε_m/k, VDW LJ	R_σ	R_ε
Ar–He	3.0104 3.0869	61.88 69.36	1.0254	1.1208
Ar–Ne	3.0975 3.1360	76.99 79.46	1.0124	1.0321
Ar–Kr	3.5478	142.55	1.0013	1.0005
Ar–Xe	3.7522 3.7723	175.44 175.65	1.0053	1.0012

Table IV. Relative Differencies (%) Between the Sound Velocities Calculated from the Pure-Gas Values [4] When the VDW and the LJ Approximations Are Used and the Present Experimental Velocity Data as a Function of the Reduced Density ρ^*

	$\Delta V^*/V^*$ (%)		
ρ^*	VDW	LJ	Mixture
0.75	7.3	18.8	Ar–He
	2.8	8.3	Ar–Ne
	−0.8	−0.1	Ar–Kr
	−2.9		Ar–Xe
0.85	10.7	23.5	Ar–He
	4.4	10.2	Ar–Ne
	−1.4	−0.7	Ar–Kr
	−2.4	0.5	Ar–Xe
0.95		21.6	Ar–He
		7.5	Ar–Ne
	−1.2	−0.5	Ar–Kr
	−2.0	0.9	Ar–Xe
1.05		−0.2	Ar–Kr
		1.1	Ar–Xe

calculated velocities are not very sensitive to the parameters and thus no improvement by a best adjustment can be expected. On the other hand, the introduction in the Lorentz–Berthelot rules of two deviation parameters, k_σ and k_ε, gives better results, as it has been proved by Barreiros et al. [9]: $\sigma_{12} = 0.5k_\sigma(\sigma_{11} + \sigma_{22})$, $\varepsilon_{12} = k_\varepsilon(\varepsilon_{11} + \varepsilon_{22})^{1/2}$. In the case of the argon–krypton mixture the values $k_\sigma = 0.979$ and $k_\varepsilon = 1.002$ are convenient. The

Table V. Influence of the Parameters k_σ and k_ε on the Relative Deviations $\Delta V^*/V^*$ for Argon–Light Gas Mixtures

	$\Delta V^*/V^*$ (%), LJ	
ρ^*	Ar–He	Ar–Ne
0.75	−1.2	−1.6
0.95	1.5	0.2
k_σ	0.880	0.951
k_ε	0.900	0.951

introduction of such parameters leads to the acceptable agreement presented in Table V: the deviations are, at most, equal to $\pm 1.6\%$, with the k_σ and k_ε parameters values also given in this table.

4. CONCLUSION

The change of the sound velocity of equimolar noble gases mixtures with pressure has been determinated at pressures up to 800 MPa. With an accuracy of 0.2%, the results provide not only reliable basic thermodynamic data, but also useful references to check the validity of the one-fluid model for gas mixtures.

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