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Precise Determination of the Compressibility Factor of Methane, Nitrogen, and Their Mixtures from Refractive Index Measurements[1]

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We show that the absolute determination of the refractive index, when combined with an expansion technique for obtaining the higher-order coefficients of the Lorentz–Lorenz expansion, leads to precise values of density. A grating interferometer has been developed for the refractive index measurements as a function of pressure. The advantage of a grating interferometer is that it performs a reversible counting and generates a DC compensated signal from the interference fringes. The pressure is also measured with an interferometer, previously calibrated with an oil-type precision piston gauge. For the precise determination of the compressibility factor, the absolute measurement of the refractive index is combined with the differential technique to determine the refractivity virial coefficients of the Lorentz–Lorenz expansion. The compressibility factors of methane, nitrogen, and their mixtures have been determined at 323.15 K for pressures up to 335 bar. The optical method for the determination of the compressibility factor not only is shown to be precise, but also has the ability to produce numerous experimental points in a short time as compared to other methods.

KEY WORDS: compressibility factor; grating interferometer; refractive index; refractivity virial coefficient.

1. INTRODUCTION

The purpose of this paper is to show the possibility of determining precisely the compressibility factor from refractive index measurements. Up to now,

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the most commonly used methods for the determination of the compressibility factor have been the Burnett expansion technique and constant- or variable-volume methods [1, 2]. We intend to show that the determination of the compressibility factor based on the measurement of the refractive index is not only simple and fast, but also precise. This is particularly true if, in addition to the absolute measurements of the refractive index and pressure, we measure independently the second and third refractivity virial coefficients.

Much progress has been made [3–11] in refractive index measurements in the last few years in several laboratories. The recent differential measurement of the second and third refractivity virial coefficients should lead to better precision in the compressibility factor.

In this paper we present compressibility factors obtained from refractive index measurements for methane, nitrogen, and their mixtures.

In the next section we develop the relevant mathematical equations and explain the experimental procedure. We then give comparative results from different methods.

2. MATHEMATICAL DEVELOPMENT

The compressibility factor Z is given by

$$Z = \frac{P}{\rho RT} \tag{1}$$

where P is the pressure, ρ is the molar density, R is the universal gas constant, and T is the absolute temperature.

We intend to determine ρ from the Lorentz–Lorenz equation:

$$LL = [(n^2 - 1)/(n^2 + 2)]\, \rho^{-1} = A_n + B_n \rho + C_n \rho^2 + \cdots \tag{2}$$

where n is the refractive index and A_n, B_n, and C_n are, respectively, the first, second, and third refractivity virial coefficients. Equation (2) can also be written as

$$L_n = (n^2 - 1)/(n^2 + 2) = A_n \rho + B_n \rho^2 + C_n \rho^3 + \cdots \tag{3}$$

The first approximation for the density is given by

$$\rho_1 = (L_n/A_n) \tag{4}$$

With this value of density we get the first approximation for the compressibility factor

$$Z_1 = (P/RT)(A_n/L_n) \tag{5}$$

The second approximation for ρ is given by

$$\rho_2 = (L_n/A_n) - (B_n/A_n)(L_n/A_n)^2 \tag{6}$$

Replacing Eq. (6) in Eq. (1) we get for the compressibility factor

$$Z_2 = (P/RT)[(A_n/L_n) + (B_n/A_n)] \tag{7}$$

The third approximation for density, given by

$$\rho_3 = \frac{L_n}{A_n} - \frac{B_n}{A_n}\left(\frac{L_n}{A_n}\right)^2 + \frac{2B_n^2 - A_n C_n}{A_n^2}\left(\frac{L_n}{A_n}\right)^3 \tag{8}$$

leads to

$$Z_3 = \frac{P}{RT}\left(\frac{A_n}{L_n} + \frac{B_n}{A_n} + \frac{C_n L_n}{A_n^2} - \frac{B_n^2 L_n}{A_n^3}\right) \tag{9}$$

3. OPTICAL ARRANGEMENT

We measure the refractive index of gaseous methane as a function of pressure with a grating interferometer. The differential technique [3–8] combined with the interferometric refractive index measurements is used to determine B_n and C_n independently.

Figure 1 gives a schematic diagram of the optical arrangement. The advantage of a grating interferometer is that it performs a reversible counting and generates a DC compensated signal from the interference fringes.

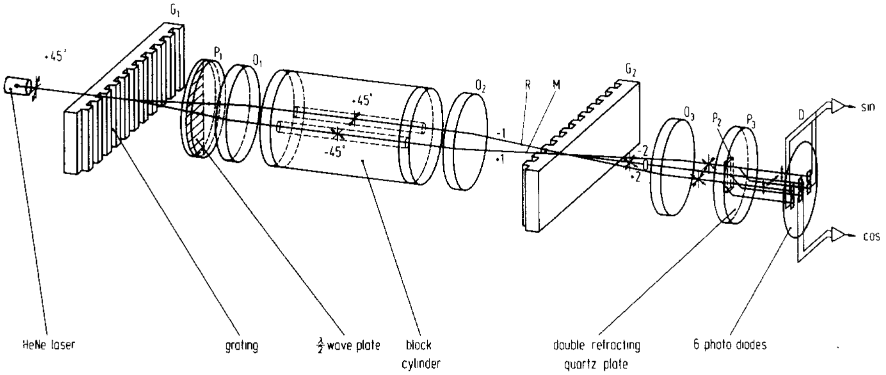

Fig. 1. Schematic diagram of the grating interferometer.

A linearly polarized He–Ne laser light passes through the first grating (G_1), producing numerous diffraction orders. Two symmetrical beams of the first diffraction order are selected such that one of them acts as a reference beam (R) and the other as a measuring beam (M). One of the beams passes through a $\lambda/2$ plate (P_1) such that the planes of polarization of the two beams are now perpendicular to each other. The two beams made parallel by the first objective (O_1) then enter the cylinder block, where one goes through the measuring cell and the other through the reference cell. This ensures that, to a great extent, the variation in length due to change in pressure is compensated. The two cells of the cylinder block are arranged symmetrically around the optical axis and are immersed in a temperature-controlled bath. A second objective (O_2) is used to focus the two beams on the second grating (G_2). The planes of polarization of the two beams are not effected by the two gratings.

The beams focused on the second grating produce two diffraction patterns superimposed on one another. Among the resultant diffractions only three superposed orders ($0, \pm 2$) have enough contrast so that they can be converted to electrical signals at a later stage.

The three beams rendered parallel by the lens (O_3) impinge on a double refracting quartz plate (P_3) in order that three pairs of push–pull modulated signals be produced. The six signals are inphase and antiphase. To produce quadrature signals ($\pm$sin, $\pm$cos) for the rotating electric field, we incorporate a $\lambda/4$ wave plate (P_2) in the path of the zero order of diffraction.

We have developed for our interferometer an array of six photodiodes with very similar dependence on dark currents and temperature coefficients. These photodiodes arranged in a matrix (D) not only transform the optical signals into electrical signals but also simplify mechanical adjustments and shorten the amplifier connections.

The central pair of the push–pull modulated electrical signals, which is in quadrature with the other two pairs, is introduced into two inputs of a differential amplifier. We introduce the combination of the remaining pairs of push–pull modulated electrical signals into the inputs of another differential amplifier. The amplitude of the quadrature signal is approximately equal to the sum of the amplitudes of the other two signals. The signals introduced in the differential amplifiers are combined in such a way that the DC parts of the signals are compensated. The two outputs of the differential amplifiers, when combined in a detector, produce a DC compensated rotating electrical field. This rotating electrical field operates a reversible counter and digitizes each change of one wavelength into 256 parts.

4. EXPERIMENT

4.1. Experimental Procedure

Accurate determination of the compressibility factor involves precision measurements of L_n, P, T, A_n, B_n, and C_n [Eq. (9)]. Measuring the pressure at the same time as the refractive index increases the efficiency of data taking. To ensure that the pressure is measured as fast as the refractive index, we developed an interferometric technique [12]. The interferometer for the pressure measurement is of the same type as the refractive index interferometer and was previously calibrated by the Physikalisch-Technische Bundesanstalt (PTB), Braunschweig (FRG), with an oil-type precision piston gauge (manufactured by Ruska, U.S.A.). Nitrogen of exceptionally high purity (99.9995%) is used for the calibration as the measuring gas for the pressure interferometer. The uncertainty in the pressure measurement has been determined by PTB to be 5×10^{-5}.

The absolute refractive index is obtained by counting the changes in the interference fringes while venting the fluid to vacuum. This reference to vacuum is necessary because interferometric measurements record only changes in the refractive index.

Absolute refractive indices are calculated from laboratory measurements by means of the formula

$$n = (K\lambda/l) + 1 \tag{10}$$

where K is the total fringe count to vacuum, λ is the vacuum wavelength of light, and l is the spacer length at the temperature of the fluid.

The manner of counting the fringes for the pressure measurement is the same as in the case of the refractive index.

4.2. Determination of A_n, B_n, and C_n

The first refractivity virial coefficient (A_n) is obtained by making an absolute measurement of the refractive index (n) as a function of pressure (P) [5–7, 9–11]. Replacing ρ in terms of P in Eq. (2), we obtain

$$[(n^2 - 1)/(n^2 + 2)][RT/P] = A_n + (B_n - A_n B_P)(P/RT) + \cdots \tag{11}$$

where B_P, the second pressure virial coefficient, is given by the expansion

$$(P/RT) = \rho + B_P \rho^2 + \cdots \tag{12}$$

When one plots the left side of Eq. (11) against P/RT, one can determine A_n from the intercept. Although B_n appears in the second term, this absolute method cannot be used for a precision determination of B_n. Since B_n is a small fraction of the second term in Eq. (11), an error as small as 2% in $(B_n - A_n B_P)$ could lead to an error [13] as large as 100% in B_n. In our case, we determine B_n and C_n by using an expansion technique.

The expansion technique and the relevant mathematical equations have been discussed in detail in the preceding article [14].

5. RESULTS AND DISCUSSION

Table I includes the present experimental values of A_n, B_n, and C_n for methane, nitrogen, and their mixtures.

In Tables II and III, we give the values of compressibility factors calculated for three different approximations and values of the refractive index as a function of pressure for methane and nitrogen. Z_1 is calculated only by including the first term (A_n) of the Lorentz–Lorenz function [Eq. (1)]. Z_2 is calculated by taking the first two coefficients (A_n and B_n) [Eq. (7)] and Z_3 is given by the first three coefficients (A_n, B_n, and C_n) [Eq. (9)]. In Table IV, we give the third approximation, Z_3, for five different mixtures of methane and nitrogen.

For methane, the compressibility factor Z_3 gives the best agreement with the experimental values of Douslin *et al.* [15] and Trappeniers *et al.* [16] with respect to Goodwin's [17] equation of state (Fig. 2) up to our highest measured pressure (286 bar). The second approximation for the compressibility factor (Z_2) also gives good agreement up to 100 bar. Even using only the first approximation for the compressibility factor (Z_1), we see that the deviation from other experimental values at the highest pressure (286 bar) does not exceed 0.4% (Table II).

Table I. Refractivity Virial Coefficients of Methane, Nitrogen, and Methane–Nitrogen Mixtures

Gas (mole fraction)	Temp. (K)	λ (nm)	$A_n \times 10^6$ ($m^3 \cdot mol^{-1}$)	$B_n \times 10^{12}$ ($m^6 \cdot mol^{-2}$)	$C_n \times 10^{18}$ ($m^9 \cdot mol^{-3}$)
N_2			4.446 ± 0.001	0.64 ± 0.08	-107 ± 5
13.52% $CH_4 + N_2$			4.734 ± 0.001	1.0 ± 0.2	-124 ± 13
25.02% $CH_4 + N_2$			4.979 ± 0.001	1.5 ± 0.3	-152 ± 23
38.69% $CH_4 + N_2$	323.15	633.0	5.270 ± 0.001	2.0 ± 0.3	-166 ± 20
49.92% $CH_4 + N_2$			5.509 ± 0.002	2.6 ± 0.4	-194 ± 42
89.76% $CH_4 + N_2$			6.358 ± 0.002	5.1 ± 0.4	-296 ± 46
CH_4			6.576 ± 0.002	5.83 ± 0.15	-326 ± 10

Table II. Refractive Index and the First Three Approximations of the Compressibility Factor of Gaseous CH_4 as a Function of the Pressure at 323.15 K

P (bar)	n	Z_1	Z_2	Z_3
10.696	1.0039845	0.98621	0.98657	0.98657
15.499	1.0058109	0.98018	0.98069	0.98067
20.210	1.0076256	0.97426	0.97493	0.97490
24.673	1.0093647	0.96880	0.96961	0.96957
30.469	1.0116533	0.96181	0.96282	0.96275
35.590	1.0137028	0.95577	0.95694	0.95685
40.258	1.0155927	0.95040	0.95173	0.95161
45.116	1.0175826	0.94489	0.94637	0.94622
50.263	1.0197134	0.93925	0.94091	0.94072
55.276	1.0218123	0.93387	0.93570	0.93546
60.002	1.0238111	0.92894	0.93092	0.93065
65.456	1.0261410	0.92344	0.92561	0.92528
70.368	1.0282591	0.91869	0.92101	0.92063
80.491	1.0326791	0.90944	0.91211	0.91160
90.270	1.0370096	0.90130	0.90429	0.90365
100.673	1.0416692	0.89353	0.89687	0.89606
110.723	1.0462064	0.88698	0.89065	0.88967
120.702	1.0507282	0.88147	0.88549	0.88431
130.538	1.0551848	0.87708	0.88140	0.88001
140.792	1.0598121	0.87357	0.87823	0.87661
150.919	1.0643442	0.87120	0.87621	0.87434
160.678	1.0686556	0.87003	0.87536	0.87324
170.807	1.0730649	0.86982	0.87549	0.87309
180.842	1.0773468	0.87069	0.87669	0.87400
189.884	1.0811219	0.87233	0.87865	0.87568
201.419	1.0858150	0.87556	0.88225	0.87893
211.247	1.0896943	0.87926	0.88628	0.88264
221.029	1.0934404	0.88377	0.89113	0.88716
231.090	1.0971723	0.88920	0.89689	0.89258
241.005	1.1007279	0.89528	0.90331	0.89865
251.066	1.1042104	0.90215	0.91051	0.90550
261.256	1.1076135	0.90973	0.91843	0.91305
271.386	1.1108751	0.91784	0.92689	0.92113
281.121	1.1138970	0.92614	0.93551	0.92938
286.680	1.1155749	0.93108	0.94064	0.93430

Table III. Refractive Index and the First Three Approximations of the Compressibility Factor of N_2 as a Function of the Pressure at 323.15 K

P (bar)	n	Z_1	Z_2	Z_3
10.696	1.0026563	0.99995	1.00001	1.00001
15.499	1.0038493	1.00008	1.00016	1.00016
20.210	1.0050192	1.00029	1.00040	1.00039
24.673	1.0061270	1.00057	1.00070	1.00068
30.469	1.0075647	1.00105	1.00121	1.00118
35.590	1.0088332	1.00158	1.00177	1.00172
40.258	1.0099882	1.00215	1.00236	1.00231
45.116	1.0111882	1.00283	1.00307	1.00300
50.263	1.0124571	1.00365	1.00392	1.00384
55.276	1.0136900	1.00455	1.00485	1.00475
60.002	1.0148495	1.00549	1.00581	1.00569
65.456	1.0161840	1.00668	1.00703	1.00689
70.368	1.0173820	1.00785	1.00823	1.00807
80.491	1.0198378	1.01056	1.01099	1.01076
90.270	1.0221916	1.01355	1.01403	1.01376
100.673	1.0246729	1.01712	1.01766	1.01732
110.723	1.0270453	1.02096	1.02155	1.02115
120.702	1.0293751	1.02513	1.02578	1.02530
130.538	1.0316439	1.02960	1.03030	1.02974
140.792	1.0339785	1.03462	1.03538	1.03473
150.919	1.0362515	1.03993	1.04074	1.04000
160.678	1.0384100	1.04537	1.04623	1.04540
170.807	1.0406162	1.05134	1.05225	1.05132
180.842	1.0427663	1.05757	1.05854	1.05749
189.884	1.0446724	1.06344	1.06446	1.06331
201.419	1.0470610	1.07127	1.07235	1.07107
211.247	1.0490570	1.07822	1.07936	1.07796
221.029	1.0510081	1.08540	1.08659	1.08507
231.090	1.0529772	1.09304	1.09428	1.09263
241.005	1.0548809	1.10079	1.10209	1.10031
251.066	1.0567750	1.10889	1.11024	1.10832
261.256	1.0586549	1.11732	1.11872	1.11666
271.386	1.0604862	1.12590	1.12736	1.12515
281.121	1.0622109	1.13433	1.13584	1.13350
286.680	1.0631806	1.13923	1.14077	1.13833

Table IV. Third Approximation of the Compressibility Factor (Z) for the Mixtures of CH_4–N_2 as a Function of the Pressure at 323.15 K

P (bar)	Z Mixture composition, mol % methane				
	13.52	25.02	38.69	49.92	89.76
9.965	0.99877	0.99763	0.99594	0.99451	0.98847
14.966	0.99823	0.99670	0.99414	0.99172	0.98305
19.963	0.99776	0.99580	0.99245	0.98931	0.97789
23.961	0.99763	0.99510	0.99121	0.98747	0.97381
29.960	0.99737	0.99423	0.98937	0.98492	0.96769
33.964	0.99732	0.99372	0.98826	0.98313	0.96375
39.960	0.99733	0.99309	0.98676	0.98083	0.95805
44.955	0.99752	0.99272	0.98566	0.97904	0.95340
49.950	0.99773	0.99248	0.98466	0.97738	0.94885
54.951	0.99811	0.99229	0.98375	0.97586	0.94451
59.945	0.99854	0.99224	0.98299	0.97445	0.94028
64.948	0.99909	0.99230	0.98237	0.97321	0.93624
69.947	0.99976	0.99265	0.98189	0.97208	0.93232
74.945	1.00056	0.99293	0.98152	0.97110	0.92861
79.949	1.00141	0.99337	0.98126	0.97025	0.92509
84.942	1.00241	0.99387	0.98116	0.96955	0.92173
89.946	1.00350	0.99451	0.98115	0.96899	0.91857
94.938	1.00469	0.99528	0.98133	0.96858	0.91561
99.942	1.00601	0.99615	0.98159	0.96832	0.91286
104.934	1.00740	0.99713	0.98201	0.96822	0.91034
109.938	1.00892	0.99826	0.98256	0.96827	0.90799
114.930	1.01055	0.99948	0.98325	0.96844	0.90589
119.935	1.01225	1.00082	0.98407	0.96879	0.90401
124.926	1.01408	1.00227	0.98501	0.96926	0.90234
129.927	1.01601	1.00385	0.98611	0.96989	0.90092
134.917	1.01801	1.00552	0.98731	0.97067	0.89972
139.927	1.02024	1.00733	0.98866	0.97159	0.89875
144.920	1.02246	1.00923	0.99011	0.97268	0.89803
149.923	1.02475	1.01124	0.99172	0.97389	0.89751
154.915	1.02717	1.01336	0.99344	0.97529	0.89725
159.919	1.02967	1.01560	0.99529	0.97680	0.89721
164.910	1.03226	1.01793	0.99726	0.97843	0.89740
169.915	1.03493	1.02037	0.99935	0.98021	0.89782
174.906	1.03771	1.02290	1.00155	0.98212	0.89846
179.910	1.04057	1.02554	1.00388	0.98418	0.89933
184.901	1.04352	1.02827	1.00632	0.98634	0.90039
189.905	1.04654	1.03111	1.00887	0.98865	0.90168
194.898	1.04965	1.03403	1.01153	0.99108	0.90318
199.901	1.05285	1.03705	1.01431	0.99364	0.90489
204.889	1.05613	1.04015	1.01716	0.99629	0.90678
209.994	1.05954	1.04341	1.02021	0.99914	0.90891

Table IV. *(Continued)*

P (bar)	Z Mixture composition, mol % methane				
	13.52	25.02	38.69	49.92	89.76
214.896	1.06290	1.04663	1.02324	1.00199	0.91115
219.901	1.06641	1.05000	1.02642	1.00501	0.91361
224.883	1.06999	1.05344	1.02967	1.00813	0.91623
229.886	1.07367	1.05697	1.03304	1.01137	0.91904
234.876	1.07738	1.06056	1.03650	1.01470	0.92200
239.884	1.08119	1.06425	1.04005	1.01814	0.92513
244.870	1.08499	1.06800	1.04367	1.02166	0.92839
249.865	1.08889	1.07182	1.04737	1.02528	0.93181
254.865	1.09285	1.07571	1.05117	1.02900	0.93537
259.870	1.09689	1.07968	1.05506	1.03281	0.93906
264.859	1.10098	1.08371	1.05899	1.03670	0.94288
269.864	1.10511	1.08780	1.06303	1.04068	0.94683
274.852	1.10929	1.09194	1.06710	1.04472	0.95089
279.858	1.11355	1.09616	1.07133	1.04886	0.95508
284.847	1.11784	1.10043	1.07554	1.05306	0.95935
289.850	1.12220	1.10476	1.07984	1.05735	0.96374
294.840	1.12659	1.10913	1.08419	1.06168	0.96823
299.846	1.13104	1.11357	1.08861	1.06611	0.97282
304.836	1.13552	1.11805	1.09308	1.07059	0.97748
309.840	1.14006	1.12260	1.09762	1.07514	0.98224
314.827	1.14462	1.12716	1.10219	1.07973	0.98707
319.833	1.14925	1.13180	1.10685	1.08439	0.99201
324.821	1.15391	1.13646	1.11152	1.08911	0.99698
329.818	1.15859	1.14118	1.11626	1.09385	1.00205
334.818	1.16333	1.14594	1.12104	1.09862	1.00710

In Fig. 3 we show comparative values of Z_3 for methane, nitrogen, and their mixtures.

We have conclusively proved that in the case of methane, using differential measurement for B_n and C_n and using the first three coefficients (A_n, B_n, and C_n) of the Lorentz–Lorenz expansion for calculating the density, one can obtain accurate values for the compressibility factor.

6. CONCLUSION

The reason the determination of the density from refractive index measurements was erroneous in the past [18] is that the Lorentz–Lorenz function is not independent of density. For obtaining a more precise value

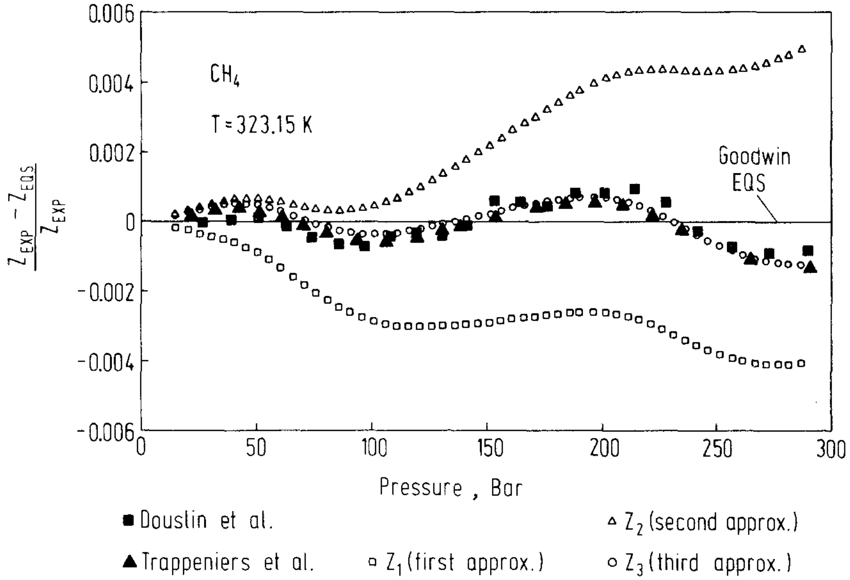

Fig. 2. Deviations of experimental values of the compressibility factor Z_{EXP} from Z_{EQS} values calculated using the Goodwin equation of state as reference

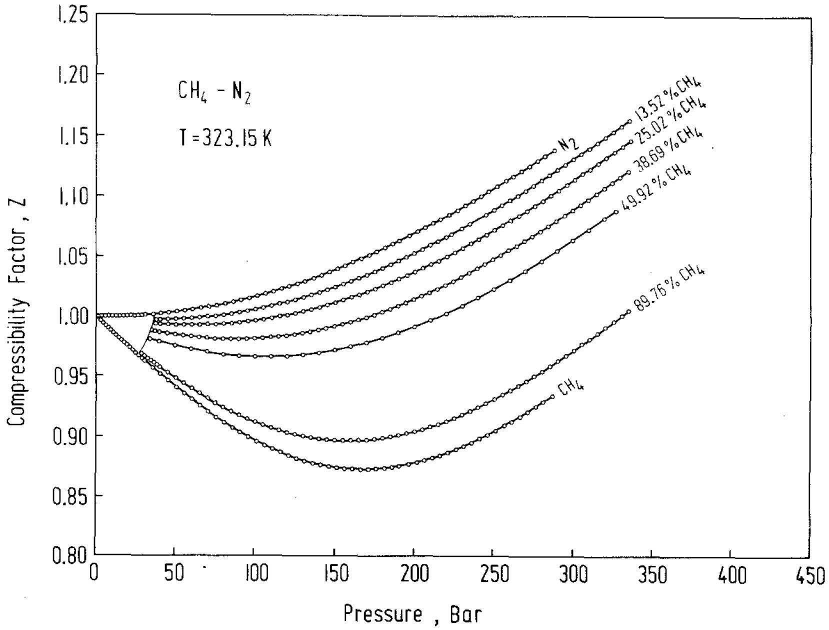

Fig. 3. Compressibility factor from refractive index measurements for CH$_4$, N$_2$, and mixtures of CH$_4$-N$_2$ at 323.15 K.

of density, one has to include higher terms in the Lorentz–Lorenz expansion. We have shown that using an absolute measurement of n as a function of P for the determination of B_n and C_n [Eq. (1)] is prone to large errors. The expansion technique permit us to obtain accurate values for the higher-order terms of the Lorentz–Lorenz expansion. This technique combined with the absolute measurements of the refractive index as a function of pressure leads to values of the compressibility factor comparable to the best PVT values. Thus, the optical method, when used properly, not only is precise for the determination of density but also has the ability to produce numerous experimental points of the compressibility factor (Fig. 3) in a short time as compared to other methods.

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