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The sound velocity of an equimolar mixture of CH_4 and He from 2 kbar to 8 kbar and from 273 K to 318 K

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Abstract

By using a phase-comparison pulse-echo technique, the sound velocity of an equimolar mixture of methane and helium has been measured at temperatures between 273 K and 318 K and at pressures up to 8 kbar. The overall accuracy in the sound velocity is expected to be better than 0.1%.

1. Introduction

Previously the sound velocity of He-N_2 and $\text{N}_2\text{-CH}_4$ has been measured at our laboratory up to 10 kbar [1,2]. Ross variational perturbation (VT) theory has been applied to determine the parameters of the effective EXP-6 potential function for these binary systems. Using these parameters and VT theory we calculated the fluid–fluid separation behavior. Many sets of parameters, that all lead to reasonable agreement between calculation and experiment, have been used in a trial-and-error manner to predict fluid–fluid phase separation. However, the calculated fluid–fluid demixing pressure is always far too low compared to the experimental value [3].

This result raised several questions concerning the validity of an approach that uses VT. For instance, is the one-fluid assumption really applicable; or is an effective-pair potential able to represent many-body interactions? Can a nitrogen molecule be treated like a sphere? This last question is of obvious concern since we used an effective EXP-6 potential that represents interactions of spherical molecules. To answer the last question, He-CH_4 is a good reference system because both pure components have spherical molecules. So if the calculations give good results for this system, the deviations in case of He-N_2 are probably due to the angular dependence of the intermolecular interaction in nitrogen.

2. Experiment

2.1. Experimental principle and set-up

The details about the experimental method and equipment have been published elsewhere [1,2,4] and hence only an outline is given here.

The phase-comparison pulse-echo technique is used in this experiment, the principle of which is as follows. The experiment starts with the application of an electrical pulse, produced by a transmitter, to the electrodes of an X-cut quartz transducer. Because of the piezoelectric effect, the transducer is excited into a thickness mode of vibration and generates a longitudinal sound pulse. This pulse propagates in the gaseous mixture into opposite directions and is reflected by two reflectors, mounted at both ends of the pressure vessel at different distances from the transducer. After an appropriate time τ , a second pulse is introduced into the medium such that the echo of the first pulse, travelling along the longer path, and the echo of the second pulse, passing the shorter path, coincide at their arrival at the transducer. The difference in transit time τ can then be better determined in case the echoes arrive at the transducer with opposite phase and cancel each other. Complete cancellation can be realized by means of adjusting the transit time of the second pulse, by tuning the pulse frequency, and by adjusting the amplitudes of the two echoes to match each other. In this way the transit time τ can be measured with an uncertainty of 0.01%. Moreover, the difference between the two path lengths of the echoes has been pre-determined as a function of pressure and temperature in the range of our interest with an uncertainty of 0.03%. The sound velocity can then easily be calculated.

The main parts of the equipment are the ultrasonic cell, a high pressure vessel, a cryostat, a high-pressure generating system, and an electronic system. The ultrasonic cell is the key part of the apparatus. It consists of a hollow copper cylinder provided with an X-cut quartz transducer and two reflectors. The transducer, which has aluminum electrodes on both sides, is clamped at its edges between a conical copper support and a conical ring in the middle of ultrasonic cell. Two copper reflectors are fixed at the two ends of the cell at distances from the transducer of, respectively, 20.617 and 29.647 mm. The ultrasonic cell is suspended inside the pressure vessel by means of a suspension rod.

The cryostat is of the vacuum-type and designed for temperatures between 100 K and room temperature. It consists of a high-pressure vessel enclosed by a demountable stainless-steel vacuum jacket. Between the vessel and the jacket a chromium-plated copper radiation shield has been mounted. The whole system is immersed in a bath of liquid nitrogen contained in a Dewar vessel.

The high-pressure vessel is made of Ni–Cr–Mo steel. It holds both the ultrasonic cell and sample gas during the experiment. Two gastight electrical feedthroughs [5] are fixed in the closure head. A thick copper plate is mounted on top of the pressure vessel to provide good thermal contact. The temperature is

regulated using three heating elements fixed in the top plate together with a Pt-resistance wire as the temperature sensor. This sensor is part of a Thomson bridge. The high-pressure vessel is suspended from the top by means of a stainless steel tube whose lower end is silver soldered to a copper flange, held tight against the copper plate by means of a nut. All electrical leads are brought out of the vacuum space by means of electrovac feedthroughs. The high pressure stainless-steel inlet capillary, fitted to the closure head by a compression technique, is guided by the spacer and is brought out of the vacuum chamber through a brass cylinder.

The temperature of the pressure vessel is controlled by balancing the heat loss, mainly through the copper cold finger with the heat input through the heating elements. The temperature can be regulated within 0.01 K around the preset temperature by means of a proportional-integrating temperature regulation system. The temperature can be measured with an accuracy of 0.002 K by means of a calibrated glass-enclosed Pt resistance, fixed in the bottom part of the pressure vessel. The temperature gradient from the top to the bottom of the pressure vessel is monitored during the experiment by means of two copper-constantan thermocouple junctions fixed at the top and bottom of the vessel. At low temperatures the difference over the full length of the pressure vessel is kept smaller than 0.02 K. The maximum difference of about 0.02 K occurs at 273.15 K because of the large temperature difference between the sample gas and the liquid nitrogen.

The high-pressure generating system is a 15 kbar Harwood gas compressor. A manganin gauge, calibrated up to 10 kbar against a dead weight tester, is used to measure the pressure. The uncertainty increases from 0.001 kbar at 2 kbar to 0.007 kbar at 8 kbar. At high pressures the uncertainty increases due to hysteresis and zero-point shift. During each experimental cycle the reading of the manganin gauge at 2 kbar is compared with the value recorded by a dead weight pressure balance to check the offset of the gauge.

By using a gate circuit consisting of a pulse-former and timer, two successive pulses are cut out of a continuous 10 MHz signal generated by an oscillator which is locked by a 1 MHz synthesizer. The pulse width, the separation time between the two pulses and the repetition time can be adjusted with the timer, while the amplitude of the second pulse can be reduced with the pulse-former. The amplitudes and the separation of the pulses as well as their echoes are displayed on an oscilloscope to enable fine-tuning of the interference.

2.2. *Experimental procedure*

The equipment is only designed to determine the sound velocity of a homogeneous mixture. In case of a fluid–fluid phase separation, the low-density fluid would be floating on top of the other fluid. The sound velocity is determined along an isotherm and at decreasing pressure. Since the pressure decrease is

realized by releasing some sample from the top of the pressure vessel, a fluid–fluid phase separation would definitely cause a change in the composition of the sample. On the other hand, fluid–fluid demixing is very difficult to detect in this experiment. During such a process, the composition changes only gradually. This also results in a gradual change of the sound velocity. It is difficult to distinguish between this effect and the changes in w due to the change in pressure introduced by performing the experiment. Therefore one should be sure that phase transitions do not occur in the experimental range.

Streett et al. [6], have investigated the fluid–fluid phase equilibrium of He–CH₄ up to 10 kbar in an extensive temperature range. Their investigation shows that fluid–fluid demixing occurs in an equimolar mixture at 4.4, 5.6, 7.4, and 9.4 kbar for temperatures of respectively 244, 256, 273, and 290 K. This phase diagram limits our experiment to a temperature range above 273 K in order to obtain data in a sufficiently large pressure range along each isotherm.

Therefore, we also performed experiments at 308 and 318 K to increase the temperature range. This was done by the removal of liquid nitrogen from the Dewar vessel and opening the vacuum jacket to air. But we restricted the maximum temperature range to 318 K for two reasons. Firstly, the heating power is not enough to obtain even higher temperatures. Secondly, the temperature gradient from the top to the bottom of the high-pressure vessel was increasing because in this case no cold finger was present to remove excessive heat. Nevertheless, it turned out that up to 318 K no excessive temperature gradients occurred as shown by the thermal couple readings. It seemed that air convection within the “vacuum” jacket helped to balance the temperature.

The experiment was started by filling the high-pressure vessel with a mixture up to the highest experimental pressure as discussed above (Streett’s phase diagram). This procedure was chosen because the manganin pressure gauge had also been calibrated with decreasing pressure. The temperature was fixed at a predetermined value and the system was equilibrated. After the mixture reached thermal equilibrium, the frequency of the transmitter was adjusted until a complete cancellation of the reflected echoes had been achieved by destructive interference. Then the temperature, the pressure, and several sequential null frequencies were determined. Subsequently some sample mixture was released to reach a new equilibrium at a lower pressure and the same series of measurement was repeated. The experiment was continued along an isotherm by repeating the above-mentioned procedure until about 2 kbar. Because of larger uncertainties in the pressure measurement as well as a mismatch of the acoustical impedance the data are less accurate below 2 kbar; it is too difficult to pursue experiments below 1 kbar in this apparatus due to damping.

The measurement have been performed along four isotherms (273.15, 298.15, 308.15 K and 318.15 K). The values for the sound velocity have been determined in the pressure range between 2 kbar to 8 kbar depending on the demixing pressures.

3. Results

The mixture of methane and helium used in this investigation was purchased from Messer Griesheim Nederland B.V. The composition is specified to be 50.0 ± 0.2 mole percent methane and 50.0 ± 0.2 mole percent helium.

Isotherms of the experimental sound velocity data as a function of pressure are shown in Fig. 1. The pressure and temperature behaviour of the sound velocity is in general quite similar to that in other binary systems such as HE–N₂ and N₂–CH₄ [1,2]. A decrease of the temperature would cause an increase of the sound velocity. Temperature decrease has more effect on the sound velocity at low pressure. At 2 kbar, this effect is about -1.4 , and -2.1 m/(s K) in the temperature range between 308 and 318 K, and between 273 and 298 respectively. At 7.5 kbar, this effect is about -0.5 and -0.2 m/(s K) in the respective temperature ranges. The tendency of the temperature effect is reversed at 7.5 kbar. An increase of pressure would result in an increase of the sound velocity. At 318.15 K, this effect is 276.2 m/(s kbar) and 151.5 m/(s kbar) in the pressure ranges between 2 and 4 kbar, and between 4 and 6 kbar, respectively.

In order to check the reproducibility, two runs have been performed at 298.15 K with different gas fillings (the same composition) and a time lag of two weeks. The consistency of the two runs is better than 0.09%.

The raw data are fitted with a polynomial of the form

$$p = \sum_{k=0}^3 a_k w^k \quad (1)$$

by the least-squares method, where p is the pressure in kbar and w is sound

Fig. 1. Experimental data along isotherms between 273 K and 318 K.

Table 1
Coefficients of Eq. (1) along respective isotherms

<i>T</i> (K)	<i>a</i> ₀	<i>a</i> ₁	<i>a</i> ₂	<i>a</i> ₃	std%
318.15	−0.714772E + 0	0.141340E − 2	−0.252316E − 6	0.314544E − 9	0.01
308.15	−0.165463E + 1	0.300280E − 2	−0.115464E − 5	0.476603E − 9	0.04
298.15	−0.567641E + 0	0.124665E − 2	−0.223043E − 6	0.314724E − 9	0.01
298.15	−0.867671E + 0	0.160233E − 2	−0.350328E − 6	0.328352E − 9	0.02
273.15	−0.265976E + 1	0.449638E − 2	−0.193300E − 5	0.601750E − 9	0.04

Two experimental runs at 298.15 K are represented in this table.

velocity in m/s. The coefficients as well as the standard deviations of each fit are given in Table 1. The standard deviation given in the last column is defined as

$$\text{std} = \sqrt{\frac{\sum_{i=1}^N [(w_{\text{cal}} - w_{\text{exp}})/w_{\text{exp}}]^2}{N - m - 1}}, \tag{2}$$

where *N* and *m* are the number of data points in the fitting and the number of coefficients determined from the fit, respectively. The subscripts cal and exp denote the calculated and experimental results respectively. The number of experimental points varies depending on the isotherm. Table 1 shows that the standard deviation is less than 0.05%. Furthermore, the deviation between the raw data and the values of the sound velocity calculated with Eq. (1) at the corresponding pressures is given in Fig. 2 which shows that Eq. (1) is in good agreement with the experimental results.

Since the number of experimental points is too large to list in a table, the sound velocity at some rounded values of pressure, calculated from Eq. (1), is presented in Table 2. It should be pointed out that some of the sound velocity data in Table

Fig. 2. Comparison between the experimental sound velocity and the values calculated with Eq. (6).

Table 2
The sound velocity of an equimolar mixture of methane and nitrogen along several isotherms

p (kbar)	T (K)			
	318.15	308.15	298.15	273.15
2.0	1535.7	1549.8	1530.6	1582.6
2.5	1698.7	1714.0	1715.9	1745.7
3.0	1842.4	1859.2	1862.5	1891.1
3.5	1971.2	1988.9	1988.9	2021.1
4.0	2088.1	2106.0	2102.5	2138.3
4.5	2195.3	2212.7	2207.0	2244.8
5.0	2294.6	2310.9	2304.7	2342.3
5.5	2387.1	2401.8	2397.1	2432.3
6.0	2473.9	2486.5	2485.2	2515.9
6.5	2555.7	2565.9	2569.7	2594.0
7.0	2633.1	2640.8	2651.3	2667.3
7.5	2706.7	2711.6	2730.3	
8.0	2776.9	2778.8	2807.2	

Numbers in *italic* are extrapolated values by less than 0.35 kbar.

2 are extrapolated values obtained from Eq. (1). However, these values are still reliable since the range of extrapolation is rather small (less than 0.35 kbar).

4. Summary

Because of the lack of literature data concerning this binary system in this range of pressure, it is impossible to compare the present results with those of other authors. However, measurements of the mixture at 298.15 K suggest that the reproducibility of the sound velocity data is better than 0.09%. It is not as good as those in previous studies [1,2]. This uncertainty is mostly due to the uncertainty of the manganin gauge, used in the pressure measurement. The uncertainties of the measurements in the distance l and the echo transit time difference τ are 0.03% and 0.01%, respectively. The accuracy in the temperature measurement is about 0.01 K. Considering the small temperature dependence of w this can be neglected. The accuracy of the pressure determination is 0.05% of the reading plus 0.05 kbar and gives the largest contribution to the uncertainty in w . The overall uncertainty in sound velocity is expected to be about 0.1%.

In Fig. 3, the methane and helium data of Kortbeek et al. [7,8] as well the mixture data of this work are plotted for several pressures at 298.15 K. It should be noted that at 300 K the sound velocity of methane is larger than that of the helium (lighter molecule). Moreover, it is shown that the value of the sound velocity of this binary system does not always change monotonously with the concentration at constant temperature and constant pressure. The deviation from a linear behaviour is not very large at 8 kbar, but rather obvious at 2 kbar, where a clear minimum is observed. Such a pronounced minimum has previously been

Fig. 3. Sound velocity of pure methane, pure helium and the equimolar mixture at 298.15 K and various pressures.

observed only in the helium–xenon system [9]. Other systems like methane–krypton [10], helium–argon [9], and helium–nitrogen [1] show only a tendency to form a minimum. In general in systems where the pure components have a very large difference in molecular mass (helium–xenon) such a minimum exists in the isobaric sound velocity curves along the concentration axis. When the difference in molecular masses is moderate and when the concentration of the heavier component is more than sixty mole percent, the curves tend to be flat and nearly parallel to the concentration axis, as shown in the helium–argon system [9]. Not only the mass of the molecule is important. In fact, the sound velocity also depends on the compressibility, and the thermal expansion coefficient. Therefore, the behaviour of the sound velocity in mixtures can be very complicated. Considering its molecular mass the critical temperature of CH_4 is rather high, as a result the volumetric behaviour at room temperature is different from that of e.g. nitrogen and argon and thus the sound velocity.

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References

- [1] W. Zhang and J.A. Schouten, *Fluid Phase Equilibria* 79 (1992) 211.
- [2] W. Zhang and J.A. Schouten, *Physica A* 189 (1992) 493.

- [3] W. Zhang, J.P.J. Michels and J.A. Schouten, to be published.
- [4] P.J. Kortbeek, M.J.P. Muringer, N.J. Trappeniers and S.N. Biswas, *Rev. Sci. Instrum.* 56 (1985) 1269.
- [5] J.A. Schouten, N.J. Trappeniers and W. Goedegebuure, *Rev. Sci. Instrum.* 50 (1979) 1652.
- [6] W.B. Streett, A.L. Erickson and J.L.E. Hill, *Phys. Earth Planet. Interiors* 6 (1972) 69.
- [7] P.J. Kortbeek, J.J. van de Ridder, S.N. Biswas and J.A. Schouten, *Int. J. Thermophys.* 9 (1988) 425.
- [8] P.J. Kortbeek and J.A. Schouten, *Int. J. Thermophys.* 11 (1990) 455.
- [9] Y. Hanayama, *J. Phys. Soc. Japan* 46 (1979) 328.
- [10] M. Kimura, Y. Hanayama and T. Nishitake, *Jpn. J. Appl. Phys.* 26 (1987) 1366.