Compressibility of Helium-Nitrogen Mixtures

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MIXTURES OF HELIUM and nitrogen at pressures to 2700 p.s.i. and higher play an important part in processes used for the separation of helium from natural gas. Effective engineering design and control of these processes require a knowledge of the compressibility factors of helium-nitrogen mixtures.

Considerable work has been done on the compressibilities of binary systems. Helium-hydrogen mixtures have been studied by Gibby and coworkers (*4*) and helium-carbon dioxide by Harper and Miller (*5*). Bartlett (*1*, *2*) and Verschoyle (*9*) have worked extensively on mixtures of hydrogen and nitrogen. Recently, the helium-nitrogen system has been studied by Pfefferle, Goff, and Miller (*8*) and by Kramer and Miller (*6*), who presented virial coefficients for the system at 86° F. and pressures to 125 atm.

Compressibility factors for the helium-nitrogen system, at pressures higher than those used by Kramer and Miller, were obtained at 70° F. at pressures to 4000 p.s.i.a. An evaluation of the dependence of the compressibility factor Z for mixtures upon both temperature and pressure was beyond the scope of the present work; for practical design, however, a knowledge of the variation of Z with pressure at a single temperature is helpful.

APPARATUS

The Burnett (*3*) method was used in this work. Data obtained by this method are conservatively estimated as being accurate to 0.1%. Temperatures were maintained within ±0.05° F. of the desired value, and pressures were measured to the nearest 0.01 p.s.i.

MATERIALS

Helium used in this study was Bureau of Mines' Grade-A helium having an analyzed purity of 99.995%. The nitrogen was obtained from a local distributor; its purity was 99.9%. These gases were used without further purification in preparing the mixtures studied.

PREPARATION OF MIXTURES

Work with helium-nitrogen and other gas mixtures at this laboratory has indicated that, unless special mixing techniques are used, a long period of time is required to obtain complete equilibration. As an example of the difficulty in obtaining homogeneous mixtures, the preparation of a 2.7-97.3 He-N_2 mixture may be cited. A cylinder of nitrogen containing 0.7 mole % He was available, at a pressure of 800 p.s.i.g., and the calculated amount of helium was added to this cylinder to produce the desired equilibrium mixture. The cylinder was placed in a special cradle so that it could be turned upside down readily, and a sample of gas was removed 2 hours after the cylinder was inverted. The cylinder was then turned upright and allowed to stand for 30 minutes before another sample was removed. This procedure was continued, turning the cylinder end-over-end and withdrawing samples at 30-minute intervals. The change in composition of the mixture with time is shown in Figure 1. The experiment was interrupted after 4.5 hours, and the following morning, 20.5 hours later, the gases were equilibrated, consecutive analyses indicating constant composition at 2.7% He. Equilibrium may have been reached earlier, and the experiment was incomplete in this sense, but it does show how, on inversion, the helium flowed from one end to the other with little mixing.

To avoid this mixing problem in the present work, several cylinders were equipped with internal mixing devices. The valve was removed from each cylinder and a rod 1/4 inch in diameter and long enough to extend to nearly to the bottom of the cylinder was silverbrazed to the valve. Captive on the rod, but free to slide the full length of the rod, was a four-bladed paddle of spring steel. The valve was reinstalled in the cylinder, and the cylinder was then placed on the cradle and turned end-over-end. During the rotation, the paddle drops the length of the cylinder and mixes the

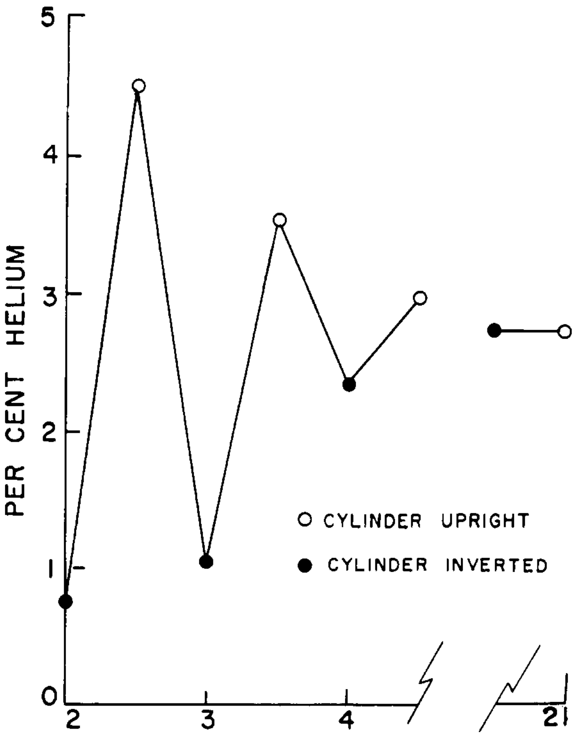

Figure 1. Change in helium concentrations observed during preparation of a helium-nitrogen mixture.

gases. Mixtures can be equilibrated in 30 minutes by this procedure, as indicated by consecutive mass spectrometer analyses. The desired mixtures were prepared by evacuating the mixing cylinder, admitting the minor component first and, finally, the other component until the desired total pressure was obtained.

EXPERIMENTAL DATA AND RESULTS

Experimental compressibility factors were determined for 15 mixtures of helium and nitrogen and for each of the pure components at 70° F. and at pressures to 4000 p.s.i.a. The data were obtained by the treatment given by Burnett in his original article (*3*). Volume ratios, N, were determined by making calibration runs with pure helium.

The parabolic equation

$$Z = 1 + BP + CP^2 \qquad (1)$$

was fitted to the experimental data by the least squares method (*10*). In this equation Z = the compressibility factor (PV/RT), and P = the pressure in p.s.i.a. Z factors computed by Equation 1, at each experimental pressure, using the coefficients thus obtained, were compared with the experimental data, and these results are shown in Table I. The table also includes the per cent deviation at each pressure and the average per cent deviation for each mixture over the entire pressure range. Greatest deviations for individual pressures were observed with 80.1% N_2 for which the deviation was +0.25% at 4016 p.s.i.a., and the 93.6% N_2 mixture for which the deviation was -0.24% at 2534 p.s.i.a. The over-all deviation for the total of 168 experimental pressures was within the range +0.1 to -0.1% for 80% of the cases. Maximum average per cent deviation for the mixtures was $\pm 0.14\%$ for 93.6% N_2. Sixty-seven per cent of the mixtures exbited average per cent deviations ranging from ± 0.01 to $\pm 0.07\%$.

Table I shows that, within the limits of experimental error, a linear relationship between Z and P was observed for mixtures containing nitrogen concentrations through 10.2%. In these cases C in Equation 1 is zero and the equation becomes

$$Z = 1 + BP \qquad (2)$$

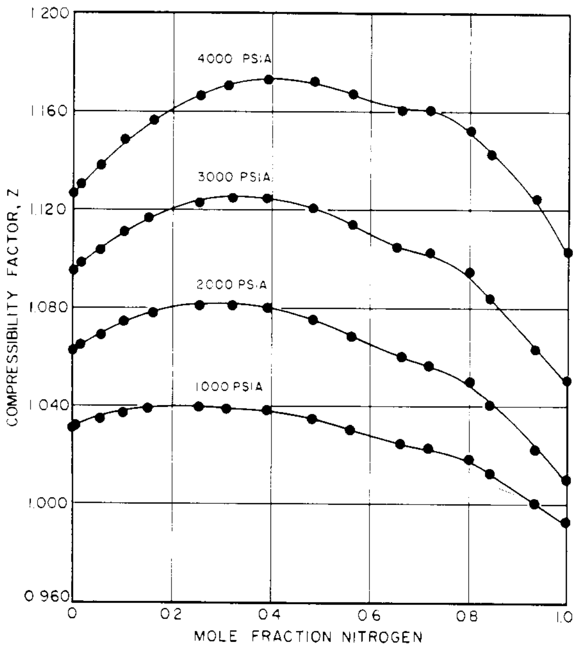

Figure 2. Isobaric compressibility factors for helium-nitrogen mixtures at 70° F.

The values of B and C given in Table I are not considered as "true" virial coefficients, because they were computed from a closed equation of state. A graphical treatment of the data gave no better results because of lack of data at near atmospheric pressure. For these reasons plots of B and C *vs.* composition are not included in this article; the Z data, however, are considered to have a maximum error of $\pm 0.1\%$.

Figure 2 is a plot of four compressibility isobars and shows an interesting feature of the helium-nitrogen system—that is, that over a wide range of compositions, the compressibility factor for the mixture is greater than that of either pure component. This effect is most pronounced in

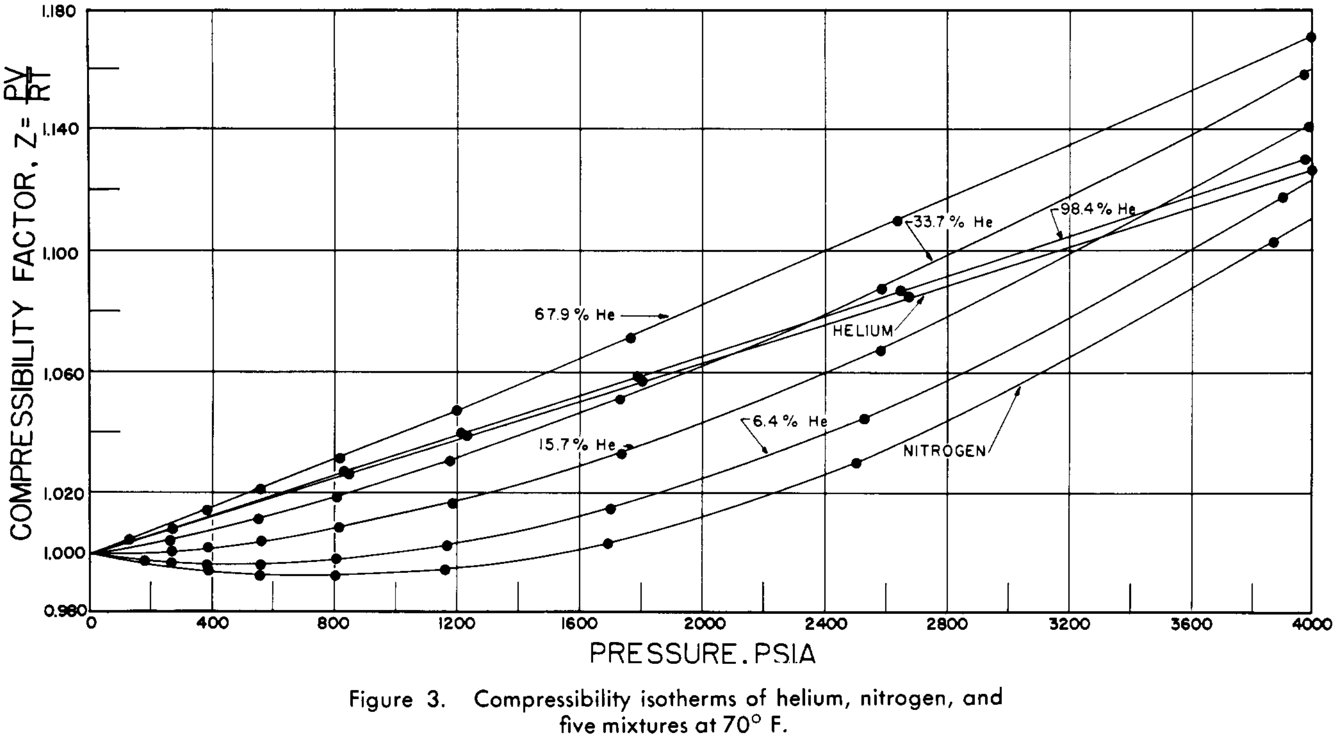

Figure 3. Compressibility isotherms of helium, nitrogen, and five mixtures at 70° F.

Table I. Compressibility Data for Helium-Nitrogen Mixtures, at 70° F.

	Pressure, P.S.I.A.	Exptl. Compressibility Factor Z	Calcd. Compressibility Factor[a]	% Dev.
0% N_2	4004.4	1.1268	1.1269	+ 0.01
$B = 3.1683 \times 10^{-5}$	2675.9	1.0850	1.0849	−0.01
$C = 0$	1809.8	1.0574	1.0573	−0.01
$N = 1.4410$	1234.0	1.0390	1.0391	+ 0.01
	846.14	1.0266	1.0268	+ 0.02
	582.43	1.0183	1.0185	+ 0.02
	401.95	1.0126	1.0127	+ 0.01
	277.90	1.0089	1.0088	−0.01
	192.38	1.0064	1.0061	−0.03
	133.22	1.0042	1.0042	− ...
			Av.	±0.01
0.6% N_2	3986.6	1.1282	1.1280	−0.02
$B = 3.2118 \times 10^{-5}$	2662.8	1.0858	1.0855	−0.03
$C = 0$	1800.7	1.0580	1.0578	−0.02
$N = 1.4409$	1227.7	1.0394	1.0394	− ...
	841.80	1.0269	1.0270	+ 0.01
	579.38	1.0184	1.0186	+ 0.02
	399.82	1.0126	1.0128	+ 0.02
	276.44	1.0087	1.0089	+ 0.02
	191.34	1.0059	1.0061	+ 0.02
	132.60	1.0047	1.0043	−0.04
			Av.	±0.02
1.6% N_2	3979.7	1.1302	1.1301	−0.01
$B = 3.2691 \times 10^{-5}$	2656.5	1.0871	1.0868	−0.03
$C = 0$	1795.4	1.0587	1.0587	− ...
$N = 1.4410$	1223.7	1.0398	1.0400	+ 0.02
	838.78	1.0271	1.0274	+ 0.03
	577.19	1.0185	1.0189	+ 0.04
	398.27	1.0127	1.0130	+ 0.03
	275.34	1.0091	1.0090	−0.01
	190.61	1.0063	1.0062	−0.01
	132.08	1.0050	1.0043	−0.07
			Av.	±0.03
5.7% N_2	4008.8	1.1384	1.1383	−0.01
$B = 3.4489 \times 10^{-5}$	2668.8	1.0919	1.0920	+ 0.01
$C = 0$	1802.7	1.0626	1.0622	−0.04
$N = 1.4407$	1227.3	1.0422	1.0423	+ 0.01
	840.99	1.0289	1.0290	+ 0.01
	578.55	1.0198	1.0200	+ 0.02
	399.19	1.0137	1.0138	+ 0.01
	275.93	1.0095	1.0095	− ...
	190.98	1.0066	1.0066	− ...
	132.30	1.0046	1.0046	− ...
			Av.	±0.01
10.2% N_2	4034.1	1.1499	1.1502	+ 0.03
$B = 3.7234 \times 10^{-5}$	2678.4	1.1001	1.0997	−0.04
$C = 0$	1803.9	1.0676	1.0672	−0.04
$N = 1.4409$	1226.4	1.0458	1.0457	−0.01
	838.91	1.0308	1.0312	+ 0.04
	576.71	1.0211	1.0215	+ 0.04
	397.65	1.0145	1.0148	+ 0.03
	274.75	1.0099	1.0102	+ 0.03
	190.20	1.0074	1.0071	−0.03
	131.73	1.0054	1.0049	−0.05
			Av.	±0.03
16.1% N_2	3993.3	1.1563	1.1558	−0.04
$B = 3.8966 \times 10^{-5}$	2643.2	1.0128	1.1031	+ 0.03
$C = .01535 \times 10^{-9}$	1777.9	1.0688	1.0693	+ 0.05
$N = 1.4409$	1208.6	1.0469	1.0471	+ 0.02
	826.96	1.0322	1.0322	− ...
	568.40	1.0222	1.0221	−0.01
	391.88	1.0155	1.0153	−0.02
	270.74	1.0109	1.0105	−0.04
			Av.	±0.03
25.6% N_2	4076.1	1.1700	1.1701	+ 0.01
$B = 3.9276 \times 10^{-5}$	2683.6	1.1102	1.1097	−0.05
$C = .60298 \times 10^{-9}$	1799.2	1.0727	1.0727	− ...
$N = 1.4412$	1220.2	1.0485	1.0488	+ 0.03
	833.71	1.0325	1.0331	+ 0.06
	572.52	1.0218	1.0227	+ 0.09
	394.38	1.0144	1.0156	+ 0.12
	272.35	1.0096	1.0107	+ 0.11
	188.32	1.0061	1.0074	+ 0.13
	130.40	1.0040	1.0051	+ 0.11
			Av.	±0.07
32.1% N_2	4022.6	1.1714	1.1718	+ 0.03
$B = 3.8327 \times 10^{-5}$	2644.6	1.1097	1.1090	−0.06
$C = 1.0859 \times 10^{-9}$	1772.5	1.0717	1.0713	−0.04
$N = 1.4409$	1202.5	1.0476	1.0477	+ 0.01
	822.00	1.0318	1.0322	+ 0.04
	564.73	1.0214	1.0219	+ 0.05
	389.27	1.0145	1.0151	+ 0.06
	268.92	1.0099	1.0104	+ 0.05
	186.07	1.0068	1.0071	+ 0.03
	128.89	1.0049	1.0049	− ...
			Av.	±0.04
39.1% N_2	3995.0	1.1729	1.1732	+ 0.03
$B = 3.6641 \times 10^{-5}$	2619.1	1.1080	1.1075	−0.05
$C = 1.6819 \times 10^{-9}$	1756.0	1.0704	1.0695	−0.08
$N = 1.4409$	1190.8	1.0459	1.0460	+ 0.01
	814.21	1.0304	1.0309	+ 0.05
	559.54	1.0204	1.0210	+ 0.06
	385.78	1.0137	1.0144	+ 0.07
	266.56	1.0092	1.0099	+ 0.07
	184.45	1.0063	1.0069	+ 0.06
	127.76	1.0043	1.0047	+ 0.04
			Av.	±0.05
48.5% N_2	3818.5	1.1621	1.1627	+ 0.05
$B = 3.2280 \times 10^{-5}$	2506.7	1.0992	1.0979	−0.12
$C = 2.7053 \times 10^{-9}$	1681.8	1.0626	1.0620	−0.06
$N = 1.4409$	1142.7	1.0403	1.0404	+ 0.01
	782.35	1.0263	1.0270	+ 0.07
	538.17	1.0172	1.0182	+ 0.10
	371.26	1.0111	1.0124	+ 0.13
	256.75	1.0076	1.0085	+ 0.09
	177.74	1.0051	1.0058	+ 0.07
	123.16	1.0035	1.0040	+ 0.05
			Av.	±0.08
56.3% N_2	3986.4	1.1660	1.1670	+ 0.09
$B = 2.6733 \times 10^{-5}$	2603.8	1.0973	1.0954	−0.17
$C = 3.7986 \times 10^{-9}$	1744.4	1.0593	1.0582	−0.10
$N = 1.4409$	1185.0	1.0369	1.0370	+ 0.01
	811.61	1.0233	1.0242	+ 0.09
	558.55	1.0147	1.0161	+ 0.14
	385.53	1.0092	1.0109	+ 0.17
	266.63	1.0056	1.0074	+ 0.18
	184.63	1.0034	1.0050	+ 0.16
	127.97	1.0021	1.0035	+ 0.14
			Av.	±0.13
66.3% N_2	3975.0	1.1582	1.1592	+ 0.09
$B = 1.9902 \times 10^{-5}$	2590.7	1.0877	1.0856	−0.19
$C = 5.0665 \times 10^{-9}$	1737.0	1.0508	1.0499	−0.09
$N = 1.4409$	1182.0	1.0303	1.0306	+ 0.03
	810.92	1.0185	1.0194	+ 0.09
	558.80	1.0113	1.0127	+ 0.14
	386.11	1.0068	1.0085	+ 0.17
	267.26	1.0042	1.0057	+ 0.15
	185.16	1.0025	1.0039	+ 0.14
	128.41	1.0017	1.0027	+ 0.10
			Av.	±0.12

[a] Computed by equation $Z = 1 + BP + CP^2$, where B and C have the values indicated, and P is expressed in p.s.i.a.

Table I. Continued

	Pressure, P.S.I.A.	Exptl. Compressibility Factor Z	Calcd. Compressibility Factor [a]	% Dev.
72.0% N_2	4027.4	1.1603	1.1627	+ 0.21
$B = 1.7466 \times 10^{-5}$	2618.4	1.0872	1.0848	−0.22
$C = 5.6956 \times 10^{-9}$	1754.4	1.0499	1.0482	−0.16
$N = 1.4412$	1194.1	1.0298	1.0290	−0.08
	819.26	1.0183	1.0181	−0.02
	564.63	1.0114	1.0117	+ 0.03
	390.14	1.0072	1.0077	+ 0.05
	269.99	1.0045	1.0051	+ 0.06
	187.02	1.0028	1.0035	+ 0.07
	129.62	1.0017	1.0024	+ 0.07
			Av.	±0.10
80.1% N_2	4015.6	1.1506	1.1535	+ 0.25
$B = 1.2302 \times 10^{-5}$	2605.7	1.0760	1.0759	−0.01
$C = 6.4566 \times 10^{-9}$	1748.4	1.0406	1.0412	+ 0.06
$N = 1.4412$	1192.3	1.0227	1.0239	+ 0.12
	819.61	1.0132	1.0144	+ 0.12
	565.75	1.0079	1.0091	+ 0.12
	391.37	1.0049	1.0058	+ 0.09
	271.08	1.0031	1.0038	+ 0.07
	187.89	1.0020	1.0025	+ 0.05
	130.27	1.0012	1.0017	+ 0.05
			Av.	±0.09
84.3% N_2	3993.6	1.1417	1.1426	+ 0.08
$B = 0.54984 \times 10^{-5}$	2589.7	1.0670	1.0649	−0.20
$C = 7.5610 \times 10^{-9}$	1739.6	1.0330	1.0325	−0.05
$N = 1.4412$	1188.1	1.0167	1.0172	+ 0.05
	817.86	1.0087	1.0096	+ 0.09
	565.10	1.0045	1.0055	+ 0.10
	391.22	1.0022	1.0034	+ 0.12
	271.13	1.0010	1.0021	+ 0.11
	188.01	1.0003	1.0013	+ 0.10
	130.41	1.0000	1.0008	+ 0.08
			Av.	±0.10
93.6% N_2	3906.9	1.1179	1.1184	+ 0.04
$B = -0.85547 \times 10^{-5}$	2533.8	1.0446	1.0421	−0.24
$C = 9.9437 \times 10^{-9}$	1708.3	1.0148	1.0144	−0.04
$N = 1.4409$	1171.3	1.0026	1.0036	+ 0.10
	809.25	0.9981	0.9996	+ 0.15
	560.79	0.9966	0.9983	+ 0.17
	389.09	0.9963	0.9982	+ 0.19
	270.12	0.9967	0.9984	+ 0.17
	187.55	0.9971	0.9987	+ 0.16
	130.23	0.9976	0.9991	+ 0.15
			Av	±0.14
100.0% N_2	3872.1	1.1028	1.1045	+ 0.15
$B = -1.8103 \times 10^{-5}$	2509.2	1.0298	1.0279	−0.18
$C = 11.645 \times 10^{-9}$	1696.7	1.0033	1.0028	−0.05
$N = 1.4409$	1167.2	0.9945	0.9948	+ 0.03
	808.36	0.9925	0.9930	+ 0.05
	561.27	0.9929	0.9935	+ 0.06
	390.21	0.9946	0.9947	+ 0.01
	271.14	0.9959	0.9960	+ 0.01
	188.46	0.9974	0.9970	−0.04
	130.90	0.9982	0.9978	−0.04
			Av.	±0.06

the 4000 p.s.i.a. isobar, where $Z_{\text{mixt.}}$ is greater than Z_{He} or Z_{N_2} for nitrogen concentrations ranging to slightly above 90%. The effect decreases with decreasing pressure, and at 1000 p.s.i.a. occurs only from zero to approximately 50% N_2.

the 4000 p.s.i.a. isobar, where $Z_{\text{mixt.}}$ is greater the Z_{He} or Z_{N_2} for nitrogen concentrations ranging to slightly above 90%. The effect decreases with decreasing pressure, and at 1000 p.s.i.a. occurs only from zero to approximately 50% N_2.

This phenomenon is also demonstrated in Figure 3, a plot of Z *vs.* P for pure nitrogen and helium, and for five representative mixtures. The mixtures containing 98.4 and 67.9 mole % He exhibit greater Z values than either pure component over the entire pressure range. The mixture containing 15.7% He has Z values lying between those of the pure components over a part of the pressure range and exceeds the Z value of helium above 3300 p.s.i.a. A crossover also occurs for 6.4% He at approximately 4050 p.s.i.a. For the mixture containing 33.7 mole % He, the crossover occurs at 2170 p.s.i.a. A mixture containing 99.4% He exhibited, over the entire pressure range, a significantly higher compressibility factor than that of pure helium. The data for this mixture fall about halfway between those for pure helium and the 98.4% mixture.

The additive volume rule does not apply to computation of compressibility data for these mixtures, as this rule limits Z for mixtures to values lying between those for the pure components. Elevation of compressibility data above values predicted by the additive pressure and additive volume rules was observed in argon-ethylene by Masson and Dolley (*7*) and in hydrogen-helium systems by Gibby, Tanner, and Masson (*4*). The latter workers found, as was observed in the present study, that the compressibility of the mixture could exceed that of either pure component. A comment concerning this maximum in the compressibility of the mixture has been given by Kramer and Miller (*6*). The maximum denotes that the mixture is less compressible at this composition than at any other.

Consideration is being given to extending this work to pressures of approximately 10,000 p.s.i.a. Supplementary apparatus will be incorporated to enable accurate pressure measurements at pressures near atmospheric. Investigations at higher pressures will be helpful in obtaining a better understanding of the helium-nitrogen system, and accurate low-pressure data would enable evaluation of virial coefficients.

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