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THE COMPRESSIBILITY OF GASEOUS MIXTURES OF HELIUM-NITROGEN AND HELIUM-DEUTERIUM AT HIGH PRESSURES

by

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ABSTRACT

The compressibilities of gaseous mixtures of helium-nitrogen and helium-deuterium were determined in the pressure range from 100 atm. to 1400 atm. at 25° C. The compressibility of pure helium was also determined in the same pressure range at 25° C.

The experimental data were fitted to a four-term virial equation by the method of least squares, and the resulting virial coefficients are listed. Some of the experimental compressibility factors are then compared with the corresponding compressibility factors determined by an additive volume method.

ACKNOWLEDGMENTS

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I. Introduction

The compressibility of many pure gases has been determined experimentally over very wide ranges of temperature and pressure; however, there has been little work published on the experimental compressibility of gaseous mixtures at high pressures. This report outlines the experimental determination of the compressibility of five mixtures of helium-nitrogen and three mixtures of helium-deuterium up to 1400 atm. at 25° C.

The existing experimental data on the compressibility of pure helium did not cover the desired pressure range (100 atm.-1400 atm.) at 25° C. These helium data were obtained by the technique described below and are listed in this report. The compressibility of pure nitrogen at 25° C was also checked using the apparatus and technique described below. These data are compared with the data reported by Michels and co-workers(1) for the compressibility of pure nitrogen at 25° C over the same pressure range.

II. Experimental

The apparatus used in this experiment is shown schematically in Fig. 1. The gas mixtures to be studied were prepared by introducing pure nitrogen or deuterium into an H-size cylinder of helium at pressures from 500 psi to 1500 psi. The mixture in the cylinder was allowed to stand for at least 24 hours. The individual mixtures were sampled and analyzed at least twice during each series of compressions and were found to be homogeneous.

The mixture was compressed to the desired pressure in the 200-cc high-pressure vessel and allowed to reach thermal equilibrium. When thermal equilibrium was attained, the pressure was read on the 30-kpsi Heise gauge. (The Heise gauge was filled with hydraulic fluid and separated from the pneumatic system with a mercury-filled "U" tube when deuterium was present in the system.) The mixture was then expanded into the 8-liter low-pressure vessel and again allowed to reach thermal equilibrium. The pressure was measured with the electromanometer. After the pressure in the 8-liter volume had been determined, the mixture was sampled by expansion into an evacuated vessel for analysis. The system was then allowed to bleed down to atmospheric pressure, and the cycle could then be repeated.

All of these pressure measurements were made relative to atmospheric pressure. Before a series of compressions was performed with a given mixture, the pressure vessels were evacuated. A small amount of the specific mixture to be studied was added, and the system was allowed to bleed down to atmospheric pressure. This method was used to eliminate the need to evacuate the 8-liter pressure vessel before every compression.

Both pressure vessels were immersed in a temperature-controlled water bath, maintained at 25.01 ± 0.01° C as determined with a platinum resistance thermometer.

The ratio of the pressure vessel volumes was determined by the following technique. The 8-liter volume was pressurized with helium to approximately 200 psi (these pressures varied during the many expansions required in this determination) and the 200-cc volume evacuated. The pressure was read on the electromanometer, and the gas then expanded into the 200-cc volume. The subsequent pressure was again recorded with the electromanometer. The ratio of the pressures was then a direct measure of the ratio of the volumes. The change in the compressibility factor of the helium due to these small pressure changes was determined to be negligible and was not considered in the volume ratio determination. This measurement accounted for all of the small volumes included in the system (electromanometer chamber, valves, tubing, etc.) as it was subsequently used in the compressibility measurements.

The change of the volume ratio with increased pressures was less than the resolution of this experiment. Experiments with pure nitrogen, for which the compressibility is well known, in the pressure range of 150 atm. to 1700 atm. showed no change in the volume ratio within the limits of the accuracy of the initial low-pressure determination of the volume ratio.

The 30-kpsi Heise gauge used to measure the pressure of the mixture in the 200-cc vessel was calibrated with a piston gauge and found to have an accuracy of ± 0.30% of the reading, or better, over the desired pressure range. The 500-psi electromanometer was also calibrated with a piston gauge and found to be linear to within 0.05% of full scale.

The mixtures were compressed with a Pressure Products Incorporated 30,000-psi diaphragm compressor.

The helium-nitrogen mixtures were analyzed with a CEC 21-620 gas mass spectrometer. The accuracy of the mixture analysis was better than ± 1.0%. The helium-deuterium mixtures were analyzed with a gas chromatograph. The accuracy of the mixture analysis using this method was estimated to be ± 2.0%.

The compressibility factor $Z(P) = PV/RT$ as a function of pressure can be determined with this experimental apparatus by the following equation:

$$Z(P) = Z(Po)\ (1 + v)^{-1} \frac{P}{Po}$$

where P is the pressure attained in the 200-cc high-pressure vessel,. Po is the equilibrium pressure after the gas has been expanded into the 8-liter vessel, Z(Po) is the compressibility factor of the mixture at the low-pressure Po, and v is the ratio of the 8-liter volume to the 200-cc volume.

The value of the volume ratio v was found to be 42.58 ± 0.10 by the previously described method. Because of this large volume ratio, the equilibrium pressure Po after expansion ranged from 5 to 20 atmospheres. The compressibility factor Z(Po) of the mixtures at these low pressures was then determined by the following techniques. For the case of helium-nitrogen mixtures, low-pressure compressibility data were available.[(2)] The second virial coefficient (B_{mix}) was determined from these published data and substituted into the following two-term virial equation:

$$Z(Po) = 1 + B_{mix}\ Po.$$

For the case of helium-deuterium mixtures, Z(Po) was determined using a method of additive volumes as follows:

$$Z(Po) = (1 - C)Z_{He} + CZ_{N}$$

where C is the mole fraction of nitrogen in the mixture and Z_{He} and Z_{N} are the compressibility factors of pure helium and pure nitrogen, respectively, at pressure Po.

The error introduced by using this method is small for low-pressure data (e.g., an error of less than 0.1% in Z(Po) at 10 atm. can be determined from the variation in the second virial coefficient with composition of the He-D_2 mixture). The compressibility factors Z_{He} and Z_N used in this determination were obtained from Michels' work.[1,3]

III. Results

The compressibility factors determined by this experiment are listed in Tables I and II. The experimental data for helium-nitrogen mixtures are plotted in Fig. 2.

As previously mentioned, experimental data on the compressibility of pure helium were not available over the desired pressure range. These data were obtained by the above mentioned technique and are also listed in Table I. These experimental data are shown in Fig. 2. The low-pressure Z(Po) for pure helium was obtained from Michels'[3] work. The three data points for pure nitrogen shown in Table I and Fig. 2 were determined by the same technique as a control to obtain a comparison with Michels' data on pure nitrogen.

The compressibility factor Z(P) can be expressed in a virial expansion of the powers of the pressure as follows:

$$Z(P) = 1 + BP + CP^2 + DP^3 + \ldots.$$

These data were fitted to a four-term virial equation by the method of least squares, and the virial coefficients are listed in Table III. Plots of these coefficients vs. mole concentration of the mixtures are shown in Figs. 4 and 5. The calculated values of the compressibility factors using these coefficients in the virial equation are listed in Tables I and II.

For the purpose of comparison, two experimental compressibility isotherms of helium-nitrogen mixtures are plotted in Fig. 3 with the compressibility isotherms of the same mixtures as calculated by the method of partial volumes (Amagat's Law).

$$Z(P) = (1 - C)Z_{He} + CZ_{N}.$$

Z(P) is the compressibility factor of the mixture at the pressure P, C is the mole fraction of nitrogen in the mixture, and Z_{He} and Z_{N} are the compressibility factors for pure helium and nitrogen, respectively, in the pressure P.

IV. Summary

It should be pointed out that the virial coefficients reported here are useful only for interpolating between experimental data points. Until accurate low-pressure experimental data become available for these mixtures, the absolute values of the second virial coefficients B cannot be determined accurately. The least squares determination of the remaining virial coefficients depends strongly on the values of B. Consequently, the extrapolation of the compressibility isotherms of the mixtures above the experimental data using these coefficients cannot be justified.

As shown in Fig. 3 the experimental values of Z are higher than those values of Z predicted by the method of partial volumes for a given mixture. This held true for all of the mixtures studied in this experiment. The partial volume method of calculating the compressibility of mixtures does not take into account the interaction effects of dissimilar molecules. This can be shown by examination of the plots of the virial coefficients in Figs. 4 and 5. The virial coefficients predicted by the partial volume technique lie along the straight line drawn between the end points of the curves in Figs. 4 and 5. The difference between the experimental coefficients and those coefficients predicted by partial volumes can be attributed to the unique interactions between various combinations of the dissimilar molecules of the mixture.

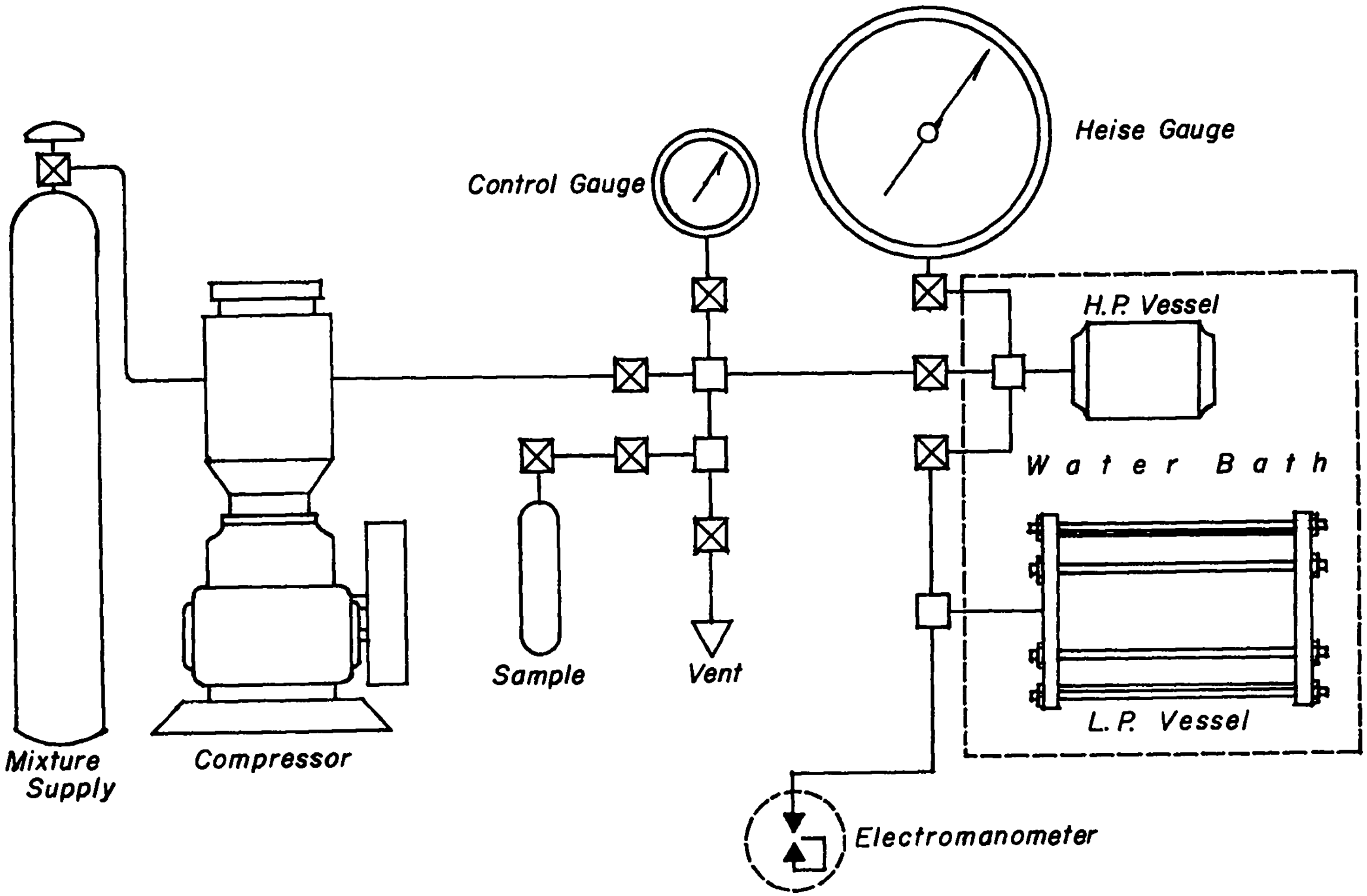

Fig. 1. System Schematic.

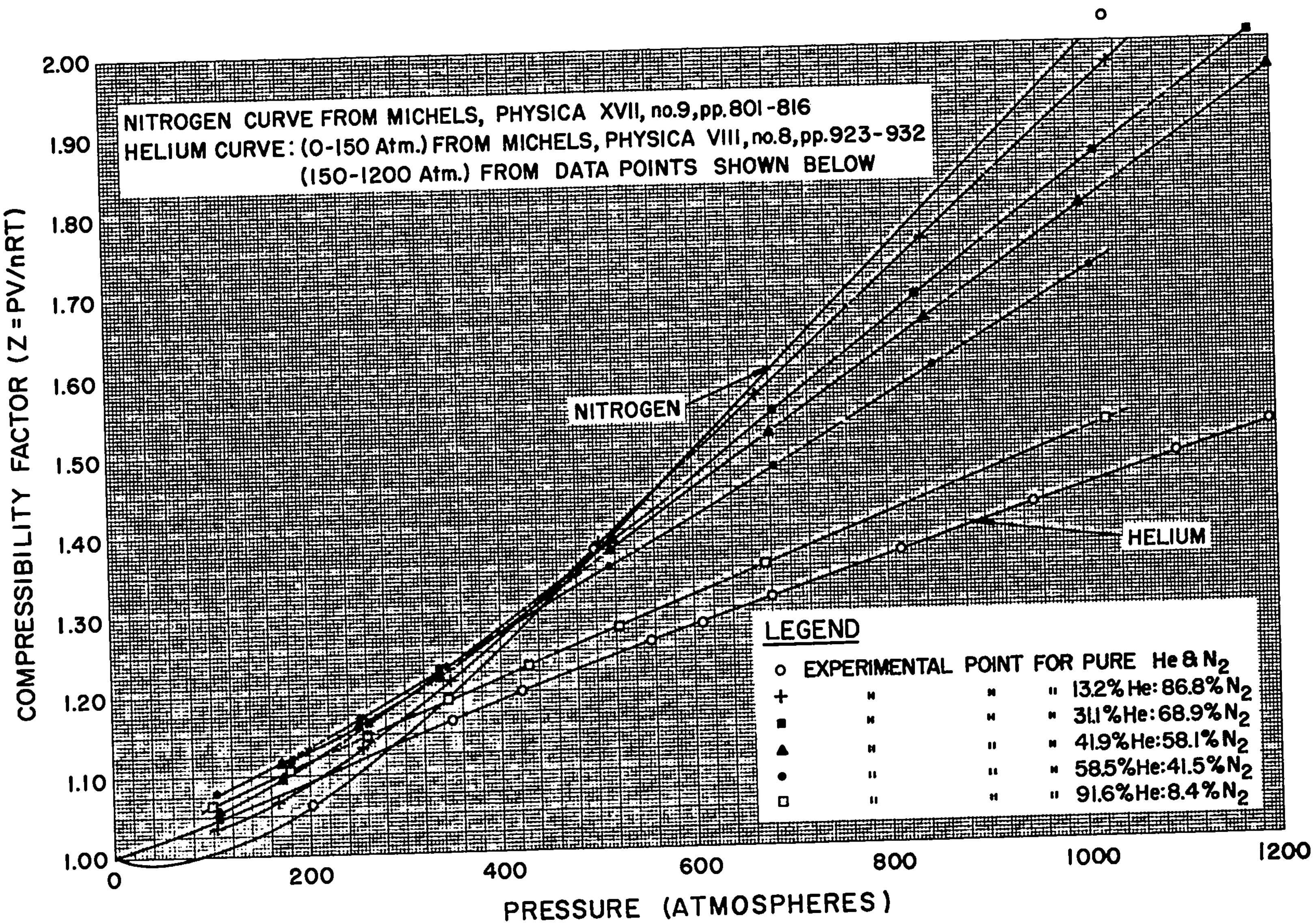

Fig. 2. Compressibility Data for Helium-Nitrogen Mixtures at 25° C.

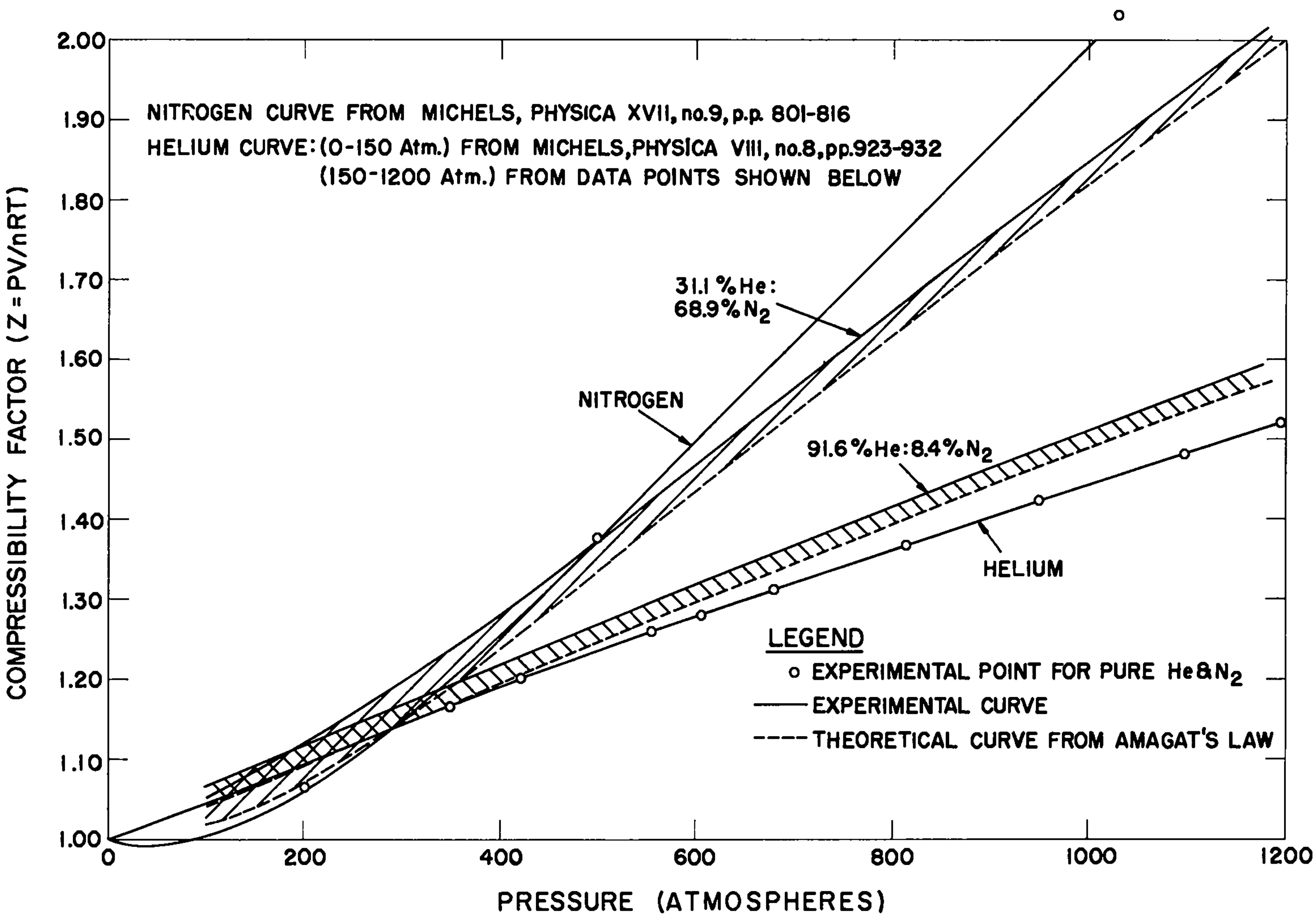

Fig. 3. Experimental Compressibility Data Compared with Compressibility Predicted by Partial Volumes (Amagat's Law) for Helium-Nitrogen Mixtures.

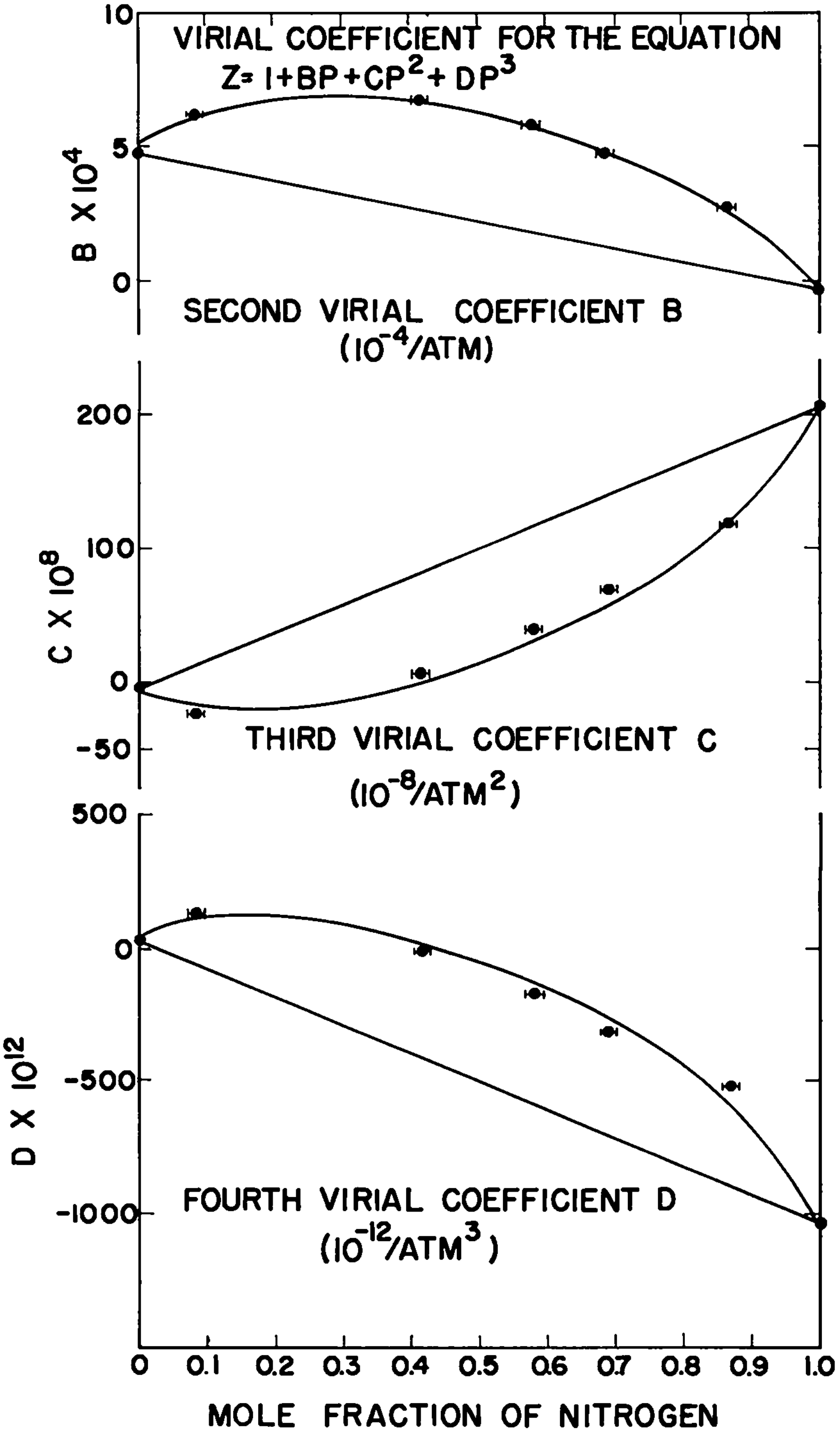

Fig. 4. Virial Coefficients for Helium-Nitrogen Mixtures.

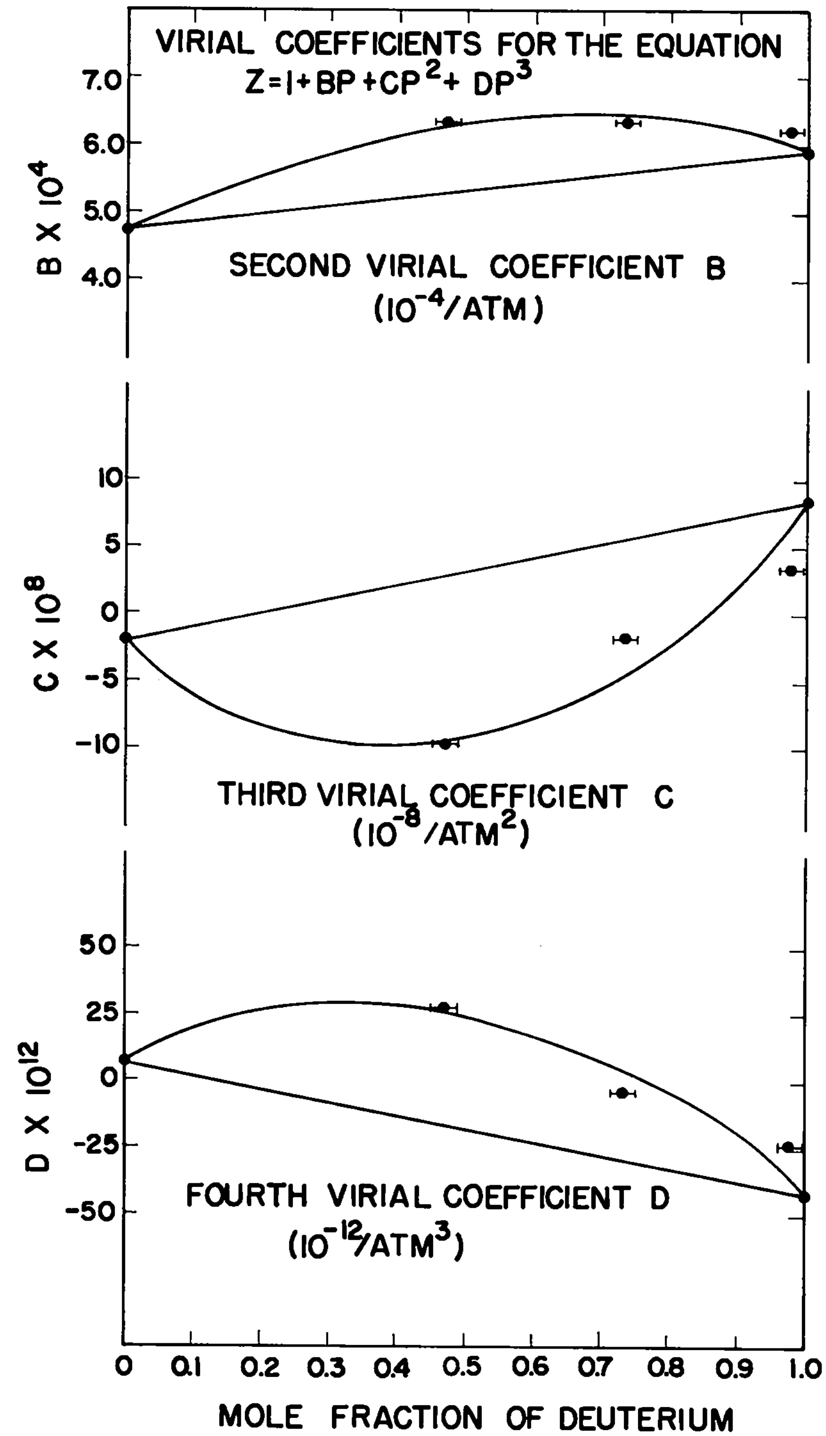

Fig. 5. Virial Coefficients for Helium-Deuterium Mixtures.

Table I

Compressibility Factor Z = PV/RT for Helium-Nitrogen Mixtures

Mole Fraction of Helium	Pressure (Atmospheres)	Experimental Z	Calculated Z $Z=1+BP+CP^2+DP^3$
1.00	1579.7	1.668	1.667
	1357.8	1.583	1.584
	1195.9	1.520	1.519
	1097.2	1.481	1.481
	951.99	1.424	1.423
	815.13	1.366	1.368
	679.27	1.311	1.311
	606.97	1.279	1.279
	554.91	1.256	1.257
	420.18	1.201	1.197
	353.16	1.167	1.167
0.916	1024.1	1.523	1.524
	675.35	1.354	1.349
	523.27	1.275	1.277
	428.69	1.227	1.232
	343.29	1.191	1.189
	258.23	1.146	1.146
	177.25	1.105	1.103
	100.03	1.062	1.060
0.585	1008.4	1.715	1.716
	842.41	1.593	1.592
	683.86	1.476	1.476
	512.04	1.354	1.352
	342.27	1.230	1.233
	251.77	1.170	1.170
	175.22	1.115	1.118
	103.77	1.077	1.069
0.419	1195.9	1.964	1.963
	999.25	1.795	1.796
	840.36	1.656	1.656
	676.37	1.514	1.511
	514.08	1.372	1.372
	332.74	1.218	1.225
	251.43	1.164	1.164
	169.98	1.115	1.106
	102.07	1.058	1.061

Table I (Continued)

Mole Fraction of Helium	Pressure (Atmospheres)	Experimental Z	Calculated Z $Z=1+BP+CP^2+DP^3$
0.311	1181.37	2.013	2.012
	1015.24	1.863	1.866
	833.22	1.688	1.691
	681.14	1.544	1.541
	511.02	1.381	1.377
	336.83	1.223	1.223
	259.93	1.164	1.162
	173.18	1.096	1.099
	103.43	1.049	1.055
0.132	1209.5	2.161	2.155
	1037.0	1.973	1.983
	837.64	1.752	1.756
	666.17	1.561	1.553
	500.82	1.377	1.367
	341.59	1.210	1.209
	252.79	1.130	1.135
	167.39	1.066	1.076
	99.01	1.034	1.038
0.000 (Nitrogen)	1031.6	2.035	2.0264*
	498.77	1.379	1.3708*
	202.44	1.068	1.0590*
0.000 (Nitrogen)**	9.8119	0.9988	0.999
	50.034	0.9965	1.003
	75.240	0.9990	1.008
	99.790	1.005	1.015
	199.69	1.057	1.065
	300.47	1.147	1.145
	400.04	1.255	1.246
	501.17	1.375	1.365
	601.55	1.498	1.494
	700.06	1.620	1.624
	802.69	1.747	1.757
	901.46	1.868	1.876
	1002.1	1.992	1.983

*Calculated from virial coefficients reported by Michels, Lunbeck, and Wolkers.(1)

**These experimental compressibility factors for pure nitrogen were taken from Michels'(1) work and used to determine the virial coefficients of nitrogen shown in Table III.

Table II

Compressibility Factor Z = PV/RT for Helium-Deuterium Mixtures

Mole Fraction of Helium	Pressure (Atmospheres)	Experimental Z	Calculated Z $Z=1+BP+CP^2+DP^3$
0.532	1350.0	1.742	1.743
	998.20	1.563	1.562
	679.10	1.394	1.394
	516.50	1.307	1.305
	344.00	1.206	1.208
	176.60	1.115	1.109
0.267	1360.2	1.819	1.818
	1184.7	1.718	1.719
	1052.7	1.642	1.642
	856.00	1.526	1.526
	674.60	1.419	1.418
	511.40	1.317	1.318
	341.60	1.216	1.214
	147.30	1.087	1.093
	103.40	1.070	1.065
0.022	1358.3	1.857	1.856
	1239.8	1.784	1.785
	1092.8	1.693	1.695
	998.20	1.636	1.636
	849.20	1.543	1.542
	683.20	1.438	1.436
	510.00	1.324	1.325
	341.60	1.216	1.217
	170.10	1.103	1.107
	108.50	1.073	1.068
0.000	100.50	1.058	1.061
(Deuterium)*	200.00	1.120	1.122
	300.00	1.185	1.185
	400.00	1.249	1.249
	500.00	1.315	1.314
	600.00	1.380	1.379
	800.00	1.510	1.509
	1000.00	1.637	1.638
	1200.00	1.762	1.763
	1400.00	1.884	1.884

*These experimental compressibility factors for pure deuterium were taken from Michels'[4] work and used to determine the virial coefficients for deuterium shown in Table III.

Table III

Virial Coefficients of Mixtures

The experimental compressibility data were fitted to the four-term virial expansion:

$$Z(P) = 1 + BP + CP^2 + DP^3.$$

The coefficients B, C, and D as determined by the method of least squares are shown below.

Nitrogen-Helium Mixtures

Mole Fraction of Helium	$B \times 10^4$	$C \times 10^8$	$D \times 10^{12}$
0.000	-0.4515	206.362	-1038.01
0.132	2.6745	118.520	-509.81
0.311	4.6230	69.703	-307.68
0.419	5.6436	39.016	-157.69
0.585	6.6345	5.1163	-5.2288
0.916	6.1769	-23.463	127.777
1.000	4.6851	-2.0844	5.4190

Deuterium-Helium Mixtures

Mole Fraction of Helium	$B \times 10^4$	$C \times 10^8$	$D \times 10^{12}$
0.000	5.9545	8.4750	-42.342
0.022	6.2468	3.6030	-23.684
0.267	6.3274	-1.7548	-3.8619
0.532	6.3464	-9.9300	+ 27.286
1.000	4.6851	-2.0844	5.4190

The data for pure deuterium and pure nitrogen used in this calculation were obtained from Michels'[1,4] work.

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