Pressure-Volume-Temperature Data for Neon from 80–130° K and Pressures to 2000 Atmospheres

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The gas expansion method has been used in an experimental study of the equation of state of neon, at temperatures from 80–130° K, and at pressures to 2000 atm. The isotherms have been fitted to polynomial equations, and these have been used to calculate values of the dimensionless ratio, Z ($Z = PV/RT$), and isothermal compressibility at regular intervals of pressure. The results are compared to published data at pressures below 300 atm.

Experimental studies of the equation of state of neon at low temperatures have been reported by Crommelin et al. (*1*), Holborn and Otto (*4, 5*), Sullivan and Sonntag (*13*), and Gibbons (*2*). McCarty and Stewart (*8*) have fitted selected data for neon to an equation of state of the Strobridge (*12*) type, which they have used to calculate certain thermodynamic properties of neon over the temperature range 25–300° K and pressures up to 200 atm.

In this paper, experimental equation of state data are reported for neon at five temperatures between 80° and 130° K, and pressures from 75 to 2000 atm. These data have been obtained by the method of gas expansion, in which a small quantity of fluid is confined in a cell of known volume at the desired pressure and temperature, and then expanded into a large volume at room temperature. Precise measurement of pressure and temperature in this volume allows the mass of the fluid to be calculated from the known equation of state at low pressures.

EXPERIMENTAL

A schematic diagram of the gas expansion apparatus is shown in Figure 1. It is similar to one used in earlier density measurements for liquid argon (*10*) and liquid nitrogen (*11*).

The procedure followed to obtain each experimental point is as follows: With valves 3 and 4 closed, neon gas from the cylinder, *K*, is admitted to the high pressure cell, *C* (volume about 3.6 cc), and the pressure is boosted to the desired value by the two-stage diaphragm compressor, *D*, and the intensifier, *I*, which is driven by the hydraulic pump, *H*. Neon also enters the "dummy line," *L*, which is sealed at its lower end and is equal in volume to line *N* connected to cell *C*. These lines are 0.062 in. o.d. × 0.01 in. i.d. stainless steel, with a total internal volume of about 0.06 cc, about 1.7% of the cell volume. The manganin gauge, *M*, and Wheatstone bridge, *R*, provide rapid pressure measurement for setting the desired pressure, and final measurement is made with the Ruska dead weight gauge, *W*. A differential pressure indicator, *P*, separates the gas system from the oil in the dead weight gauge. Pressures measured by this system are accurate to within ±0.01%. Temperatures in the cryostat, *A*, are controlled to within ±0.01° K and are measured by an NBS-calibrated platinum resistance thermometer, *T*, used in conjunction with a Mueller bridge and electronic null detector. Temperatures reported here are accurate to within ±0.01° K.

While the cell and connecting lines are being pressurized, expansion volumes V_1 and V_2 are evacuated and the residual pressure is measured by the low-pressure gauge, *G*. This gauge is a Texas Instruments precision pressure gauge with a fused quartz Bourdon tube, having a range of 1–1.66 atm and an accuracy of ±0.01%. V_1 and V_2 are in a continuously stirred water bath, *B*, maintained at 25° ± 0.01° C.

After recording the temperature and pressure of the neon in *C*, valves 1, 2, and 5 are closed, and the connecting lines between valves 1–4 are evacuated through 7. Valves 6 and 7 are closed and 1–4 are opened, allowing the neon from the dummy line, *L*, and the cell, *C*, to expand into V_2 and V_1, respectively. The final pressures in these volumes (about 1.5 atm or less) are measured by *G*, and the number of moles of gas in each volume is calculated from the first two terms of the virial equation for neon at 25° C. Quantities of gas remaining in the connecting lines and the cell, whose volumes and temperatures are known, are also calculated. These "noxious volumes" amount to about 0.1% of the total expansion volume in each case, so errors associated with these corrections are small.

The number of moles of gas in V_2 and its connecting lines is subtracted from that in V_1 and its connecting lines (including *C*) to give the number of moles expanded from *C*. This value, combined with the known volume of *C* (corrected for temperature and end pressure effects), gives the density of the neon at the pressure and temperature measured before expansion—in other words, one *PVT* point is obtained from a single expansion. The method is not so cumbersome as it may seem. The apparatus can be set in operation in about 1 hr, and *PVT* points can be measured at a rate of one every 20–30 min.

Research grade neon, supplied by the Linde Division, Union Carbide Corp., was used in these experiments. A trace analysis by the method of gas chromatography showed that the purity of this neon exceeded 99.97%.

Extensive tests of the apparatus indicate that the measured densities are reproducible to within a few parts in ten thousand, in agreement with estimates made by standard methods of error analysis. Since errors in temperature and pressure measurements are small, the principal

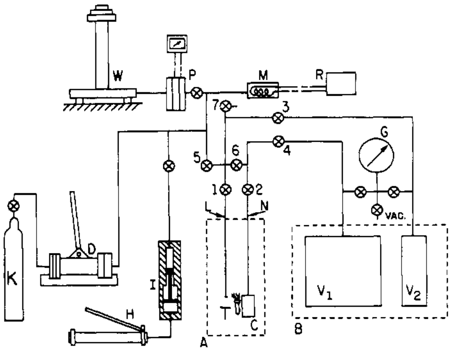

Figure 1. Diagram of the apparatus

source of absolute error in this apparatus—as in nearly all methods commonly used for *PVT* measurement (*6*)—is the uncertainty in the volume of the system. The expansion volumes were calibrated by careful weighing of the containers, first when evacuated and then after filling with distilled, deaerated water at 25° C. Volumes of the lines connected to the expansion volumes V_1 and V_2 were measured by cross expansion of gas at about 1 atm pressure. These volumes are less than 0.1% of the expansion volumes in each case. The volume of the high pressure cell, *C*, was determined by differential weighing with mercury, and changes in volume due to thermal and pressure effects were calculated by standard methods. The errors in the original volume determinations are estimated to be ±0.05%, but the error in estimating the volume change due to thermal contraction of the cell between room temperature and 100° K is about the same order of magnitude. A total absolute error of 0.1–0.2% is indicated for the calibration of the apparatus from first principles.

To reduce the probable absolute error, it was decided to check the original calibration of the apparatus by measuring the densities of saturated liquid argon,and liquid nitrogen at several temperatures near 100° K, and comparing these with published values. After studying data from several sources, this author concluded that the most accurate values available for the saturation densities of argon and nitrogen are as follows: for argon, the data of Mathias et al. (*7*), reproduced to within a few parts in ten thousand by Terry et al. (*14*) and by Michels et al. (*9*); and, for nitrogen, the data of Terry et al. (*14*), reproduced to within a few parts in ten thousand by Goldman and Scrase (*3*).

The apparatus described here was used to measure liquid argon and nitrogen densities at several pressures just above saturation and at temperatures near 100° K. The resulting density vs. pressure curves were then extrapolated to the saturation pressure to obtain the saturated liquid densities. (The error involved in this extrapolation is less than 0.01%.) The resulting values showed a systematic deviation of about 0.25% from the "best" values described above. A correction to the volume of the cell, *C* (considered to be the most probable source of error), was then made to bring these values into agreement. In other words, the entire apparatus was recalibrated at a temperature of 100° K, using saturated argon and nitrogen as standards. The absolute accuracy of the data reported here is estimated to be better than 0.1%.

RESULTS AND DISCUSSION

Table I gives values of pressure and the dimensionless ratio $Z = PV/RT$ for each of the five experimental isotherms. The data for each isotherm have been fitted to a polynomial in pressure by the method of least squares. The coefficients for each isotherm, and the maximum and standard deviations of the experimental values from the polynomials, are shown in Table II. These polynomials describe the isotherms only within the range of pressures covered in the experiment. Since the low pressure range is not included, the constant, *A*, is not equal to 1. Calculated values of *Z* and β (the isothermal compressibility), at pressure intervals of 100 atm, are shown in Table III. Values of β are not listed for extreme values of *P* because they are subject to errors arising from distortion of the fitted curves near the end points.

A measure of the smoothness of the experimental isotherms is shown by a plot of calculated values of β at 90° K, in Figure 2. Further evidence of internal smoothness is shown in Figure 3, in which calculated values of β are cross-plotted against temperature at four pressures, from 300–1700 atm.

Table IV gives a representative comparison of values of *Z*, from Table III, with the published results of other investigators. Comparison with the results of Holborn and Otto, possible only in the narrow pressure range from 75

Table I. Experimental Data
($Z = PV/RT$)

T = 80° K		T = 90° K		T = 100° K		T = 110° K		T = 130° K	
P, atm	*Z*	*P*, atm	*Z*	*P*, atm	*Z*	*P*, atm	*Z*	*P*, atm	*Z*
76.365	0.90114	73.055	0.96024	75.457	0.98922	74.549	1.00851	73.597	1.02887
175.026	0.99896	141.034	0.99024	141.306	1.02397	141.101	1.04660	143.072	1.07315
243.012	1.12482	175.024	1.02819	171.012	1.05236	175.023	1.07688	175.022	1.09910
277.001	1.19589	243.007	1.12985	209.013	1.09705	209.015	1.11277	212.141	1.13336
310.992	1.26951	276.998	1.18876	209.013	1.09705	243.005	1.15364	243.279	1.16428
344.985	1.34470	310.988	1.25092	243.955	1.14461	276.994	1.19753	276.995	1.19993
378.977	1.42039	344.984	1.31426	277.535	1.19388	310.988	1.24385	310.989	1.23798
412.970	1.49618	378.974	1.37866	310.984	1.24590	344.979	1.29210	344.981	1.27743
446.964	1.57209	412.970	1.44417	344.977	1.30104	378.972	1.34193	412.976	1.35862
480.959	1.64781	446.960	1.51016	378.969	1.35725	412.967	1.39254	446.959	1.40015
548.948	1.79773	480.956	1.57569	412.960	1.41425	446.960	1.44376	548.945	1.52749
616.941	1.94616	514.955	1.64108	446.954	1.47168	480.955	1.49519	582.940	1.57071
684.935	2.09283	548.941	1.70667	480.949	1.52974	514.950	1.54696	616.936	1.61432
752.931	2.23763	582.936	1.77239	514.943	1.58802	548.946	1.59896	650.931	1.65839
820.926	2.38062	616.933	1.83714	548.939	1.64641	582.941	1.65107	684.926	1.70164
888.927	2.52138	650.930	1.90196	582.934	1.70455	616.938	1.70330	752.937	1.78841
956.927	2.66143	684.926	1.96626	616.931	1.76259	650.935	1.75576	820.926	1.87483
956.943	2.66128	752.923	2.09425	650.928	1.82034	684.932	1.80761	888.924	1.96009
1024.946	2.79955	820.918	2.22073	684.927	1.87800	752.928	1.91168	956.923	2.04505
1092.950	2.93634	888.919	2.34582	752.923	1.99251	820.922	2.01461	1024.932	2.13013
1228.967	3.20494	956.919	2.46965	820.917	2.10623	888.925	2.11612	1092.946	2.21409
1364.993	3.46904	1024.925	2.59200	888.917	2.21883	956.925	2.21710	1228.973	2.38032
1569.052	3.85671	1092.931	2.71349	956.924	2.33030	1024.929	2.31744	1365.008	2.54366
1773.124	4.23611	1228.950	2.95251	1024.925	2.44045	1092.935	2.41722	1569.063	2.78481
		1364.979	3.18719	1092.929	2.54983	1228.953	2.61367	1773.135	3.02164
		1569.039	3.53252	1228.947	2.76554	1364.981	2.80689	2045.262	3.33588
		1773.115	3.86967	1364.980	2.97811	1569.041	3.09143		
		2011.231	4.25568	1569.039	3.29010	1773.116	3.37001		
				1773.115	3.59627	2045.249	3.73507		
				2045.247	3.99717				

Table II. Coefficients for Neon Isotherms

$(Z = A + BP + CP^2 + DP^3 + EP^4 + FP^5 + GP^6 + HP^7 + IP^8 + JP^9 + KP^{10})$

	Temperature, ° K				
	80°	90°	100°	110°	130°
Maximum deviation	0.388×10^{-3}	0.371×10^{-3}	0.327×10^{-3}	0.391×10^{-3}	0.517×10^{-3}
Standard deviation	0.102×10^{-3}	0.098×10^{-3}	0.089×10^{-3}	0.150×10^{-3}	0.194×10^{-3}
A	0.983225	1.04852	1.02477	1.01592	1.01003
$B \times 10^{-4}$	−25.5356	−24.7680	−11.9687	−5.51171	0.0827598
$C \times 10^{-5}$	2.38491	2.11535	1.12765	0.685546	0.381871
$D \times 10^{-8}$	−6.70334	−5.89678	−2.40663	−1.10273	−0.645753
$E \times 10^{-11}$	11.8679	10.6380	3.02046	0.585743	0.601496
$F \times 10^{-14}$	−13.8895	−12.9732	−2.08344	0.978473	−0.121170
$G \times 10^{-17}$	10.8345	10.7772	0.411159	−2.22031	−0.416927
$H \times 10^{-20}$	−5.53135	−6.00484	0.493488	2.01589	0.537341
$I \times 10^{-23}$	1.75542	2.14493	−0.425900	−0.991489	−0.305891
$J \times 10^{-27}$	−3.08854	−4.43397	1.37049	2.58557	0.871834
$K \times 10^{-31}$	2.23443	4.02882	−1.66046	−2.80475	−1.00664

Table III. Calculated Values of Z and β at Even Values of Pressure

	T = 80° K		T = 90° K		T = 100° K		T = 110° K		T = 130° K	
P, atm	Z	$\beta \times 10^3$ atm^{-1}	Z	$\beta \times 10^3$ atm^{-1}	Z	$\beta \times 10^3$ atm^{-1}	Z	$\beta \times 10^3$ atm^{-1}	Z	$\beta \times 10^3$ atm^{-1}
100	0.90991	. . .	0.96285	. . .	0.99660	. . .	1.01899	. . .	1.04318	. . .
200	1.04192	3.259	1.06243	3.629	1.08590	3.862	1.10300	4.004	1.12181	4.164
300	1.24544	1.587	1.23035	1.847	1.22866	2.057	1.22867	2.213	1.22557	2.421
400	1.46728	0.976	1.41928	1.144	1.39239	1.291	1.37296	1.414	1.34257	1.598
500	1.68999	0.691	1.61247	0.802	1.56257	0.905	1.52426	0.998	1.46622	1.143
600	1.90939	0.527	1.80479	0.607	1.73356	0.682	1.67750	0.752	1.59292	0.866
700	2.12494	0.423	1.99479	0.483	1.90343	0.541	1.83063	0.594	1.72061	0.686
800	2.33666	0.352	2.18194	0.399	2.07142	0.444	1.98264	0.487	1.84800	0.563
900	2.54461	0.301	2.36611	0.339	2.23708	0.376	2.13289	0.411	1.97429	0.475
1000	2.74900	0.262	2.54737	0.293	2.40025	0.325	2.28106	0.355	2.09916	0.409
1100	2.95014	0.232	2.72591	0.259	2.56105	0.285	2.42723	0.310	2.22261	0.357
1200	3.14832	0.208	2.90194	0.231	2.71986	0.252	2.57175	0.274	2.34482	0.315
1300	3.34360	0.189	3.07558	0.208	2.87698	0.226	2.71491	0.244	2.46588	0.281
1400	3.53604	0.174	3.24697	0.190	3.03234	0.205	2.85660	0.221	2.58570	0.254
1500	3.72621	0.158	3.41641	0.173	3.18561	0.189	2.99628	0.204	2.70399	0.232
1600	3.91513	0.143	3.58413	0.159	3.33662	0.175	3.13364	0.189	2.82070	0.213
1700	4.10281	0.135	3.74997	0.149	3.48632	0.158	3.26971	0.171	2.93654	0.193
1800	. . .	. . .	3.91313	. . .	3.63703	. . .	3.40728	. . .	3.05317	. . .
2000	. . .	. . .	4.23622	. . .	3.93900	. . .	3.68458	. . .	3.28835	. . .

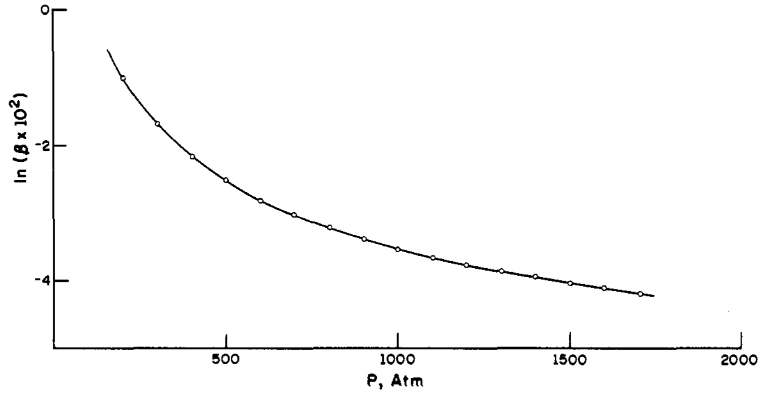

Figure 2. Plot of β vs. P at 90° K (from Table III)

to 100 atm, shows that values of Z reported here are systematically higher than those of Holborn and Otto by about 0.4%. In the pressure range 100–300 atm, the reported values of Z are lower than those of Sullivan and Sonntag (except for the point at 80° K and 200 atm) by an average of about 0.4%. The data of Crommelin et al. (*1*) and of Gibbons (*2*) lie outside the range of this experiment; however, it is to be noted that Gibbons' data at 70° K differ from those of Sullivan and Sonntag by as much as 2%. The calculated values of McCarty and Stewart, at 200 atm, are lower than those reported here by about 1%.

Differences of a few tenths of a percent are not uncommon between equation-of-state measurements from independent experiments, especially where cryogenic fluids are concerned (*2, 3, 6, 10, 14*), even though these differences exceed the precision of each experiment by about an order of magnitude. The very nature of the experiment makes it difficult

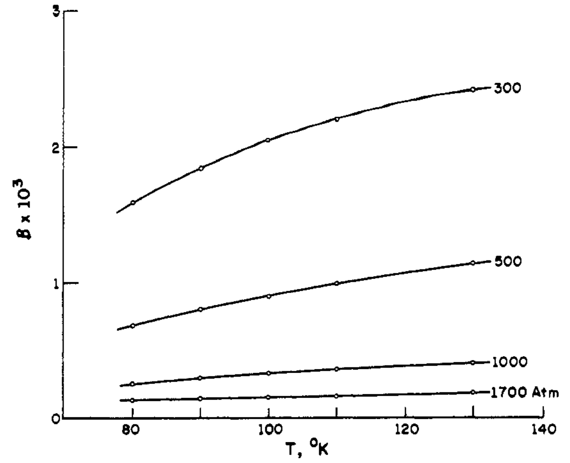

Figure 3. Calculated values of β (Table III) cross-plotted as isobars to show internal consistency of data

Table IV. Comparison of Selected Values of Z with Published Data

	Temperature		
	80° K	100° K	120° K
P = 100 atm			
This work	0.9099	0.9966	1.0340
Holborn and Otto (*4, 5*)	. . .	0.994	1.030
Sullivan and Sonntag (*13*)	0.9165	1.0000	1.0352
McCarty and Stewart (*8*)	0.905	0.992	1.027
P = 200 atm			
This work	1.0419	1.0859	1.1160
Sullivan and Sonntag (*13*)	1.0391	1.0907	1.1181
McCarty and Stewart (*8*)	1.031	1.077	1.102
P = 300 atm			
This work	1.2454	1.2287	1.2275
Sullivan and Sonntag (*13*)	1.2465	1.2353	1.2323

to achieve high absolute accuracy (*6*). It is difficult to suggest specific causes for the differences in the results reported here and those of other investigators. Holborn and Otto used a method similar to that used here, while Sullivan and Sonntag used a Burnett apparatus which does not require volume determination for any part of the equipment. It should be emphasized again that the absolute accuracy of the results reported here is expected to be equal to that of the argon and nitrogen data used in calibrating the apparatus. This calibration procedure is simple, and its advantage is obvious. If other investigators adopted argon (or another appropriate standard) as a low-temperature calibrating medium, the problem of small systematic differences between the results of independent experiments could certainly be reduced, if not eliminated.

Small systematic errors do not impair the usefulness of a given set of data for calculating thermodynamic properties, as long as the data are internally smooth and consistent. The derivatives which appear most often in equations used to calculate thermodynamic properties are $(\partial V/\partial P)_T$, $(\partial V/\partial T)_P$, and $(\partial^2 V/\partial T^2)_P$. If reliable values of these derivatives are to be obtained, experimental data should not scatter from fitted curves by more than a few parts in 10,000. If an equation of state is to be fitted to data from several different experiments, however, then systematic differences must be smoothed out, either before or during the curve-fitting process. If this is not done, artificial distortions will appear in the surface represented by the equation, resulting in erroneous values for calculated thermodynamic properties.

LITERATURE CITED

(1) Crommelin, C. A., Martinez, J. P., Onnes, H. K., *Commun. Phys. Lab. Univ. Leiden*, No. 154a (1919).
(2) Gibbons, R. M., *Cryogenics*, **9**, 251 (1969).
(3) Goldman, K., Scrase, N. G., *Physica*, **45**, 1 (1969).
(4) Holborn, L., Otto, J., *Z. Physik*, **33**, 1 (1925).
(5) Holborn, L., Otto, J., *ibid.*, **38**, 359 (1926).
(6) Levelt-Sengers, J. M. H., "Physics of High Pressure and the Condensed Phase," Chap. 3, North Holland, Amsterdam, the Netherlands, 1965.
(7) Mathias, E., Onnes, H. K., Crommelin, C. A., *Leiden Commun.*, 131A (1912).
(8) McCarty, R. D., Stewart, R. B., "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," p 84, The American Society of Mechanical Engineers, New York, N. Y., 1965.
(9) Michels, A., Levelt, J. M. H., DeGraaff, H., *Physica*, **24**, 659 (1958).
(10) Streett, W. B., Staveley, L. A. K., "Advances in Cryogenic Engineering," Vol 13, p 363, Plenum, New York, N. Y., 1968.
(11) Streett, W. B., Staveley, L. A. K., *J. Chem. Phys.*, **50**, 2302 (1969).
(12) Strobridge, T. R., *Nat. Bur. Stand. Tech. Note No. 129*, 1962.
(13) Sullivan, J. A., Sonntag, R. E., "Advances in Cryogenic Engineering," Vol 12, p 706, Plenum, New York, N. Y., 1967.
(14) Terry, M. J., Lynch, J. T., Bunclark, M., Mansell, K. R., Staveley, L. A. K., *J. Chem. Thermodynamics*, 1, 413 (1969).

RECEIVED for review March 27, 1970. Accepted March 11, 1971. This work was supported by a grant from the U. S. Army Research Office, Durham, N. C.