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Measurement of the Compressibility and Sound Velocity of Neon up to 1 GPa[1]

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The density of neon has been determined at 298.15 K as a function of pressure from 80 MPa to 1 GPa. The precision of the measurements is 0.03 %, while the estimated absolute accuracy is between 0.05 and 0.09 %. The sound velocity has been measured between 98 and 298 K with intervals of 25 K and at pressures up to 1 GPa, with an accuracy generally better than 0.06 %. The adiabatic compressibility and the ratio of the specific heats are calculated by combining *pVT* with velocity-of-sound data at 298 K. Several equations of state are fitted to the density data at 298.15 K.

KEY WORDS: compressibility; equation of state; high pressure; neon; *pVT*; sound velocity.

1. INTRODUCTION

At our institute, mixtures containing neon are studied under high pressure. The interpretation requires a good knowledge of the behavior of the pure components under these conditions. However, the number of investigations of the thermodynamic properties of neon under pressure is very limited [1–6]. Therefore, we have studied the *pVT* behavior and the sound velocity in the pressure range up to 1 GPa. The combined measurement of the compressibility and the sound velocity of neon as a function of pressure has been used to determine other important properties such as the adiabatic compressibility and the ratio of specific heats.

The availability of accurate density and velocity-of-sound data at higher pressures is a challenge to test empirical and semiempirical equations of state. Moreover, there is also an increasing demand for these

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data, both from the field of computer experiments [molecular dynamics (MD) and Monte Carlo simulations (MC)] and from statistical mechanical perturbation and integral equation theories.

2. EXPERIMENTAL

The method and the equipment for the determination of the compressibility isotherms of gases up to 1 GPa have been described previously [7]. The method involves the expansion of the gas from an initially pressurized vessel of volume V_A into an evacuated vessel V_B of nearly the same volume. Two types of measuring methods are used: total expansions and stepwise expansion runs. In the case of a total expansion, the pressure after the expansion is equal in both vessels. In a stepwise expansion run the gas is partly expanded. The pressure in V_B increases with each expansion, while the pressure in V_A decreases, and after the last expansion, the pressure in both vessels becomes equal. After each expansion, the pressure is recorded in both vessels, on the high-pressure side (vessel V_A) by a manganin gauge and on the low-pressure side (vessel V_B) with a Michels' pressure balance via a differential pressure meter. The density on the high-pressure side is calculated from the density on the low-pressure side, which in its turn is obtained from the literature. We used the results of Michels et al. [1], which were obtained with a piezometer in the temperature range from 273 to 423 K and at pressures up to almost 300 MPa, with an accuracy of the compressibility factor of about 0.01 %. These data were also used to determine the volume ratio V_B/V_A of the pressure vessels. The pressure distortion coefficients β_A and β_B [$\beta \equiv (1/V)(\partial V/\partial p)_T$] of the pressure vessels were determined previously by calibration with argon up to 280 MPa.

The velocity of sound was measured with the well-known phase comparison pulse-echo technique, operating with one X-cut quartz transducer and two reflectors at unequal distances, having a ratio of 3:2. Two successive longitudinal sound-wave pulses of about 6 μs are introduced in the pressurized fluid by applying two electrical pulses to the transducer, produced by a synthesiser, a pulse former, and a timer. At certain frequencies, the so-called null frequencies, the phase difference between the echo of the first pulse, reflected by the distant reflector, and the echo from the second pulse, reflected by the near reflector, equals $(2n+1)\pi$, where the integer n is the order of interference. The two echoes cancel each other, provided that the amplitudes are equal. From these null frequencies, one can calculate very accurately the difference in transit time of the sound pulses necessary to cover the difference in path lengths. The systematic error in the sound velocity in this method is estimated to be less than

0.02% and random errors are caused mainly by the uncertainty in the pressure measurement. The null frequencies range from 9.5 to 10.5 MHz. Details of the equipment and the metod can be found elsewhere [8].

The gas under investigation was purchased from L'Air Liquide and was stated to be 99.99% pure.

3. RESULTS

In the pressure range from 80 MPa to 1 GPa, three runs of stepwise expansions, consisting of, respectively, 3, 17, and 7 steps and 19 total expansions, were performed at 298.15 K. These 46 data points, together with 10 points between 80 and 235 MPa of Michels et al. [1], were fitted to a polynomial of the type

$$p = \sum_{i=0}^{5} a_i \rho^i \tag{1}$$

The standard deviation is found to be 0.03%. By combining the random and the systematic error as given in Ref. 7, the total accuracy of the data is

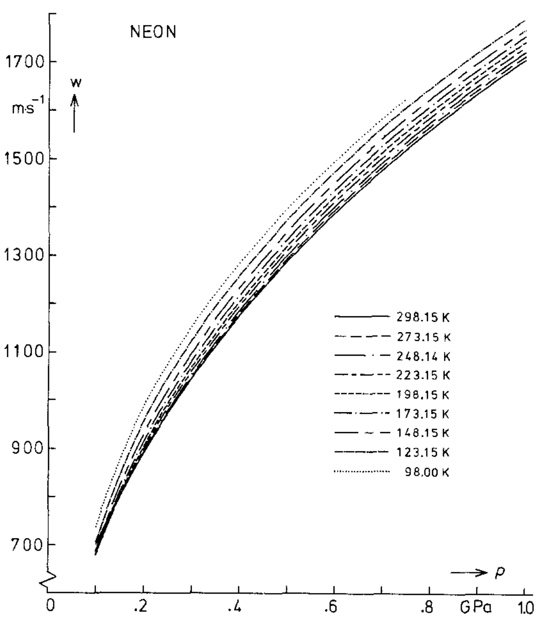

Fig. 1. Sound velocity in neon as a function of pressure at several temperatures.

found to be 0.05% at 400 MPa, 0.06% at 700 MPa, and about 0.09% at 1 GPa.

The sound velocity measurements were carried out in steps of 50 MPa from 1 GPa down to 250 MPa and in steps of 25 MPa below 250 MPa, in the temperature range from 98 to 298 K. In Fig. 1 the isotherms are given, whereas in Fig. 2 the isobars are shown. The values of the sound velocity at round pressures along the isotherms were obtained by fitting the experimental data to polynomials: $p = \sum_{i=0}^{n} a_i w^i$, where $n = 4$ for the isotherms between 298 and 223 K, $n = 5$ in the range 173–148 K, and $n = 6$ below 148 K. The standard deviations of the sound velocity isotherms, due to random errors, range from 0.02 to 0.04%. As the systematic errors are estimated to be about 0.02%, the overall accuracy will generally be better than 0.06%. Due to the mismatch of the acoustic impedance between the quartz transducer and the sample, the lowest pressure at which the sound velocities were determined was 97 MPa. The isotherm of 98.15 K terminates at 760 MPa, obviously below the melting pressure (819 MPa) [11]. From the density (ρ) and the sound velocity (w) one obtains the adiabatic compressibility χ_S ($\equiv 1/\rho w^2$). The polynomial expression, Eq. (1), was used to calculate the derivative of the density with respect to pressure, in order to obtain the isothermal compressibility χ_T [$\equiv (1/\rho)(\partial\rho/\partial p)_T$]. The ratio of χ_T over χ_S provides γ, the ratio of specific heats ($\gamma = \chi_T/\chi_S =$

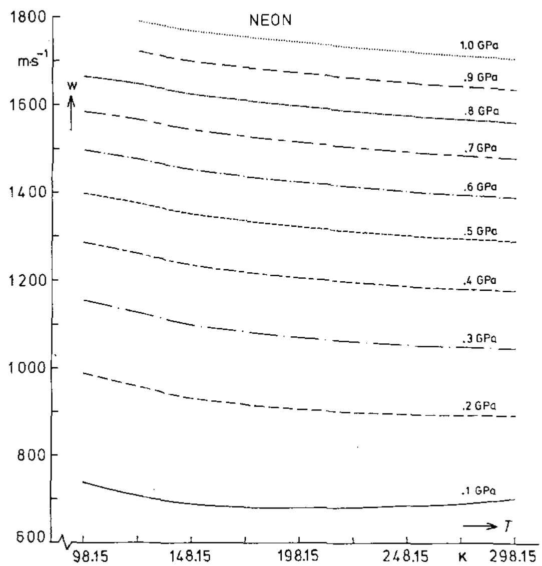

Fig. 2. Sound velocity in neon as a function of temperature at several pressures.

Table I. Thermodynamic Properties of Neon at 298.15 K

p (MPa)	ρ $(\mathrm{kmol \cdot m^{-3}})$	w $(\mathrm{m \cdot s^{-1}})$	$\chi_T \times 10^5$ $(\mathrm{MPa^{-1}})$	$\chi_S \times 10^5$ $(\mathrm{MPa^{-1}})$	γ
100	26.572	697.18	652.03	384.52	1.696
150	34.020	800.89	378.83	227.58	1.665
200	39.743	891.76	256.68	157.13	1.634
250	44.368	972.97	189.53	118.23	1.603
300	48.238	1046.62	148.02	93.98	1.575
350	51.563	1114.13	120.27	77.58	1.550
400	54.476	1176.56	100.63	65.85	1.528
450	57.070	1234.71	86.12	57.07	1.509
500	59.409	1289.19	75.01	50.29	1.492
550	61.540	1340.48	66.28	44.91	1.476
600	63.498	1388.98	59.26	40.53	1.462
650	65.311	1435.00	53.51	36.92	1.449
700	66.999	1478.82	48.72	33.89	1.437
750	68.580	1520.66	44.67	31.31	1.427
800	70.067	1560.70	41.21	29.10	1.416
850	71.471	1599.12	38.23	27.17	1.407
900	72.802	1636.06	35.63	25.48	1.398
950	74.067	1671.63	33.34	23.99	1.390
1000	75.274	1705.95	31.32	22.67	1.382

C_p/C_V). In Table I the thermodynamic properties at 298.15 K and at round values of the pressure with intervals of 50 MPa are given. The ratio of specific heats γ is a monotonously decreasing function of pressure. The sound velocities for all isotherms at round values of the pressure are given in Table II.

4. COMPARISON WITH PREVIOUS WORK

4.1. Compressibility

At pressures below 170 MPa, we used the data of Michels et al. [1] as reference data. Up to 235 MPa, Michels' data are consistent with our measurements, but the density at Michels' highest pressure (286 MPa) is 0.3 % lower, and therefore, this point is omitted in the combined fitting. This deviation can be explained by the fact that there is a sharp increase in the viscosity in the pressure-transmitting balance oil above 260 MPa at room temperature, giving rise to pressure gradients. This was observed in recent calibrations of the pressure balance against a 30-m mercury column up to 300 MPa, following the cumulative method of Bett et al. [12].

Table II. Velocity of Sound (in $m \cdot s^{-1}$) in Neon at Various Pressures (in MPa)

	T (K)								
p (MPa)	298.15	273.15	248.15	223.15	198.15	173.15	148.15	123.15	98.15
100	697.18	689.93	683.37	768.84	676.98	679.30	686.51	703.01	735.76
150	800.89	798.30	796.92	797.41	801.01	808.22	821.32	841.91	873.44
200	891.76	891.80	892.92	897.17	903.08	914.39	930.00	951.60	985.69
250	972.97	974.70	977.51	984.18	991.31	1003.95	1020.27	1043.10	1076.42
300	1046.62	1049.54	1053.66	1061.83	1069.74	1082.58	1099.00	1122.53	1153.95
350	1114.13	1117.95	1123.13	1132.21	1140.69	1153.49	1169.83	1193.38	1222.87
400	1176.56	1181.11	1187.11	1196.76	1205.70	1218.52	1234.75	1257.77	1285.65
450	1234.71	1239.85	1246.48	1256.50	1265.82	1278.77	1294.91	1317.05	1343.70
500	1289.19	1294.82	1301.90	1312.18	1321.83	1334.96	1351.01	1372.17	1397.89
550	1340.48	1346.52	1353.91	1364.39	1374.33	1387.61	1403.55	1423.78	1448.77
600	1388.98	1395.36	1402.95	1413.58	1423.77	1437.11	1452.93	1472.39	1496.71
650	1435.00	1441.67	1449.39	1460.13	1470.52	1483.82	1499.48	1518.36	1542.00
700	1478.82	1485.72	1493.52	1504.34	1514.89	1528.02	1543.50	1561.99	1584.86
750	1520.66	1527.74	1535.61	1546.46	1557.13	1570.01	1585.27	1603.50	1625.49
800	1560.70	1567.92	1575.87	1586.70	1597.46	1610.03	1625.06	1643.08	1664.07[a]
850	1599.12	1606.43	1614.49	1625.23	1636.04	1648.32	1663.11	1680.90	
900	1636.06	1643.42	1651.64	1662.22	1673.05	1685.12	1699.66	1717.08	
950	1671.63	1679.01	1687.46	1697.79	1708.60	1720.63	1734.94	1751.74	
1000	1705.95	1713.32	1722.08	1732.06	1742.82	1755.06	1769.16	1784.99	

[a] Extrapolated value.

In Fig. 3 the relative deviations of the data of Maslennikova et al. [4] and of Vidal et al. [5] from our data are shown. The first authors measured the molar volume up to 700 MPa at four isotherms between 298.15 and 423.15 K. No experimental accuracy is given. Vidal et al. measured the density of several noble gases at 298.15 K up to 1 GPa, with an accuracy of 0.2%. Considering the fact that the values at 0.9 and 1 GPa are extrapolated, the agreement is good. The shape of the deviation curve at about 300 MPa is very similar to that of helium [10].

4.2. Sound Velocity

A comparison of the present results for the sound velocities with those of other authors is shown in Fig. 4. Our sound velocities are systematically 0.2% higher than the values of Vidal et al. and 0.7% higher than those of Pitaevskaya and Bilevich [3]. This is outside the range of combined errors, as Vidal et al. claim an accuracy of 0.1%, and Pitaevskaya and Bilevich 0.3%. The sound velocities of Michels et al. [2] are calculated from pVT data and this leads, just as was the case for argon [8] and for nitrogen [9], to deviations of about 0.5%. Not shown in Fig. 4 is a comparison with the data of Kimura et al. [6], who measured the sound velocity at 295 K up to 3.5 GPa. Their sound velocities are generally higher than our values but scatter by about 2%. There are no experimental sound velocity data at elevated pressures and below 295 K known to the present authors.

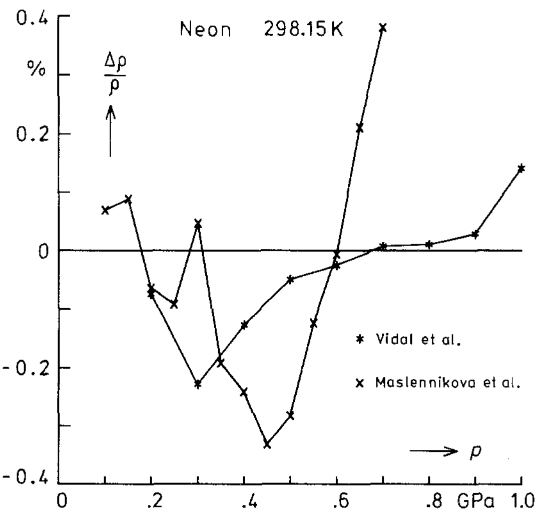

Fig. 3. Comparison between previous and present density data at 298.15 K.

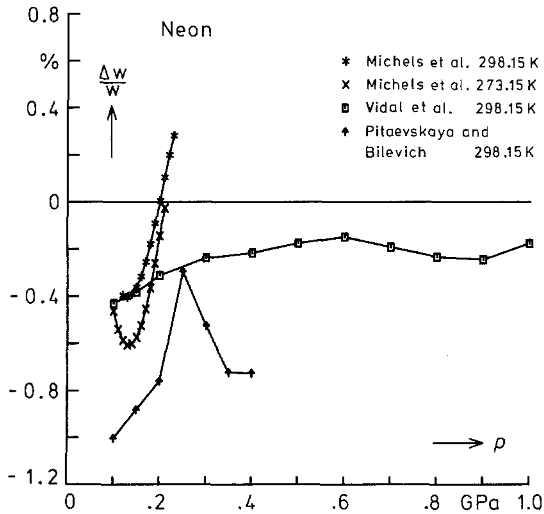

Fig. 4. Comparison between previous and present sound velocity data up to 1 GPa.

4.3. Ratio of Specific Heats

As could be expected from the comparison of density and sound velocity, the data of Vidal et al. are, except at 1 GPa, within 1% in good agreement with our results. Vidal et al. report a small increase in γ at 1 GPa, but this is an artifact, due to an increase in error by the extrapolation of the densities.

5. ANALYSIS OF THE RESULTS

The sound velocity in neon has an intermediate character between helium and argon. As shown in a previous paper [10], helium has a gas-like character, represented by a positive slope of $(dw/dT)_p$, even at pressures up to 1 GPa for higher temperatures and even up to 200 MPa at 98 K. In neon, the isobars below 200 MPa show a minimum, which shifts with increasing pressures to higher temperatures, as can be seen in Fig. 2. Above 250 MPa the remaining branch in the temperature interval has a negative slope, corresponding to a liquid behavior. In gases such as argon and nitrogen, only negative slopes of sound velocity versus temperature are encountered above 100 MPa, in this temperature range.

6. EQUATION OF STATE

Several equations have been proposed for simple dense gases. Most equations are of a purely empirical nature, whereas others are based on theoretical assumptions concerning the interaction of the molecules. An empirical equation of state of the type $\rho = \rho(p)$, which was also applied to compressibility data for nitrogen [9] and helium [10], was fitted to 56 data points in the range 80–1000 MPa:

$$\rho = A + Bp^{-1} + Cp^{-2} + Dp^{-m} \tag{2}$$

The values of the parameters, as found from a least-squares analysis are $A = -3.804069 \times 10^2$, $B = 1.76453164 \times 10^2$, $C = 9.22182148 \times 10^3$, $D = 3.1847333 \times 10^2$, and $m = -0.0518$, where p is expressed in MPa and ρ is in $\mathrm{kmol \cdot m^{-3}}$. The standard deviation is 0.04%, but the distribution of the deviations is not completely random. Another type gave slightly better results:

$$\rho = A + Bp + Cp^{-1} + Dp^{-2} + E\ln(p) \tag{3}$$

with $A = -8.27117 \times 10^1$, $B = 1.3247468 \times 10^{-3}$, $C = 4.59960151 \times 10^2$, $D = 4.07671502 \times 10^3$, and $E = 2.26108174 \times 10^1$. The standard deviation is 0.035% and the deviations above 250 MPa are randomly distributed. Below 80 MPa both equations are less suitable.

A semiempirical equation expressing the compressibility factor Z in terms of volume, which was applied earlier to argon [7] and nitrogen [9], was fitted to the experimental data, extended with data of Michels et al., to cover a pressure range of 35–1000 MPa:

$$Z = pV/RT = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 + aV^{-1} + bV^{-m} \tag{4}$$

where a, b, and m are adjustable parameters, V is the volume in $\mathrm{m^3 \cdot kmol^{-1}}$, and η is the packing fraction, defined by $\eta = (1/6)\,\pi d^3(N/V)$, N being Avogadro's number and d the rigid-sphere diameter. The first term on the right-hand side represents the hard-sphere contibution of Carnahan and Starling and the other two terms give the contribution due to attractive forces. From a least-squares procedure the following values were obtained: $a = -5.7076777 \times 10^{-3}$, $b = 2.8256729 \times 10^{-7}$, $m = 3.505$, and $d = 2.41 \times 10^{-10}$ m. The standard deviation is 0.1%, which is about the experimental error of the present measurements.

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