

RESULTS

The results are presented in Tables IV and V and in Figure 1. It should be remembered that the *B-W-R* equation gave a poor fit to the *P-V-T* points above 60 atm., so the tabulated and graphed results are probably not accurate much above 60 atm.

The internal consistency of the results was checked by using the relations:

$$\left(\frac{\partial \ln P}{\partial H}\right)_s = \frac{1}{P\bar{V}}$$
$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

The slopes measured on the appropriate graphs were compared with the quantities on the right hand side of the above equations. Agreement was within 0.4% at the 10 points that were checked. The error introduced into the entropy and enthalpy owing to the use of the *B-W-R* equation of state is estimated at about 1% in the enthalpy and 0.5% in the entropy. This error was estimated by observing the variation in *H* and *S* as the *B-W-R* equation was made to fit the experimental data more and more closely.

NOMENCLATURE

A, B, C, D = constants in the modified Antoine equation

A₀, B₀, C₀,

a, b, c, α, γ = constants in the Benedict-Webb-Rubin equation of state

H = enthalpy of real gas state, B.t.u./lb.

H^o = enthalpy of ideal gas state, B.t.u./lb.

ΔH_v = latent heat of vaporization, B.t.u./lb.

P = absolute pressure, atm.

P_c = critical pressure, atm.

R = gas constant for isopentane

S = entropy of real gas state, B.t.u./lb., ° R.

S^o = entropy of ideal gas state, B.t.u./lb., ° R.

t = temperature, ° F.

T = absolute temperature, ° R., = *t* ° F. + 459.688

V = specific vapor volume, cu. ft./lb.

V_g = specific volume of saturated vapor, cu. ft./lb.

V_l = specific volume of saturated liquid, cu. ft./lb.

z = compressibility factor, *pV/RT*

LITERATURE CITED

- (1) Altschul, M., *Z. Physik. Chem.* **11**, 577 (1893).
- (2) Benedict, Manson, Webb, G.B., Rubin, L.C., *Chem. Eng. Progr.* **47**, 419 (1951).
- (3) Brough, H.W., Schlinger, W.B., Sage, B.H., *Ind. Eng. Chem.* **43**, 2442 (1951).
- (4) Isaac, Reginald, Li, Kun, Canjar, L.N., *Ibid.*, **46**, 199 (1954).
- (5) Pawlewski, B., *Ber.* **15**, 2143 (1882).
- (6) Rossini, F.D., *et al.*, "Selected Values of Properties of Hydrocarbons and Related Compounds," Am. Petrol. Inst. Research Project 44, Table 32-2 (1.200) - t - E, 1960.
- (7) Rossini, F.D., *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Am. Petrol. Inst. Research Project 44, Table 1U-E, 1953.
- (8) *Ibid.*, Table 1d-E.
- (9) *Ibid.*, Table 1K-E.
- (10) Schumann, S.C., Aston, J.G., Sagenkahan, M., *J. Am. Chem. Soc.* **64**, 1039 (1942).
- (11) Silberberg, I.H., McKetta, J.H., Kobe, K.A., *J. CHEM. ENG. DATA* **4**, 323 (1959).
- (12) Vohra, S.P., Kobe, K.A., *Ibid.*, p. 329.
- (13) Washburn, E.W., *et al.*, "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. III, p. 244, McGraw-Hill, New York, 1928.
- (14) Willingham, C.B., Taylor, W.J., Pignocco, J.M., Rossini, F.D., *J. Res. Natl. Bur. Std.* **35**, 219 (1945).
- (15) Young, S., *Proc. Phys. Soc. London* **13**, 602 (1894).
- (16) Young, S., *Sci. Proc. Roy. Dublin Soc.* **12**, 374 (1909).

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Compressibility Factors for Helium-Nitrogen Mixtures

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Experimental compressibility factors for the helium-nitrogen system from -140° to 0° C. up to 500 atm. were determined by the Burnett method. A total of 1186 compressibility factors for the two pure components and six mixtures are reported. Derived thermodynamic properties of this system are compared with recent calorimetric determinations.

THIS PAPER presents compressibility factors for the helium-nitrogen system from 0° to 140° C. at pressures to 500 atm. Compressibility data for this system have been reported by a number of previous investigators, but no data in the present temperature range have been published. Pfefferle, Goff, and Miller (13), Kramer and Miller (6), and

Witonsky and Miller (17) have published data on the helium-nitrogen system at temperatures from 30° to 475° C. and at pressures to 100 atm. Other data have been collected by Ku (7) at 38.48° and 100° C. up to 295 atm. Miller, Brandt, and Stroud (10) report compressibility factors at 70° F. up to 4000 p.s.i.a. Such an abundance of data has been published for pure helium and pure nitrogen that it will be left to the writers of monographs to review these data. The present authors collected data for the pure components

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mainly for the sake of having an internally consistent set of data available for the helium-nitrogen system at low temperature.

EXPERIMENTAL METHOD

The compressibility factors presented in this paper were collected using the Burnett method (1). Temperature and pressure are the only variables measured when using this method. The temperature was measured with a Leeds and Northrup calibrated platinum resistance thermometer and a Type G1 Mueller Bridge to an accuracy approaching $\pm 0.01^\circ\text{C}$. of the International Temperature Scale. The pressure was measured with a set of two Ruska piston gages with ranges from 5 to 2400 p.s.i.g. and 30 to 12,000 p.s.i.g. The effective area of both gages was calibrated as a function of pressure by direct comparison to similar gages which had been calibrated by the National Bureau of Standards to $\pm 0.01\%$. Details of the original apparatus are given by

Mueller and coworkers (11, 12), and the apparatus, as modified for use in this study, is described by Canfield and coworkers (2, 3).

The gas mixtures were prepared from U. S. Bureau of Mines Grade A helium and Matheson's prepurified grade of nitrogen. The composition of the mixtures and the purity of the helium and nitrogen were determined by several mass spectrographic analyses and an experimental determination of molecular weights. The recommended compositions are presented in Table I. A complete discussion of the purity and composition analyses has been published (2).

RESULTS

Compressibility factors were determined for pure helium, pure nitrogen, and six helium-nitrogen mixtures whose compositions are given in Table I. In each case, isotherms were measured at 0° , -50° , -90° , -115° , -130° , and -140°C .

Table I. Experimental Compressibility Factors

$T = 273.15^\circ\text{K}$.		$T = 223.13^\circ\text{K}$.		$T = 183.15^\circ\text{K}$.		$T = 158.15^\circ\text{K}$.		$T = 143.14^\circ\text{K}$.		$T = 133.15^\circ\text{K}$.	
P , atm.	$Z =$ PV/RT	P , atm.	$Z =$ PV/RT	P , atm.	$Z =$ PV/RT	P , atm.	$Z =$ PV/RT	P , atm.	$Z =$ PV/RT	P , atm.	$Z =$ PV/RT
Helium											
520.329	1.26434	525.808	1.33180	524.037	1.40479	532.043	1.47822	523.063	1.51931	517.286	1.55392
320.158	1.16605	317.470	1.20508	309.939	1.24504	308.424	1.28388	299.261	1.30378	293.245	1.32100
202.661	1.10654	198.651	1.13029	191.587	1.15350	188.453	1.17559	181.534	1.18650	176.933	1.19551
130.621	1.06929	127.122	1.08430	121.698	1.09831	118.895	1.11158	113.979	1.11773	110.786	1.12291
85.1711	1.04541	82.5174	1.05518	78.6385	1.06387	76.5069	1.07207	73.1064	1.07571	70.9500	1.07884
55.9599	1.02991	54.0599	1.03639	51.3719	1.04186	49.8517	1.04705	47.5245	1.04930	46.0828	1.05123
36.9518	1.01974	35.6299	1.02410	33.7988	1.02760	32.7450	1.03087	31.1594	1.03234	30.1999	1.03354
24.4801	1.01300	23.5768	1.01600	22.3402	1.01825	21.6265	1.02052	20.5431	1.02130	19.9064	1.02208
16.2535	1.00852	15.6424	1.01065	14.8120	1.01211	14.3302	1.01360	13.5941	1.01414	13.1711	1.01457
10.8080	1.00561	10.3958	1.00703	9.8402	1.00801	9.5166	1.00897	9.0162	1.00932	8.7363	1.00963
7.1939	1.00370	6.9178	1.00472	6.5465	1.00536	6.3304	1.00604	5.9903	1.00628	5.8043	1.00638
4.7918	1.00250	4.6067	1.00314	4.3588	1.00352			3.9833	1.00409	3.8607	1.00427
3.1931	1.00172	3.0697	1.00220	2.9044	1.00247			2.6510	1.00279	2.5698	1.00292
417.210	1.21432	418.874	1.26752	425.300	1.33198	418.459	1.38074	420.118	1.42123	408.996	1.44275
260.389	1.13608	257.445	1.16762	256.520	1.20399	248.890	1.23055	246.570	1.25123	238.617	1.26240
166.317	1.08791	162.889	1.10743	160.478	1.12897	154.454	1.14443	151.866	1.15621	146.438	1.16210
107.822	1.05745	104.976	1.06993	102.710	1.08313	98.3806	1.09254	96.2733	1.09976	92.6383	1.10283
70.5727	1.03778	68.4524	1.04596	66.6869	1.05421	63.6882	1.06008	62.1042	1.06450	59.7069	1.06633
46.4846	1.02496	44.9765	1.03035	43.6992	1.03561	41.6580	1.03932	40.5190	1.04214	38.9375	1.04326
30.7451	1.01652	29.7008	1.02011	28.8090	1.02350	27.4319	1.02584	26.6296	1.02775	25.5836	1.02838
20.3897	1.01086	19.6779	1.01331	19.0676	1.01555	18.1431	1.01698	17.5840	1.01835	16.8922	1.01870
13.5483	1.00719	13.0675	1.00889	12.6531	1.01030	12.0364	1.01130	11.6464	1.01211	11.1890	1.01234
9.0131	1.00473	8.6894	1.00585	8.4106	1.00677	7.9997	1.00749	7.7301	1.00806	7.4271	1.00815
6.0013	1.00316	5.7847	1.00396	5.5975	1.00449	5.3236	1.00498	5.1375	1.00533	4.9370	1.00543
3.9983	1.00220	3.8531	1.00263					3.4177	1.00359	3.2847	1.00358
		2.5676	1.00173					2.2751	1.00252	2.1870	1.00252
Mixture A, 0.8768 Mole Fraction of Helium											
523.079	1.31512	528.125	1.38705	526.139	1.46444	526.612	1.53551	68.7748	1.06995	516.978	1.61702
316.473	1.19261	312.507	1.23027	303.816	1.26716	297.289	1.29873	44.7605	1.04489	283.330	1.32893
198.510	1.12147	193.603	1.14268	185.851	1.16180	179.851	1.17742	29.3805	1.02917	169.078	1.18951
127.299	1.07824	123.246	1.09069	117.533	1.10133	113.100	1.10971	19.3855	1.01898	105.629	1.11477
82.7612	1.05106	79.7798	1.05867	75.8035	1.06479	72.7329	1.06961	12.8360	1.01245	67.6977	1.07181
54.2783	1.03361	52.1824	1.03836	49.4823	1.04196	47.4035	1.04489	8.5175	1.00814	44.0342	1.04590
35.8003	1.02224	34.3591	1.02526	32.5461	1.02740	31.1525	1.02926	5.6610	1.00545	28.8985	1.02977
23.7005	1.01476	22.7217	1.01672	21.5098	1.01793	20.5792	1.01915	3.7659	1.00369	19.0695	1.01947
15.7286	1.00981	15.0678	1.01108	14.2612	1.01178	13.6411	1.01261	2.5069	1.00259	12.6276	1.01281
10.4549	1.00651	10.0104	1.00731	9.4742	1.00768	9.0623	1.00835			8.3807	1.00847
6.9571	1.00433	6.6597	1.00495	6.3039	1.00518	6.0298	1.00567			5.5705	1.00566
4.6331	1.00292	4.4332	1.00320	4.1977	1.00344					3.7063	1.00387
		2.9533	1.00219	2.7972	1.00243					2.4678	1.00282
425.213	1.25710	428.435	1.31515	411.813	1.36311	412.702	1.41846	402.427	1.44622	400.830	1.47442
261.602	1.15933	258.848	1.19090	244.734	1.21402	240.832	1.24030	232.069	1.25094	228.779	1.26211
165.767	1.10136	162.358	1.11972	152.197	1.13163	148.411	1.14546	142.171	1.14968	139.514	1.15450
106.972	1.06561	104.149	1.07679	97.1828	1.08316	94.3180	1.09105	90.0695	1.09277	88.2067	1.09499
69.8233	1.04291	67.7383	1.04996	63.0462	1.05338	61.0357	1.05826	58.1745	1.05897	56.9204	1.06005
45.9118	1.02826	44.4421	1.03277	41.3063	1.03461	39.9326	1.03777	38.0065	1.03806	37.1767	1.03870
30.3330	1.01866	29.3236	1.02167	27.2312	1.02251	26.3052	1.02469	25.0075	1.02483	24.4584	1.02521
20.1034	1.01234	19.4178	1.01432	18.0284	1.01485	17.4042	1.01621	16.5283	1.01633	16.1652	1.01656
13.3515	1.00817	12.8891	1.00946	11.9638	1.00963	11.5476	1.01065	10.9546	1.01071	10.7153	1.01096
8.8800	1.00546	8.5685	1.00614	7.9569	1.00666	7.6771	1.00714	7.2748	1.00712	7.1164	1.00730
5.9110	1.00361	5.7033	1.00410	5.2956	1.00441	5.1097	1.00478	4.8371	1.00477	4.7317	1.00484
3.9373	1.00241	3.7989	1.00275	3.5275	1.00303			3.2186	1.00319	3.1491	1.00331
2.6241	1.00180	2.5317	1.00193					2.1428	1.00214		

(Continued on page 94)

With the exception of mixtures *C* and *F* at -140°C ., two series of Burnett expansions were made in order to define each isotherm. The first series was initiated at a pressure slightly in excess of 500 atm., and the second series was initiated at a pressure approximately equal to the average of the first two pressures of the first series. As a result, there were usually 24 to 26 points available for each of the 48 isotherms. Table I presents 1186 compressibility factors which define the volumetric behavior of the helium-nitrogen system from 0° to -140°C . up to 500 atm.

DISCUSSION OF RESULTS

The following methods are commonly used when attempting to establish the validity of experimental compressibility data: direct comparison with the results obtained by other investigators; fitting the data to a smooth curve, either graphically or by least squares; performing an error analysis on the experimental method; and comparison of derived thermodynamic data with the same data obtained by more direct methods. The reliability of the present results has been established by all four methods.

Because no other data for helium-nitrogen mixtures have been published in the present temperature range, comparison of results with other work is restricted to the pure components. For nitrogen at 0°C ., the average difference in compressibility factors of comparisons made at 50, 100, and 200 atm. between this work and Michels and coworkers (9) was $+0.12\%$, between this work and Holborn and Otto (5) was $+0.05\%$, and between this work and Friedman (4) was $+0.02\%$. At 0°C . and 400 atm., the present value for nitrogen is 0.2% higher than Michels and coworkers (9). For nitrogen at -50°C ., the average difference of comparisons made at 50, 100, 200, and 400 atm. between this work and Michels and others (9) was $+0.17\%$ with a maximum difference of 0.48% occurring at 50 atm. For helium at 0°C . and 25 atm., the present compressibility factor is 0.03% lower than the value obtained by White and coworkers (16), but 0.03% higher than the value given by Schneider (15). For comparisons made at 25, 50, 100, and 200 atm., the present values are an average of 0.05% higher than the results of Holborn and Otto (5) at 0°C . and at -50°C . for the first three pressures. On the basis of the above comparisons, and also more comprehensive comparisons given by Canfield (2), it was concluded that the present compressibility factors tend to be slightly higher than previous measurements. In a prior publication (3), the same trend was observed in the second virial coefficients derived from the present data.

The compressibility factors for both of the pure components and all of the mixtures have been fitted by least squares to equations of state. Canfield (2) gives the coefficients for the Leiden virial equation for each mixture at each of the six temperatures. Using equations which varied from third degree in density for helium to seventh degree for nitrogen, each isotherm was fitted to 500 atm. An indication of the smoothness or precision of the data was that the average of the absolute value of the difference between the experimental compressibility factors and those calculated from the fitted virial equations was less than 0.01% . More recently, Pfenning, Canfield, and Kobayashi (14) fitted each mixture to a modified form of the Benedict-Webb-Rubin equation of state. Included in each fit were some high temperature data of Kramer and Miller (6) and Miller, Brandt, and Stroud (10). The average deviation in the compressibility factors ranged from 2.9×10^{-4} for helium to 9.1×10^{-4} for nitrogen.

To establish the limits of error in the present results, an error analysis was performed on the Burnett method. The details of this analysis are given elsewhere (3); only the results will be restated here. At the higher limit of error, it was estimated that for nitrogen at -140°C . and 528 atm., the maximum error in the compressibility factor, due to errors in the experimental method, was $\pm 0.15\%$. At the lower limit, the maximum error for helium at 0°C . and 3.2 atm. was estimated to be $\pm 0.02\%$.

The thermodynamic properties of the helium-nitrogen system have been calculated between -220° and 100°F . to 7500 p.s.i.a. using principally the present compressibility factors (14). Mage (8) has experimentally measured the isothermal effect of pressure on enthalpy using a flow calorimeter, and he presents extensive comparisons between his work and similar values calculated from the present data. In summary, differences usually on the order of 1% were found for the isothermal effect of pressure on enthalpy (8). At the lower temperature limits of the present data, differences up to 4% were noted. Because Mage's estimated error was on the order of 0.5% , it is difficult to assign the usually observed difference of 1% to error in one work or the other.

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NOMENCLATURE

- P = absolute pressure
- R = gas constant
- T = absolute temperature, $0^{\circ}\text{C} = 273.15^{\circ}\text{K}$.
- V = volume per mole
- Z = compressibility factor

LITERATURE CITED

- (1) Burnett, E.S., *J. Appl. Mech., Trans. ASME* **58**, A136 (1936).
- (2) Canfield, F.B., Ph.D. thesis, Rice University, Houston, Tex., 1962.
- (3) Canfield, F.B., Leland, T.W., Kobayashi, R., *Adv. Cryo. Eng.* **8**, 146 (1963).
- (4) Friedman, A.S., Ph.D. thesis, Ohio State University, Columbus, Ohio, 1951.
- (5) Holborn, L., Otto, J., *Z. Phys.* **33**, 1 (1925).
- (6) Kramer, G.M., Miller, J.G., *J. Phys. Chem.* **61**, 785 (1957).
- (7) Ku, P.S., Ph.D. dissertation, Yale University, New Haven, Conn., 1960.
- (8) Mage, D.T., Ph.D. thesis, University of Michigan, Ann Arbor, Mich., 1964.
- (9) Michels, A., Lunbeck, R.J., Wolkers, G.J., *Physica* **17**, 801 (1951).
- (10) Miller, J.E., Brandt, L.W., Stroud, L., *U. S. Bur. Mines, Rept. Invest.* **5845**, 1961.
- (11) Mueller, W.H., Ph.D. thesis, Rice Institute, Houston, Tex., 1959.
- (12) Mueller, W.H., Leland, T.W., Kobayashi, R., *A.I.Ch.E. J.* **7**, 267 (1961).
- (13) Pfefferle, W.C., Goff, J.A., Miller, J.G., *J. Chem. Phys.* **23**, 509 (1955).
- (14) Pfenning, D.B., Canfield, F.B., Kobayashi, R., *J. Chem. Eng. Data* **10**, 9 (1965).
- (15) Schneider, W.G., *Can. J. Res.* **27B**, 339 (1949).
- (16) White, D., Rubin, T., Camky, P., Johnston, H.L., *J. Phys. Chem.* **64**, 1607 (1960).
- (17) Witonsky, R.J., Miller, J.G., *J. Am. Chem. Soc.* **85**, 282 (1963).

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