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COMPRESSIBILITY OF A BINARY MIXTURE OF ARGON AND NITROGEN AT DIFFERENT CONCENTRATIONS IN THE 59-590 BAR PRESSURE RANGE

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The compressibility of an argon–nitrogen mixture is measured by a variable volume piezometer. It is shown that the constant in the formula for the binary mixture compressibility depends on the pressure.

The investigation of the compressibility of gas mixtures, which is of great practical value, is associated with the problem of obtaining sufficiently exact and confident semiempirical equations of state. As is known [1], a measure of the cohesive force in the equations of state of a real gas with two parameters which were applied to mixtures is the constant a, which is related to analogous constants for pure gases a_1 and a_2, as well as the constant a_{12} characterizing the collisions between diverse molecules, by the relationship

$$a_{\mathrm{M}} = a_1x_1^2 + a_2x_2^2 + 2a_{12}x_1x_2. \tag{1}$$

Krichevskii and Kazarnovskii [2] proposed an equation of state for binary mixtures which agrees outwardly with (1):

$$Z(T,\ V) = x_1^2Z_1(T,\ V) + x_2^2Z_2(T,\ V) + 2x_1x_2Z_{12}(T,\ V), \tag{2}$$

in which Z_{12} is independent of the composition ([3] is devoted to an analysis of this equation).

It is interesting to extend (2) to the compressibility of mixtures

$$Z_{\mathrm{M}} = x_1^2Z_1 + x_2^2Z_2 + 2x_1x_2Z_{12}, \tag{3}$$

but to consider the quantity Z_{12} as an empirical constant without relating it to some analytical dependence with virial coefficients.

This paper is devoted to the measurement of the compressibility of an argon–nitrogen mixture for different compositions, pressures, and temperatures and to the verification of the possibility of using the relationship (3) to describe mixture compressibility.

The compressibility was measured by a pressure-unloaded piezometer of variable volume with a mercury level search by a gamma radiometer. The mass was measured by directly weighing a definite batch of gas transferred in special stainless steel ampoules with microvalves.

The diagram of the apparatus is shown in Figure 1. The inner tube (D = 14, d = 12 mm) is fabricated from stainless steel and submerged in a thick-walled vessel 2 with mercury. The tube 3 (D = 22.2, d = 15.5 mm) welded to the vessel 2 carries the load under pressure. The thermostatic jacket 4 is heat-insulated by the foam plastic half-rings 5. The inlet for the platinum resistance thermometer 6 is arranged up against the tube 3 in the expanded part of the thermostatic jacket.

The system component to seek the mercury level is constructed as follows. The support slab 7 in the form of a disk is fastened to the outer thick-walled tube 4 of the piezometer at a given height by using bolts not

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TABLE 1. Comparison between the Densities ($kg \cdot m^{-3}$) of Nitrogen and Argon, Measured on the Described Apparatus, and Data in the Literature, T = 290°K

P, bar	Nitrogen			Argon		
	our data	data from [5]	δ, %	our data	data from [5]	δ, %
150	170,96	171,29	0,19	264,50	265,60	0,42
200	220,61	221,63	0,46	351,11	352,73	0,46
300	305,15	306,37	0,40	503,64	505,56	0,38
400	370,92	372,30	0,37	622,45	625,39	0,47
500	422,82	424,63	0,43	714,78	718,39	0,50
600	466,30	467,07	0,16	788,37	792,39	0,51

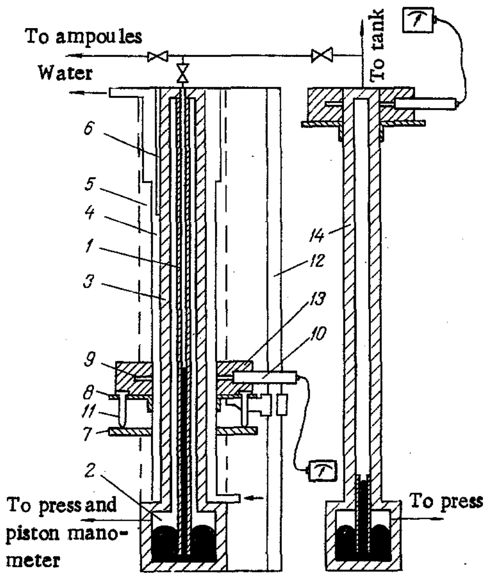

Fig. 1. Diagram of the experimental set-up.

indicated in Fig. 1. A container for the radioactive gamma-radiation source 9 and the radiometer sensor 10 is mounted on the mobile base 8. The mobile base can be displaced along the piezometer by two micrometer screws 11. The position of the moving slab is fixed by a slide gauge 12 with 0.1-mm scale divisions. The intensity of the gamma radiation incident on the radiometer sensor is regulated by the lead shield 13 with a slot of about 1 mm.

When the gamma rays overlap the mercury column, their intensity diminishes abruptly (drops to 20-30% of the initial value), as is noted on the radiometer scale. The true position of the mercury level is recorded by the beginning of the radiometer pointer motion. The accuracy of finding the height is no worse than ±0.2 mm. The experience with using such an apparatus to seek the mercury level in the customary variable-volume piezometer [4] and with piezometer data exhibited good stability of its operation and high reproducibility of the measurement results.

The piezometer volume is determined by repeated filling with distilled water at 20°C, forcing it out by mercury, and weighing the displaced volume of water on analytical balances. The dependence of the piezometer volume on the position of the mercury level there was found by the method of least squares. The maximum height of the gas column in the piezometer was 1500 mm. A correction for the volume change with temperature was inserted for other temperatures.

The gas pressure was measured by a piston-loaded manometer MP-600 of the class 0.05 with corrections for the atmospheric pressure and column height of the mercury and oil in the piezometer taken into account.

TABLE 2. Density ρ and Compressibility Coefficient Z_M of an Argon–Nitrogen Mixture for Different Pressures, Concentrations, and Temperatures

1. x_{Ar}=83,90%

T=293,15°K

p, bar	ρ, kg/m³	z_M
59,52	95,604	0,9712
78,71	127,29	0,9646
98,06	159,39	0,9597
117,88	192,26	0,9565
147,52	240,79	0,9557
176,68	287,74	0,9579
216,07	347,53	0,9699
235,60	375,50	0,9788
265,14	416,04	0,9942
294,50	453,74	1,0126
323,72	488,87	1,0331
353,05	521,42	1,0563
382,39	551,68	1,0813
411,74	579,67	1,1081
441,09	605,97	1,1356
470,46	629,81	1,1653
499,83	652,95	1,1942
530,30	674,60	1,2263
558,58	694,51	1,2547
587,96	713,64	1,2853

T=323,15°K

p, bar	ρ, kg/m³	z_M
147,71	212,44	0,9840
176,78	252,94	0,9891
206,06	292,38	0,9974
235,33	330,03	1,0091
264,63	366,16	1,0228
293,95	400,31	1,0392
323,89	433,14	1,0582
353,20	463,56	1,0783
382,52	492,38	1,0995
411,86	519,43	1,1222
441,21	545,08	1,1455
499,93	591,57	1,1960
558,67	633,35	1,2484
588,04	652,34	1,2757

T=353,15°K

p, bar	ρ, kg/m³	z_M
147,89	190,80	1,0038
177,00	226,64	1,0114
206,20	261,53	1,0211
235,45	295,54	1,0317
264,74	328,06	1,0450
294,05	359,26	1,0600
324,04	389,61	1,0771
353,34	417,86	1,0950
382,66	444,54	1,1147
411,98	470,28	1,1345
441,32	494,93	1,1547
470,67	518,00	1,1767
500,03	539,96	1,1992
529,39	560,79	1,2225
558,75	580,74	1,2460
588,12	599,49	1,2705

2. x_{Ar}=62,98%

T=293,15°K

p, bar	ρ, kg/m³	z_M
59,45	88,798	0,9760
78,66	118,11	0,9708
98,02	147,52	0,9686
117,85	177,46	0,9681
147,53	221,47	0,9710
176,70	263,53	0,9774
216,08	317,14	0,9932
235,61	342,22	1,0036
264,53	378,02	1,0201
294,46	411,49	1,0431
323,77	442,65	1,0662
353,09	471,49	1,0916
382,43	498,25	1,1188
411,78	523,08	1,1475
441,14	546,59	1,1765
470,50	568,08	1,2073
499,87	588,43	1,2383
529,24	607,39	1,2701
558,62	625,19	1,3025
588,00	642,24	1,3346

T=323,15°K

p, bar	ρ, kg/m³	z_M
147,72	196,01	0,9965
176,86	232,74	1,0049
206,08	268,28	1,0158
235,34	302,26	1,0296
264,64	334,35	1,0467
293,97	365,00	1,0650
323,92	394,24	1,0865
353,23	421,43	1,1084
382,56	447,22	1,1312
411,90	471,31	1,1557
441,25	493,73	1,1818
470,60	515,30	1,2077
499,97	532,00	1,2427
529,33	554,63	1,2620
558,70	572,50	1,2905
588,07	589,75	1,3186

T=353,15°K

p, bar	ρ, kg/m³	z_M
177,01	209,06	1,0245
206,21	240,78	1,0363
235,46	271,51	1,0494
264,75	300,79	1,0650
294,06	328,96	1,0817
324,08	355,92	1,1018
353,37	381,26	1,1215
382,69	405,40	1,1422
412,02	428,29	1,1641
441,36	450,16	1,1864
470,70	470,80	1,2098
500,06	490,40	1,2339
529,42	509,07	1,2584
558,78	526,75	1,2836
588,15	543,58	1,3093

3. x_{Ar}=41,15%

T=293,15°K

p, bar	ρ, kg/m³	z_M
59,28	81,709	0,9800
78,53	108,55	0,9773
97,92	135,38	0,9778
117,77	162,45	0,9793
147,51	201,65	0,9882
176,69	238,98	0,9987
216,08	286,54	1,0187
226,43	298,45	1,0249
235,61	308,54	1,0315
264,54	339,65	1,0521
294,36	369,75	1,0754
323,68	396,85	1,1018
353,01	422,48	1,1287
382,32	446,13	1,1576
411,70	468,22	1,1878
441,07	488,15	1,2205

4. x_{Ar}=19,25%

T=293,15°K

p, bar	ρ, kg/m³	z_M
59,27	74,538	0,9886
78,52	98,801	0,9881
97,91	122,87	0,9907
118,42	147,83	0,9960
147,48	182,31	1,0059
176,67	215,42	1,0197
216,06	257,39	1,0437
236,18	277,32	1,0589
265,21	304,56	1,0827
294,49	330,37	1,1083
323,80	354,13	1,1369
353,18	376,34	1,1667
382,46	397,02	1,1978
411,81	416,19	1,2303
441,17	434,30	1,2630
470,53	451,01	1,2972

TABLE 2. (continued)

P, bar	ρ, kg/m³	z_M
470,43	507,56	1,2520
499,80	525,31	1,2852
529,18	542,17	1,3185
558,56	558,13	1,3519
587,94	573,20	1,3856
T=323,15°K		
206,07	243,77	1,0359
235,34	273,94	1,0528
264,64	302,58	1,0718
323,82	355,27	1,1169
353,13	379,47	1,1404
382,47	401,59	1,1671
411,82	423,08	1,1928
441,16	442,98	1,2204
470,52	461,92	1,2482
499,89	479,83	1,2767
529,26	496,69	1,3058
558,63	512,61	1,3354
588,01	527,77	1,3653
T=353,15°K		
147,86	161,53	1,0292
176,99	191,04	1,0399
206,20	219,46	1,0536
235,45	246,88	1,0694
264,74	273,04	1,0872
294,06	297,98	1,1066
323,95	322,06	1,1279
353,26	344,42	1,1501
382,58	365,89	1,1725
411,92	385,98	1,1967
441,26	405,33	1,2207
470,61	423,70	1,2455
499,99	440,94	1,2715
529,34	457,43	1,2976
558,71	473,21	1,3239
588,08	487,73	1,3520

P, bar	ρ, kg/m³	z_M
499,90	466,63	1,3320
529,27	481,51	1,3667
558,65	495,60	1,4015
588,03	508,99	1,4364
T=323,15°K		
147,66	162,38	1,0256
176,82	191,82	1,0397
206,04	219,88	1,0569
235,32	246,62	1,0762
264,62	271,84	1,0980
293,95	295,73	1,1211
323,95	318,46	1,1474
353,26	339,47	1,1737
382,58	359,48	1,2004
411,19	378,19	1,2264
441,27	395,65	1,2580
470,63	412,10	1,2881
499,94	427,79	1,3182
529,36	442,43	1,3495
558,73	456,47	1,3806
588,10	469,99	1,4114
T=353,15°K		
147,83	146,67	1,0403
206,17	198,65	1,0712
235,43	222,97	1,0898
264,72	246,26	1,1095
294,04	268,32	1,1310
324,09	289,60	1,1550
382,71	328,10	1,2039
412,04	345,95	1,2293
441,38	363,02	1,2549
470,73	379,11	1,2815
500,08	394,34	1,3089
529,44	408,84	1,3366
558,81	422,69	1,3645
588,18	435,79	1,3930

The temperature was measured by a platinum resistance thermometer connected in the circuit of a unary-binary R-329 bridge with a mirror M17/4 galvanometer as zero device. The accuracy of the thermostatting was no worse than ±0.05°.

Observation of the mercury position in the mercury adjuster, which yields the initial gas pressure in the piezometer, was also performed by using the radioactive indicator with the radiometer. Since the activity of the gamma-radiation source was sufficiently low (we used Se-75), operation with it is perfectly safe.

Since the mercury search system permits finding the volume at any site of the manometer, it is sufficient to determine that volume from which the gas emerged at a given pressure. By knowing the mass of ejected gas and the volume at a given pressure, the density and the whole mass of gas in the piezometer can be computed.

Operation of the apparatus was verified by determining the density and compressibility of pure gases which have been investigated well. Values of the nitrogen and argon densities measured on our apparatus are compared in Table 1 with data in the literature.

Measured values of the helium compressibility deviate from the data in [6] by 0.2-0.3%. This indicates the reliability of operation of the apparatus and of the results obtained on it with a mean error no greater than 0.3%.

The density and compressibility of argon mixtures with nitrogen were measured on the apparatus described for different concentrations and three values of the temperature (293.15, 323.15, 353.15°K). The gas concentration in the tanks was determined on a Modernized UKh-1 chromatograph [7, 8] with ±0.2% error. The values obtained for the mixture density Z_M and compressibility are presented in Table 2.

Values of the empirical constant Z_{12} of (3) were found from the tabular data. It turns out (as should have been expected) that Z_{12} is independent of the composition but depends linearly on the pressure. The following equation for the dependence of Z_{12} on P was obtained by the method of least squares

$$Z_{12} = 0.8326 + 0.864 \cdot 10^{-3} P. \quad (4)$$

A weak dependence of Z_{12} on the temperature was detected for the temperatures studied. To set up this dependence, measurements must be performed in a broader temperature range.

The mean deviation of the measured mixture compressibilities from those calculated by means of (3) with the dependence of Z_{12} on P taken into account by means of (4) is 0.5%.

NOTATION

x is the molar fraction;
P is the pressure, bar;
V is the volume, m^3;
T is the absolute temperature, °K;
Z is the compressibility coefficient;
δ is the relative error, %;
ρ is the density, kg/m^3.

Subscripts

1, 2 are the numbers of the mixture components;
M signifies mixture.

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