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Refractivity Virial Coefficients and P, ρ, T Data of Ethylene[1]

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Virial coefficients for gaseous ethylene have been determined in the temperature range 283.15 to 373.15 K by means of a new refractive index P, ρ, T method. Measurements of the pressure and temperature dependence of the refractive index n and the density and temperature dependence of $(n-1)\rho^{-1}$ were carried out by two coupled grating interferometers. From these interferometric measurements, we determined the refractivity virial coefficients A_R, B_R, and C_R of the Lorentz–Lorenz expansion, P, ρ, T data, and the second and third virial coefficients $B(T)$ and $C(T)$ of the Leiden expansion. The deduced coefficients $B(T)$ and $C(T)$ are in excellent agreement with the accurate literature values.

KEY WORDS: ethylene; Lorentz–Lorenz expansion; P, ρ, T data; refractivity virial coefficients; virial coefficients.

1. INTRODUCTION

Up to now, the most commonly used methods for the experimental determination of the virial coefficients $B(T)$ and $C(T)$, based on P, ρ, T data have been the Burnett and Burnett-isochoric techniques [1–4]. We intend to show that determination of the virial coefficients based on measurements of the refractive index is not only simple and fast, but also accurate.

Recently, we have shown on gaseous methane that the absolute measurement of the refractive index combined with the independent determination of $(n-1)\rho^{-1}$ leads to very accurate values of density [5–7]. Since methane does not deviate much from ideal gases at room temperature, it is our intention in this paper to apply the optical technique of

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determining P, ρ, T data to a strong nonideal gas like ethylene. This gas is suitable for a comparative study because the second and third virial coefficients $B(T)$ and $C(T)$ of ethylene are extraordinarily well characterized in a temperature range from 60 K below to 170 K above the critical temperature [1]. The existence of high-quality $B(T)$ and $C(T)$ values will enable us to verify the accuracy of the virial coefficients from optical P, ρ, T measurements.

2. PRINCIPLE OF THE METHOD

From the experimental optical investigation of the P, n, T surface, one can determine accurate values of the P, ρ, T surface if, in addition to the precise measured refractive index $n(P, T)$, accurate values of the refractivity virial coefficients A_R, B_R, and C_R are known.

The refractive index n and the molar density ρ are related by the Lorentz–Lorenz (LL) expansion,

$$\mathrm{LL} = \frac{n^2-1}{n^2+2}\rho^{-1} = A_R + B_R\rho + C_R\rho^2 + \cdots \tag{1}$$

2.1. *P*, *n*, *T* Measurements and Determination of A_R

The absolute refractive index is obtained by counting the changes in the interference fringes while venting the fluid on isotherms to vacuum. This reference to vacuum is necessary because interferometric measurements record changes only in the refractive index. Absolute refractive indices $n(P, T)$ are calculated from the interference fringe count by means of the data reduction formula,

$$n(P, T) = \frac{K_n(P, T)\,\lambda_0}{l(T)} + 1 \tag{2}$$

where $K_n(P, T)$ = total fringe count while venting the sample gas isothermal from the measurement point with the pressure P to vacuum, and where λ_0 is the vacuum wavelength of the laser light, $l(T)$ is the spacer length at the temperature T of the fluid.

The first refractivity virial coefficient A_R can be determined directly by means of an independent method in which only isothermal P, n, T measurements are involved. The density in Eq. (1) can be replaced by the Leiden expansion,

$$Z = \frac{P}{\rho RT} = 1 + B(T)\rho + C(T)\rho^2 + \cdots \tag{3}$$

where $B(T)$, $C(T)$,..., are the virial coefficients of the compression factor Z. We obtain

$$RT\frac{L_n}{P}=A_R+[B_R-B(T)\,A_R]\frac{P}{RT}+\cdots \tag{4}$$

or, equivalently,

$$RT\frac{L_n}{P}=A_R+[B_R-B(T)\,A_R]\frac{L_n}{A_R}+\cdots \tag{5}$$

For convenience, the symbol L_n is used for the refraction $(n^2-1)/(n^2+2)$. When one plots isothermal refractive index data RTL_n/P vs P, Eq. (4), or RTL_n/P vs L_n, Eq. (5), one can determine A_R from the intercept with an accuracy of a few parts in 10^4.

2.2. Determination of B_R and C_R

The refractivity virial coefficients B_R and C_R can be determined by measuring the excess contribution of $(n-1)\,\rho^{-1}$ which is directly related to the refractive index virial coefficients B_n, C_n,..., defined by

$$(n-1)\,\rho^{-1}=A_n+B_n\rho+C_n\rho^2+\cdots \tag{6}$$

If one compares the coefficients of ρ^n in Eq. (6) with those in Eq. (1), it is readily shown that

$$A_R=\tfrac{2}{3}A_n \tag{7}$$

$$B_R=\tfrac{2}{3}B_n-\tfrac{1}{9}A_n^2 \tag{8}$$

$$C_R=\tfrac{2}{3}C_n-\tfrac{2}{9}A_nB_n-\tfrac{4}{27}A_n^3 \tag{9}$$

The determination of B_n and C_n consists of measuring the sum of optical path lengths of two identical sample cells, where one of them is filled with gas at density ρ_1 and the other is evacuated. When the valve between the two cells is opened, the density is halved and one measures the optical path lengths again. Because the linear term in density $(lA_n\rho\lambda_0^{-1})$ remains the same before and after the expansion and only the quadratic and higher orders change, we can determine B_n and C_n from the change of the optical path lengths. We thus get

$$\begin{aligned}\lambda_0(K_1-K_2)&=l[(n_1-1)-2(n_2-1)]\\&=l[\tfrac{1}{2}B_n\rho_1^2+\tfrac{3}{4}C_n\rho_1^3+\cdots]\end{aligned} \tag{10}$$

where n_1 and n_2 are the initial and final values of the refractive index and the products $\lambda_0 K_1$ and $\lambda_0 K_2$ are the initial and final values of the measured change of the optical path lengths referred to vacuum. Because the excess contribution of $(n-1)\rho^{-1}$ is very small, the number of fringes of K_1 and K_2 are nearly equal. To reduce the errors resulting from taking the difference between two comparable numbers K_1 and K_2, we measure directly the change of the optical path lengths during the actual expansion procedure by counting the change of the interference fringes $\Delta K = (K_1 - K_2)$. Nevertheless, one has to measure K_1, the independent variable of $\Delta K = \Delta K(K, T)$.

In practice, it is not possible to construct identical cells. The unavoidable mismatch in cell lengths and volumes leads to errors in the fringe count. The mismatch effects are eliminated by carrying out two successive expansions in opposite directions [8–10].

Using the expansion technique, the expansion from cell A to cell B gives the relation $\Delta K_{AB}(K_A, T)$. Before the expansion takes place, the initial state of the filled cell A is determined by the variable $K_A(T)$. Similarly, if cell B contains gas and cell A is evacuated, the expansion from cell B to cell A gives the relation $\Delta K_{BA}(K_B, T)$.

On adding the two relations, the systematic errors in ΔK_{AB} and ΔK_{BA} are canceled. One then obtains the relation between the measured variables and the refractive index virial coefficients B_n, C_n,..., given by Eq. (11). For convenience, the symbol F is used to represent the quantity

$$\begin{aligned} F &= \frac{\Delta K_{AB}}{K_A} + \frac{\Delta K_{BA}}{K_B} \\ &= \frac{B_n}{2A_n^2}\,[(n_A - 1) + (n_B - 1)] \\ &\quad + \frac{3A_nC_n - 4B_n^2}{4A_n^4}\,[(n_A - 1)^2 + (n_B - 1)^2] + \cdots \end{aligned} \tag{11}$$

where $n_A - 1 = K_A \lambda_0 / l$ and $n_B - 1 = K_B \lambda_0 / l$.

The measurements are carried out in such a way that K_A is nearly equal to K_B. The variable in the second term of Eq. (11) can then be written as $(n_A - 1)^2 + (n_B - 1)^2 = [(n_A - 1) + (n_B - 1)]^2/2$.

Making a least-squares fit of Eq. (11) to a polynomial in $[(n_A - 1) + (n_B - 1)]$, one can determine B_n from the slope and C_n from the curvature.

Table I. Refractivity Virial Coefficients of Ethylene at $\lambda_0 = 632.99$ nm

T (K)	$A_R \cdot 10^6$ ($m^3 \cdot mol^{-1}$)	$B_R \cdot 10^{12}$ ($m^6 \cdot mol^{-2}$)	$C_R \cdot 10^{18}$ ($m^9 \cdot mol^{-3}$)
283.15	10.6490 ± 0.0020		
288.15	10.6500 ± 0.0020		
293.15	10.6455 ± 0.0030		
298.15	10.6465 ± 0.0030		
303.00	10.6519 ± 0.0020	17.7 ± 0.4	-1280 ± 25
323.15	10.6531 ± 0.0020		
348.15	10.6540 ± 0.0020		
373.15	10.6552 ± 0.0020	17.8 ± 0.3	-1284 ± 19

3. EXPERIMENTAL APPARATUS

The experimental apparatus described in detail before [5, 8] essentially consists of two coupled interferometers. Both the absolute refractive index measurements $n(P, T)$ and the differential measurements of $\Delta K(K, T)$ to determine B_R and C_R have been carried out with the same interferometer system.

We use one interferometer for the absolute refractive index measurement of the sample. The other interferometer is used to determine the pressure by measuring the refractive index of nitrogen at a fixed temperature. The relation between the refractive index of nitrogen and the

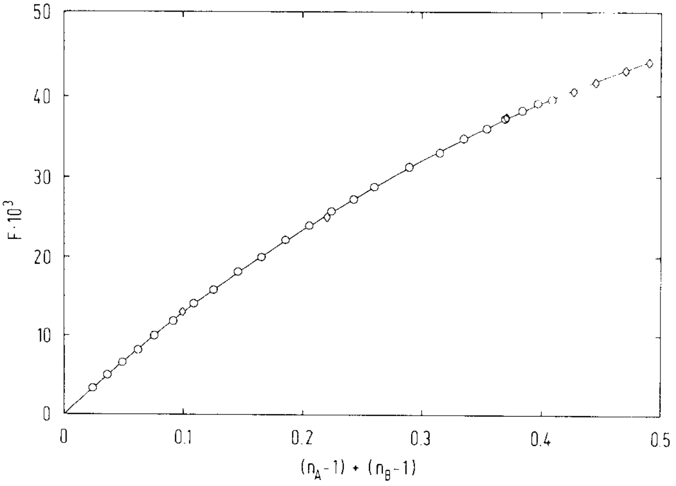

Fig. 1. Plot of the refractive index expansion function F vs $[(n_A - 1) + (n_B - 1)]$ of ethylene. (◇) 303 K; (○) 373.15 K.

Table II. The Density ρ and the Residual $B(\rho) = (P/\rho RT - 1)/\rho$ of Ethylene

	283.15 K		288.15 K		293.15 K		298.15 K	
P (MPa)	$\rho \cdot 10^{-3}$ $(\mathrm{mol \cdot m^{-3}})$	$-B(\rho) \cdot 10^{3}$ $(\mathrm{m^{3} \cdot mol^{-1}})$	$\rho \cdot 10^{-3}$ $(\mathrm{mol \cdot m^{-3}})$	$-B(\rho) \cdot 10^{3}$ $(\mathrm{m^{3} \cdot mol^{-1}})$	$\rho \cdot 10^{-3}$ $(\mathrm{mol \cdot m^{-3}})$	$-B(\rho) \cdot 10^{3}$ $(\mathrm{m^{3} \cdot mol^{-1}})$	$\rho \cdot 10^{-3}$ $(\mathrm{mol \cdot m^{-3}})$	$-B(\rho) \cdot 10^{3}$ $(\mathrm{m^{3} \cdot mol^{-1}})$
0.8	0.35957	0.15285	0.35225	0.14776	0.34529	0.14319	0.33845	0.13740
0.9	0.40764	0.15259	0.39911	0.14728	0.39102	0.14241	0.38324	0.13741
1.0	0.45649	0.15227	0.44673	0.14700	0.43743	0.14192	0.42857	0.13707
1.2	0.55670	0.15159	0.54425	0.14644	0.53240	0.14137	0.52111	0.13639
1.4	0.66036	0.15063	0.59415	0.14601	0.63018	0.14050	0.61629	0.13569
1.6	0.76803	0.14987	0.74904	0.14474	0.73111	0.13971	0.71419	0.13482
1.8	0.87995	0.14901	0.85700	0.14390	0.83546	0.13892	0.81521	0.13408
2.0	0.99663	0.14810	0.96909	0.14301	0.94335	0.13799	0.91948	0.13329
2.2	1.1185	0.14711	1.0858	0.14208	1.0554	0.13715	1.0273	0.13252
2.4	1.2464	0.14612	1.2075	0.14114	1.1717	0.13624	1.1389	0.13164
2.6	1.3810	0.14504	1.3349	0.14013	1.2928	0.13527	1.2547	0.13076
2.8	1.5231	0.14388	1.4687	0.13909	1.4193	0.13430	1.3749	0.12983
3.0	1.6741	0.14266	1.6096	0.13796	1.5517	0.13326	1.5003	0.12889
3.3	1.9205	0.14065	1.8366	0.13614	1.7629	0.13161	1.6988	0.12738
3.6	2.1972	0.13838	2.0866	0.13413	1.9922	0.12981	1.9118	0.12575
3.9	2.5154	0.13574	2.3659	0.13186	2.2434	0.12783	2.1421	0.12398
4.2	2.8953	0.13257	2.6850	0.12927	2.5225	0.12563	2.3933	0.12205
4.5	3.3774	0.12852	3.0599	0.12620	2.8376	0.12312	2.6703	0.11991
4.8	4.0738	0.12262	3.5215	0.12241	3.2019	0.12023	2.9796	0.11752
5.1			4.1388	0.11735	3.6368	0.11677	3.3313	0.11480

	303 K		323.15 K		348.15 K		373.15 K	
P (MPa)	$\rho \cdot 10^{-3}$ $(\mathrm{mol \cdot m^{-3}})$	$-B(\rho) \cdot 10^3$ $(\mathrm{m^3 \cdot mol^{-1}})$	$\rho \cdot 10^{-3}$ $(\mathrm{mol \cdot m^{-3}})$	$-B(\rho) \cdot 10^3$ $(\mathrm{m^3 \cdot mol^{-1}})$	$\rho \cdot 10^{-3}$ $(\mathrm{mol \cdot m^{-3}})$	$-B(\rho) \cdot 10^3$ $(\mathrm{m^3 \cdot mol^{-1}})$	$\rho \cdot 10^{-3}$ $(\mathrm{mol \cdot m^{-3}})$	$-B(\rho) \cdot 10^3$ $(\mathrm{m^3 \cdot mol^{-1}})$
0.8	0.33224	0.13309	0.30878	0.11573	0.28428	0.097882	0.26366	0.083614
0.9	0.37598	0.13252	0.34907	0.11571	0.32096	0.097519	0.29742	0.082978
1.0	0.42031	0.13229	0.38971	0.11539	0.35793	0.097370	0.33143	0.083008
1.2	0.51067	0.13171	0.47222	0.11480	0.43276	0.097239	0.40000	0.082621
1.4	0.60340	0.13097	0.55648	0.11437	0.50872	0.096891	0.46936	0.082252
1.6	0.69871	0.13029	0.64243	0.11373	0.58584	0.096447	0.53957	0.081992
1.8	0.79678	0.12963	0.73029	0.11318	0.66418	0.096016	0.61069	0.081835
2.0	0.89772	0.12886	0.82006	0.11254	0.74373	0.095471	0.68253	0.081364
2.2	1.0018	0.12807	0.91191	0.11196	0.82465	0.095056	0.75526	0.080936
2.4	1.1093	0.12730	1.0059	0.11131	0.90682	0.094511	0.82889	0.080540
2.6	1.2204	0.12650	1.1021	0.11067	0.99044	0.094031	0.90344	0.080154
2.8	1.3356	0.12566	1.2007	0.11002	1.0755	0.093532	0.97886	0.079718
3.0	1.4550	0.12479	1.3018	0.10933	1.1620	0.093026	1.0553	0.079307
3.3	1.6430	0.12340	1.4585	0.10827	1.2946	0.092223	1.1717	0.078698
3.6	1.8432	0.12193	1.6217	0.10715	1.4307	0.091395	1.2903	0.078041
3.9	2.0573	0.12032	1.7919	0.10600	1.5707	0.090552	1.4111	0.077365
4.2	2.2880	0.11860	1.9699	0.10481	1.7146	0.089684	1.5343	0.076701
4.5	2.5382	0.11673	2.1564	0.10356	1.8626	0.088783	1.6598	0.076016
4.8	2.8122	0.11467	2.3521	0.10224	2.0151	0.087886	1.7879	0.075320
5.1	3.1151	0.11240	2.5581	0.10085	2.1720	0.086941	1.9183	0.074602

pressure has been established by using a precision piston gauge [11]. This ensures the possibility of obtaining n and P simultaneously.

The differential measurement for $\Delta K(K, T)$ is carried out by using two interferometers. One interferometer is used to measure ΔK, which consists of two similar cells in series. The other interferometer is used to measure the total fringe count K, which consists of two similar cells in parallel. This makes it possible to obtain ΔK and K simultaneously [8].

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Measurements of $n(P, T)$ and Determination of A_R

The P, n, T measurements on ethylene cover a region where accurate experimental P, ρ, T results and deduced virial coefficients $B(T)$ and $C(T)$ are available. The measurements have been carried out on eight isotherms 283.15, 288.15, 293.15, 298.15, 303, 323.15, 348.15, and 373.15 K and pressures up to 30 MPa. Ethylene of 99.995 mol % purity was used without further purification.

For an accurate determination of A_R we measured in the lower pressure range (0.1 to 5 MPa) in steps of 0.1 MPa and of 0.5 MPa above. Each isotherm is therefore covered with 100 refractive index measurement points, generated with only one expansion run. Table I gives the experimental values of A_R, which increases about 0.1 % in the investigated temperature region.

4.2. Measurements of B_R and C_R

Procedures for the determination of B_R and C_R have been discussed elsewhere [5, 6, 8]. The coefficients B_R and C_R are functions of frequency and temperature, but up to now, no significant temperature dependence has been measured. For this purpose the measurements must be carried out to relatively high densities in order to increase the contribution of the higher-order terms and hence reduce the uncertainty of the refractivity virial coefficients.

The differential measurements were carried out on the two isotherms 303 and 373.15 K with pressures up to 32 MPa. The number of measured points, equidistant in pressure, is 23 on the 373.15 K isotherm and 9 on the 303 K isotherm, and mainly in the high-density region for the latter isotherm. The points of both isotherms lie on the same curve of the plot F versus $[(n_A - 1) + (n_B - 1)]$ (Fig. 1), and we found that in the investigated range of density the best least-squares fit for C_2H_4 was given by a polynominal of the form $y = a_1 x + a_2 x^2$. Using the polynomial of the form

Table III. Values of the Second and Third Virial Coefficients of Ethylene

T (K)	$B \cdot 10^6$ ($m^3 \cdot mol^{-1}$)						$C \cdot 10^9$ ($m^6 \cdot mol^{-2}$)				
	Douslin [12]	Waxman [2]	Trappeniers[a] [13]	Sengers[b] [1]	Wagner[c] [14]	This work	Douslin [12]	Waxman [2]	Trappeniers[a] [13]	Wagner[c] [14]	This work
283.15	−155.7			−155.8	−156.0	−155.8	7.60			7.80	7.72
288.15	−150.3			−150.2	−150.5	−150.3	7.58			7.67	7.64
293.15	−144.9		−144.8	−144.9	−145.2	−145.3	7.39		6.88	7.53	7.58
298.15	−139.8	−139.8	−139.7	−139.9	−140.1	−140.2	7.20	7.17	6.66	7.38	7.42
303				−135.2	−135.5	−135.2				7.23	6.94
303.15	−135.0		−135.0	−135.0			7.04		6.70		
323.15	−117.7	−117.6	−118.1	−117.7	−118.0	−118.0	6.54	6.56	6.67	6.62	6.58
348.15	−99.7	−99.6	−99.9	−99.6	−100.0	−100.0	5.87	5.89	5.92	5.96	5.96
373.15	−84.8	−84.6	−84.9	−84.7	−85.1	−85.1	5.32	5.28	5.23	5.45	5.40

[a] According to the analysis by Levelt Sengers and Hastings [1].

[b] Calculated values according to the correlation of Levelt Sengers and Hastings [1].

[c] According to the analysis of our data by Wagner and Setzmann [14].

$y = a_0 + a_1 x + a_2 x^2$, we found that the intercept a_0 was practically zero within the experimental error. The calculated values of B_R and C_R are listed in Table I. No temperature dependence of B_R and C_R was found in the investigated temperature region.

4.3. Determination of ρ(*P*, *T*) and the Virial Coefficients *B*(*T*) and *C*(*T*)

In Table II we give the unsmoothed values of the density $\rho(P, T)$ up to 5 MPa calculated from $n(P, T)$ data by including B_R and C_R, Eq. (1).

The temperature-dependent coefficients $B(T)$ and $C(T)$, in the infinite series, Eq. (3), were evaluated by graphical techniques based on interrelated plots of the residual quantities $B(\rho)$ and $C(\rho)$ in the relations:

$$B(\rho) = \frac{(Z-1)}{\rho} \qquad B(T) = \lim_{\rho \to 0} B(\rho) \tag{12}$$

$$C(\rho) = \frac{(Z-1)/\rho - B(T)}{\rho} \qquad C(T) = \lim_{\rho \to 0} C(\rho) \tag{13}$$

The residual $B(\rho)$, Table II, were calculated from the unsmoothed experimental values of temperature, density, and pressure. Table III gives our experimental values of $B(T)$ and $C(T)$ according to a graphical technique and a surface fit, applied by Wagner and Setzmann [14]. The two sets agree within the experimental error. For the purpose of comparison, the best virial data according to Levelt Sengers and Hastings [1] were included in Table III. Our derived values for $B(T)$ are in excellent agree-

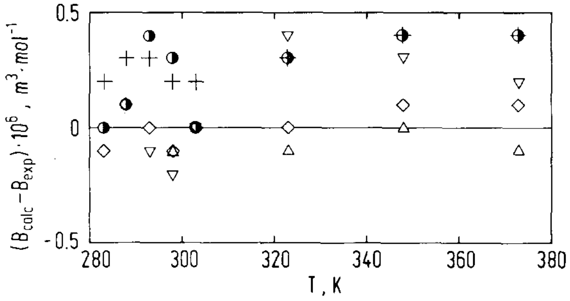

Fig. 2. The difference in the values of the second virial coefficient of ethylene calculated from the correlation of Levelt Sengers and Hastings [1] with the experimental data from four sources. (◇) Douslin and Harrison [12]; (△) Waxman and Davis [2]; (▽) Trappeniers et al. [13]; (+) Wagner and Setzmann [14], according to the analysis of our *P*, *ρ*, *T* data; (◑) this work.

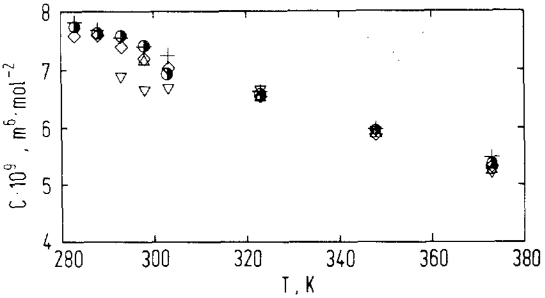

Fig. 3. The third virial coefficient of ethylene from four sources of experimental data. (◇) Douslin and Harrison [12]; (△) Waxman and Davis [2]; (▽) Trappeniers et al. [13]; (+) Wagner and Setzmann [14], according to the analysis of our P, ρ, T data; (◑) this work.

ment with the selected virial data. The maximum deviation is not more than $0.5\ cm^3 \cdot mol^{-1}$ (Fig. 2).

We have intercompared the third virial coefficients $C(T)$ of this work with the high-quality sets of Douslin and Harrison [12], Waxman and Davis [2], and Trappeniers et al. [13] in Fig. 3. This figure demonstrates that the four data sets are in mutual agreement to within the 5% level.

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