

37. W. Wilson and D. Bradley, "Speed of sound in four primary alcohols as a function of temperature and pressure," *J. Acoust. Soc. Am.*, 36, No. 2, 333-337 (1964).
38. G. W. Marks, "Acoustic velocity with relation to chemical constitution in alcohols," *Acoust. Soc., Am.*, 41, No. 1, 103-117 (1967).
39. G. S. Parks, "Thermal data on organic compounds. I. The heat capacities and free energies of methyl, ethyl and normal-butyl alcohols," *J. Am. Chem. Soc.*, 47, 338-345 (1925).
40. J. W. Williams and F. Daniels, "The specific heats of certain organic liquids at elevated temperatures," *J. Am. Chem. Soc.*, 46, No. 4, 903-917 (1924).
41. J. F. Counsell, J. L. Hales, and J. F. Martin, "Thermodynamic properties of organic oxygen compounds. Part 16. Butyl alcohol," *Trans. Faraday Soc.*, 61, No. 9, 1869-1875 (1965).
42. B. A. Grigor'ev, G. S. Yanin, and Yu. L. Rastorguev, "An experimental study of the isobaric specific heats of alcohols," *Trudy GIAP*, Issue 54, Moscow (1979), pp. 57-64.
43. G. S. Arutyunyan, S. S. Bagdasaryan, and A. M. Kerimov, "An experimental study of the isobaric specific heats of n-propyl, n-butyl, and n-amyl alcohols at various temperatures and pressures," *Izv. Akad. Nauk Az. SSR, Ser. Fiz.-Tekhn. Mat. Nauk*, No. 6, 94-97 (1981).
44. A. A. Aleksandrov, T. S. Khasanshin, and D. S. Kosoi, "The speed of sound, isochoric specific heat, and adiabatic and isothermal compression coefficients for methyl alcohol at atmospheric pressure," *Inzh.-Fiz. Zh.*, 42, No. 1, 92-98 (1982).
45. V. N. Kartsev and V. A. Zabelin, "The isothermal compressibilities of a series of n-alcohols," *Zh. Fiz. Khim.*, 52, No. 8, 2113-2114 (1978).
46. B. P. Sahli, H. Gager, and A. J. Richard, "Ultracentrifugal studies of the isothermal compressibilities of organic alcohols and alkanes: correlation with surface tension," *J. Chem. Thermodynam.*, 8, 179-188 (1976).
47. G. C. Benson and H. D. Pflug, "Molar excess volumes of binary systems of normal alcohols at 25°C," *J. Chem. Eng. Data*, 15, No. 3, 382-386 (1970).

COMPRESSIBILITY AND VIRIAL COEFFICIENTS OF METHANE-ARGON

MIXTURES

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Using the Barnett method we have measured the compressibility of methane-argon mixtures at temperatures of 373.15 and 423.15°K and pressures up to 30 MPa. The methane concentrations in the mixtures were varied from 8 to 82 mole %. We calculated the second, third, and second mixed virial coefficients.

The present article is a continuation of systematic studies of the bulk behavior of gases and gas mixtures by the Barnett method [1-4]. We measured the compressibility of methane-argon mixtures, and calculated the second and third virial coefficients of the mixtures. The values obtained for the second virial coefficients were used to calculate the second mixed virial coefficient B_{12} , which furnishes important information on the nature of the intermolecular interaction of dissimilar molecules.

The apparatus and measurement procedure were described earlier [1, 2]. The pressure was measured with MP-600 and MP-60 piston manometers of grade 0.05 accuracy, and the temperature was measured to within 0.01°C by a calibrated Beckmann thermometer. The temperature was maintained constant to within 0.005-0.01°C.

We used helium, methane, and argon with a minimum purity of 99.97% in the experiments. The mixtures were prepared in a tilting mixer provided with an electric heater. Mixing was

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TABLE 1. Compressibility Factor of Argon-Methane Mixture at 373.15°K. P is in MPa

8.35		20.05		34.85		41.94		55.57		75.97		81.91	
P	z	P	z	P	z	P	z	P	z	P	z	P	z
31.203	1.05641	23.632	1.01916	24.516	1.01641	30.251	1.04093	30.901	1.03744	25.224	0.99318	29.443	1.01126
22.851	1.02052	17.590	1.00066	18.211	0.99594	22.109	1.00353	22.497	1.99632	18.673	0.97012	21.444	0.97155
17.042	1.00396	13.236	0.99325	13.697	0.98811	16.510	0.98853	16.786	0.98062	14.072	0.96412	16.054	0.95945
12.824	0.99655	10.011	0.99096	10.365	0.98634	9.439	0.98339	12.675	0.97674	10.683	0.96549	12.163	0.95887
9.699	0.99422	7.589	0.99093	7.870	0.98786	7.176	0.98615	9.616	0.97750	8.139	0.97029	9.265	0.96348
7.348	0.99358	5.764	0.99389	5.975	0.98986	5.453	0.98859	7.321	0.98162	8.207	0.97620	7.651	0.97553
5.576	0.99464	4.375	0.99415	4.594	0.99150	4.138	0.99091	5.568	0.98493	4.730	0.98118	4.108	0.98070
4.231	0.99550	3.321	0.99544	3.447	0.99341	3.148	0.99319	4.236	0.98840	3.602	0.98562	3.128	0.98515
3.210	0.99135	2.521	0.99677	2.618	0.99503	2.397	0.99476	3.221	0.99138	2.746	0.98921	2.380	0.98860
2.435	0.99709	1.913	0.99765	1.987	0.99620	1.853	0.99585	2.448	0.99307	2.084	0.99151	1.809	0.99129
1.847	0.99789	1.451	0.99807	1.508	0.99660	1.377	0.99687	1.859	0.99468	1.583	0.99151	1.809	0.99129
1.401	0.99841							1.411	0.99594	1.583	0.99350	1.375	0.99332

TABLE 2. Compressibility Factor of Argon-Methane Mixture at 423.15°K. P is in MPa

7.90		15.15		27.62		54.98		65.10		84.54	
P	z	P	z	P	z	P	z	P	z	P	z
30.963	1.07584	28.160	1.06416	31.544	1.07635	31.056	1.06851	30.622	1.06092	31.235	1.05697
22.778	1.04383	20.789	1.03613	23.104	1.03976	22.713	1.03067	22.401	1.02359	22.764	1.01597
16.965	1.02536	15.525	1.02052	17.198	1.02078	16.913	1.01221	16.690	1.00582	16.950	0.99772
12.737	1.01531	11.673	1.01199	12.809	1.01054	12.709	1.00316	12.561	0.99838	12.760	0.98059
9.600	1.00927	8.808	1.00712	9.739	1.00550	9.600	0.99936	9.495	0.99534	9.661	0.98918
7.256	1.00615	6.673	1.00544	7.364	1.00273	7.264	0.99805	7.198	0.99541	7.329	0.98970
5.494	1.00481	5.047	1.00339	5.578	1.00185	5.514	0.99849	5.461	0.99592	5.566	0.99142
4.157	1.00271	3.802	1.00232	4.226	1.00100	4.182	0.99887	4.140	0.99659	4.226	0.99287
3.149	1.00139	2.951	1.00161	3.203	1.00069	3.170	0.99895	3.144	0.99736	3.209	0.99423
2.369	1.00139	2.194	1.00113	2.428	1.00045	2.405	0.99913	2.385	0.99779	2.436	0.99542
1.809	1.00101	1.663	1.00081	1.849	1.00030	1.823	0.99929	1.809	0.99825	1.849	0.99641

TABLE 3. Second, Third, and Second Mixed Virial Coefficients for an Argon-Methane Mixture at 373.15°K

CH ₄ content, mole %	B, cm ³ /mole	c, cm ⁶ /mole ²	B ₁₂ , cm ³ /mole
8,35	-4,1	635	-4,7
20,05	-4,7	462	-4,7
34,85	-6,6	580	-5,3
42,91	-7,7	751	-5,5
55,57	-9,6	808	-4,8
75,97	-13,7	1039	-3,9
81,91	-15,8	1120	-4,6

TABLE 4. Second, Third, and Second Mixed Virial Coefficients for an Argon-Methane Mixture at 423.15°K

CH ₄ content, mole %	B, cm ³ /mole	c, cm ⁶ /mole ²	B ₁₂ , cm ³ /mole
7,90	1,7	510	4,7
15,15	1,4	690	3,1
27,62	0,3	486	1,4
58,98	-1,6	519	3,2
65,10	-3,8	756	2,1
84,54	-7,5	1336	2,4

continued until analyses of the gas composition in the upper and lower positions of the mixer agreed. The composition of the gas was determined to within 0.1% from the molecular weight of the mixtures.

The measured values were used to calculate the compressibility factors and the virial coefficients by the analytic method proposed in [5]. In this method the experimental data are described by the equation

$$P_r Q_r = \sum_{i=1}^m A_i Q_r^{i-1}, \quad (1)$$

where $Q_r = \prod_{j=1}^r N_j$; $A_i = B_i \rho_0 RT$; P_r is the pressure at the r-th stage, T is the temperature, ρ_0

is the initial density, R is the gas constant, N_j is the instrument constant for the j-th expansion, and the B_i are the virial coefficients in the series in terms of the density. The value of N_j depends on the barometric deformation of the piezometer, and is related to the value of N_∞ at zero pressure by the equation

$$N_j = N_\infty \sum_{i=1}^n a_i P_j^{i-1} / b_i P_{j-1}^{i-1}, \quad (2)$$

where the coefficients a_i and b_i are determined by the mechanical properties of the piezometer material [6].

The values and the number of virial coefficients necessary for a given series of measurements were determined from an analysis of the sum of the squares of the deviations at each point and the standard errors of the virial coefficients [7].

Tables 1 and 2 list the values of the compressibility factor for all the mixtures investigated. The average error of the values obtained is 0.05%, and the maximum does not exceed 0.08%. The reproducibility of the results was tested by repeating all the measurements for a number of mixtures. The differences between the data of the two independent experiments did not exceed 0.02%.

The value of N_∞ was determined to within 0.005% from experiments with pure helium at each temperature. The calculated values of the compressibility factor differ from the values reported in a recent paper [8] on the measurement of the compressibility of helium by 0.01-0.02%.

Tables 3 and 4 list the values of the second, third, and second mixed virial coefficients for each mixture. The value of B_{12} was found from the equation

TABLE 5. Comparison of Values of Second Mixed Virial Coefficient of a Methane-Argon Mixture at 373.15 and 423.15°K According to Data from Various References

T, K	B_{12} cm ³ /mole	Reference	T, K	B_{12} cm ³ /mole	Reference
373,15	-4,8±0,4 -7,2 -13,1	Present work [13] [14]	423,15	2,8±0,7 -1,0 -5,4	Present work [13] [14]

Note. The values of B_{12} from [13, 14] were obtained by interpolation.

$$B_{\text{mix}} = B_{11}N_1 + 2B_{12}N_1N_2 + B_{22}N_2 \quad (3)$$

where B_{11} and B_{22} are the second virial coefficients of the pure gases, and N_1 and N_2 are the mole fractions of the components. The values $B_{11} = -4.01, 1.19$ cm³/mole for argon, and $B_{22} = -20.91, -11.24$ cm³/mole for methane at 373.15 and 423.15°K, respectively, were taken from [9-12].

The errors of the values obtained are 0.2 cm³/mole for B, 3% for C, and 0.6 cm³/mole for B_{12} . The final values of B_{12} , obtained by processing the data for all the mixtures by the method of least squares using Eq. (3), are listed in Table 5.

Since we do not know of any data in the literature on the compressibility of methane-argon mixtures at the temperatures of our measurements, we cannot compare our results with other data. However, there are two papers [13, 14] in which the coefficient B_{12} was determined from compressibility data over a wide temperature range (300-500°K) at low pressures. Table 5 shows that our values of B_{12} are in rather good agreement with those in [13], but differ widely from the values in [14].

LITERATURE CITED

1. D. S. Tsiklis, L. R. Linshits, and I. B. Rodkina, "Measurement of molar volumes of gases and gas mixtures at high pressures," *Zh. Fiz. Khim.*, **40**, 2823 (1966).
2. L. R. Linshits, I. B. Rodkina, and D. S. Tsiklis, "Measurement of the compressibility of carbon dioxide-helium mixtures by Barnett's method," *Zh. Fiz. Khim.*, **49**, 2141 (1975).
3. L. R. Linshits, I. B. Rodkina, and D. S. Tsiklis, "The molar volumes and virial coefficients of ethylene-helium mixtures," *Zh. Fiz. Khim.*, **51**, 2357 (1977).
4. L. R. Linshits, I. B. Rodkina, N. G. Tyurikova, and D. S. Tsiklis, "The molar volumes of ethylene-helium mixtures," *Zh. Fiz. Khim.*, **51**, 2948 (1977).
5. E. S. Barkan, "Determination of compressibility factor and virial coefficients by Barnett's method," *Inzh.-Fiz. Zh.*, **44**, 958 (1983).
6. A. V. Bilevich, L. F. Vereshchagin, and Ya. A. Kalashnikov, "Piezometer for determining the density of gases at high temperatures and pressures," *Prib. Tekh. Eksp.*, **3**, 146 (1961).
7. A. A. Vasserman, A. Ya. Kreizerova, and V. I. Nedostup, "Determination of the virial coefficients from experimental P-V-T data," *Teplofiz. Vys. Temp.*, **9**, 915 (1971).
8. G. S. Kell, G. E. McLaurin, and E. Whalley, "Second virial coefficient of helium from 0 to 500°C by the two-temperature gas-expansion method," *J. Chem. Phys.*, **68**, 2199 (1978).
9. A. Michels, Hub. Wijker, and Hk. Wijker, "Isotherms of argon between 0 and 150°C and pressures up to 2900 atm," *Physica*, **15**, 627 (1949).
10. N. K. Kalfoglou and J. G. Miller, "Compressibility of gases 5. The helium-argon and helium-tetrafluoromethane systems," *J. Phys. Chem.*, **71**, 1256 (1967).
11. D. R. Douslin, R. H. Harrison, R. T. Moore, and J. P. McCullough, "P-V-T relations for methane," *J. Chem. Eng. Data*, **9**, 358 (1964).
12. N. J. Trappeniers, T. Wassenaar, and J. C. Abels, "Isotherms and thermodynamic properties of methane at temperatures between 0 and 150°C and at densities up to 570 Amagat," *Physica*, **98A**, 289 (1979).
13. K. Strein, R. N. Lichtenthaler, B. Schramm, and Kl. Schäfer, "Measurement of the second virial coefficients of saturated hydrocarbons from 300-500°K," *Ber. Bunsenges, Phys. Chem.*, **75**, 1308 (1971).

14. J. Bellm, W. Reineke, Kl. Schäfer, and B. Schramm, "Measurement of second virial coefficients in the temperature range 300-500°K," *Ber. Bunsenges. Phys. Chem.*, 78, 282 (1974).

OPTICOACOUSTIC DETERMINATION OF THERMOPHYSICAL CHARACTERISTICS

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The possibilities of utilizing two-layered systems of standard and studied specimens to determine thermophysical characteristics under opticoacoustic experimental conditions are theoretically analyzed.

The opticoacoustic method of investigating solid and liquid media is based on the effect of pressure vibrations originating under the illumination of a specimen in an insulated gas-filled chamber by modulated radiation.

The magnitude and phase shift of the acoustic signal under specific conditions are related uniquely to the magnitude and phase shift of the temperature fluctuations on the specimen surface [1]. This permits utilization of the opticoacoustic method to determine thermophysical characteristics [2-6].

The thermal diffusivity coefficient is determined by exposing one surface of a plane opaque specimen and recording the magnitude or phase of the acoustic signal from the side of its second surface [2-5]. A fine strongly absorbing layer is deposited on the surface being exposed on transparent specimens. The specimen thickness should be within the limits $1.5\mu \leq l \leq (3-3.5)\mu$, where $\mu = (2\alpha/\omega)^{1/2}$ is the thermal diffusion length.

If $l > 1.5\mu$, a thermal activity coefficient $(\lambda c\rho)^{1/2}$ can be found for opaque specimens from a comparison of acoustic signals during alternate exposure of the specimen being studied and the standard [6]. But the absorption by the exposed surfaces of the specimen and standard in this case should be or is known to be the same or determined in advance by some method. In addition, the methods mentioned do not permit execution of measurements on thin specimens whose thickness is $< 1.5\mu$ in the whole frequency band utilized.

The opticoacoustic determination of thermophysical characteristics is substantially a modification of the method of plane temperature waves. For the complex determination of thermophysical characteristics in such a method, it is convenient to perform the measurements on two-layered systems consisting of test and standard specimens [7].

It is expedient to use the two-layered system also in the opticoacoustic modification of the method. For opticoacoustic measurements the two-layered system moreover permits studying materials with other optical properties since the radiation can always be directed from the side of the opaque standard. In this connection, the utilization of two-layered systems consisting of test and standard specimens to determine thermophysical characteristics under the conditions of an opticoacoustic experiment is examined in this paper for measurements from both the exposed, as well as the opposite surface.

The one-dimensional model is shown in Fig. 1. Two plane specimens of thickness l_1 and l_2 are in ideal thermal contact and communicate with external surfaces with two volumes of depths l_g and l_b . Sinusoidally modulated radiation is directed at specimen surface 2 for $x = -(l_1 + l_2)$. The radiation absorbed by the surface is converted into heat. This is equivalent to the action of a heat source of the form $I_0[1 + \exp(j\omega t)]$ on the surface.

For measurements from the specimen 2 side the volume before it should be filled with a nonabsorbing gas. When measurements are carried out from specimen 1 the volume behind it can be filled with any gas while the medium in front of specimen 2 should be transparent.

As in [1], we consider the thermal flux and temperature are continuous on the boundaries between the specimens and between each specimen and the corresponding medium, i.e., heat transfer occurs exclusively by heat conduction. Since the temperature rise in such experi-

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