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Mean Polarizabilities and Second and Third Virial Coefficients of the Gases C_2H_4, C_2H_6, and SF_6

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Mean polarizabilities $\alpha_0(\lambda_0, T)$ as well as second and third virial coefficients $B(T)$ and $C(T)$ of the equation of state of the gases C_2H_4, C_2H_6, and SF_6 have been determined from refractive index measurements with a Michelson interferometer for wavelength $\lambda_0 = 632.99$ nm in the overall ranges $250\ \mathrm{K} \leqslant T \leqslant 340\ \mathrm{K}$ and $0 \leqslant p \leqslant 3$ MPa of temperature T and pressure p. Some negative $C(T)$ values at low temperatures have been obtained. The $C(T)$ data could be fitted satisfactorily to the simple three-parameter function $C(T) = a(T - T_0) \exp[-b(T - T_0)]$, with the maximum near the critical temperature T_c. A possible correlation between $C(T)$ and the vapor pressure $p_v(T)$ is discussed.

KEY WORDS: polarizability; refractive index; virial coefficients; C_2H_4; C_2H_6; SF_6.

1. INTRODUCTION

It is well known that virial coefficients are of practical and theoretical importance, e.g., in studies related to intermolecular forces [1–3]. There exist different methods of measurement [4], which lead to a good accordance of the results of second virial coefficients $B(T)$, where T is temperature. However, in the case of third virial coefficients $C(T)$, the results of the literature are more scarce and, in most cases, full of contradictions (see, e.g., Ref. 5). Furthermore, for most investigated gases, $C(T)$ is known only in a limited temperature range, because the classical p–V–T methods of measurement have seldom been used in the undercritical temperature

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range $T < T_c$ at low pressures p, where V is the gas volume and T_c is the critical temperature. In addition, only some values of $C(T) < 0$ are known up to now. However, absolute measurements of the refractive index n as function of the molar perfect-gas density $\rho_0 \equiv p/RT$ by optical interferometry may be used with success in this temperature range, where R is the molar gas constant. This method [6], as well as the apparatus used [7], has already been described. Reliable second virial coefficients $B(T)$ have also been communicated [8]. In this paper we present third virial coefficients $C(T)$ for the first time, which have been determined by this method, too [9]. In addition, the accompanying values of mean dipole polarizabilities α_0 of the isolated molecules and second virial coefficients $B(T)$ of the investigated gases C_2H_4, C_2H_6, and SF_6 are reported.

2. EXPERIMENTS AND THEIR EVALUATION

The purity of the gases was stated to be 99.9% (SF_6), 99.99% (C_2H_4), and 99.995% (C_2H_6). The refractivity $[n(\lambda_0)-1]_p^T$ of these gases was absolutely measured with the aid of an evacuated Michelson interferometer for wavelength $\lambda_0 = 632.99$ nm (He–Ne laser). The investigated overall ranges of temperature T and pressure p were $250\ \mathrm{K} \leqslant T \leqslant 340\ \mathrm{K}$ and $0 \leqslant p \leqslant p_{\max} \leqslant 3\ \mathrm{MPa}$, respectively. The refractivity of each gas was measured isothermally for several temperatures T_i by pumping the gas in K pressure steps Δp_k very slowly completely out of the sample cell ($k = K$, $K-1, \ldots, 2, 1$, with $12 \leqslant K \leqslant 35$, the value of K depending on the maximum pressure $p_{\max}$ used). Each pressure step Δp_k corresponds to a difference Δn_k of the refractive index n:

$$\Delta n_k \equiv n_k - n_{k-1} = \lambda_0(\Delta N_k/l) \tag{1}$$

$\Delta N_k \equiv N_k - N_{k-1}$ is the change of interference fringe number (order of interference) N and can be determined directly from the interferogram registered. The quantity l is the effective length of the sample cell, which was constructed from stainless steel [$l(296.28\ \mathrm{K}) = 42.592(14)$ cm, linear thermal expansion coefficient $\gamma = 1.65 \times 10^{-5}\ \mathrm{K}^{-1}$; further details are given in Ref. 9]. Prior to the beginning of the next pressure step Δp_k, the gas was allowed to reach thermal equilibrium, and the accompanying equilibrium values p_k and T_k were measured with the precision of $|\Delta p| = 1.8 \times 10^{-4} p^*_{\max}$ and $|\Delta T| = 10$ mK. This value of ΔT is given by the uncertainty of the definition of the temperature scale. $p^*_{\max} = 3.5$ MPa is the maximum allowed pressure for the pressure transducer used. Therefore, the uncertainty of pressure measurements at low gas densities limits the accuracy of measured polarizabilities and virial coefficients (see below and Section 4.1).

According to Eq. (1), absolute values of N_k and n_k can be calculated successively ($k = 1, 2,..., K$) after the sample cell is completely evacuated ($N_0 = 0$ and $n_0 = 1$ for this reference state). The measured K data points (n_k, T_k, p_k) of each isotherm were fitted to polynomials represented by Eq. (2) of order ($m - 1$) by using a Gaussian least-squares fit:

$$LL^* \equiv \frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho_0} = \sum_{i=1}^{m} A_i \rho_0^{i-1} \tag{2}$$

where $\rho_0 \equiv p/RT$ is the molar density and LL^* is the Lorentz–Lorenz function of the corresponding perfect gas. $R = 8.31432\ \text{m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was used. The working equation (2) approximates the corresponding infinite series ($m = \infty$), which results from a combination of the virial expansions of the equation of state and the Lorentz–Lorenz function of the gas of molar density ρ [6]. At first, all K data together were fitted to Eq. (2), in order to determine the optimum value of m. For most isotherms $m = 4$ was sufficient. However, it was observed that the values of the coefficients A_i change with m in this kind of evaluation. Therefore, in order to obtain reliable and stable coefficients A_i, these were finally determined successively by linear regression of selected data sets according to Eqs. (3) and (4), beginning with $i = 1$:

$$y_i = A_i + b_i \rho_0 \tag{3}$$

with the abbreviation

$$y_i = \begin{cases} LL^*, & i = 1 \\ (y_{i-1} - A_{i-1})\, \rho_0^{-1}, & i > 1 \end{cases} \tag{4}$$

Again, a Gaussian least-squares fit was used in Eq. (3). In general, more than three of the K measured data points $(\rho_0, LL^*)_k$ could be used in Eq. (3) for each i, but each point only one time (e.g., points $k = 1$ to 4 to get A_1, points $k = 5$ to 10 to get A_2, etc.). The number of points used was given by the best-fit Eq. (3) of minimum standard deviation (see e.g., Ref. 10). By using weighting factors $w_k = 1$ and $w_k = p_k$, the unweighted and weighted sum of squares $\sum_k w_k (y_i - A_i - b_i \rho_0)_k^2$ was minimized for comparison (in Ref. 9, only unweighted fits were performed). $w_k = p_k$ was chosen, because the most important inaccuracy is the pressure measurement as mentioned above.

It should be noted that the residual and recursion procedure, given by Eqs. (3) and (4), is in accordance with the corresponding procedure, by which the virial coefficients have been defined [1]. It is worthwhile noting also that other scientists have obviously had the same difficulties in obtaining reliable and stable polynomial and virial coefficients (e.g., Refs. 11 and 12).

The coefficients A_i of the working equation (2) are related to the polarizability and virial coefficients in the following manner [6, 9]:

$$A_1 = 4\pi N_A \alpha_0(\lambda_0, T)/3 \tag{5}$$

$$A_2/A_1 \equiv B^* = b_R(\lambda_0, T) - B(T) \tag{6}$$

$$A_3/A_1 \equiv C^* = [c_R(\lambda_0, T) - C(T)] - 2B(T)\,B^*(\lambda_0, T) \tag{7}$$

$$\begin{aligned} A_4/A_1 \equiv D^* = {} & [d_R(\lambda_0, T) - D(T)] + 5B^2(T)\,B^*(\lambda_0, T) \\ & - 3B(T)[c_R(\lambda_0, T) - C(T)] - 2C(T)\,B^*(\lambda_0, T) \end{aligned} \tag{8}$$

$N_A = 6.022045 \times 10^{23}\ \text{mol}^{-1}$ is Avogadro's constant. α_0 is the mean volume dipole polarizability of an isolated molecule. B, C, D, etc., are the virial coefficients of the virial equation of state of the gas. b_R, c_R, d_R, etc., are the corresponding coefficients of the virial expansion of the Lorentz–Lorenz function $LL \equiv (n^2-1)/(n^2+2)\rho$ (the so-called optical or refractive index virial coefficients; ρ is the molar gas density). b_R was estimated by the relation [6]

$$b_R(\lambda_0, T) = A_1/4 \tag{9}$$

Comparison of this estimate with second dielectric virial coefficients and measured b_R values shows a good accordance [9] (the deviation is less than $1\ \text{cm}^3 \cdot \text{mol}^{-1}$). c_R is known only for C_2H_6 ($c_R(283\ \text{K}) = -148(5)\ \text{cm}^6 \cdot \text{mol}^{-2}$ [13], $c_R(0\,^\circ\text{C}, \ldots, 80\,^\circ\text{C}) = -139(36)\ \text{cm}^6 \cdot \text{mol}^{-2}$ [14]), but third dielectric virial coefficients $c_\varepsilon = C_\varepsilon/A_\varepsilon$ at 300 K are of the order of $-320\ \text{cm}^6 \cdot \text{mol}^{-2}$ (C_2H_4 [15]) and $-400\ \text{cm}^6 \cdot \text{mol}^{-2}$ (SF_6 [16, 17]), respectively. Because the uncertainty of the measured $C(T)$ values is in general greater, the following approximation was finally used:

$$c_R(\lambda_0, T) = 0 \tag{10}$$

The desired coefficients α_0, B, and C and their uncertainties are then estimated by

$$\begin{aligned} \alpha_0 &= 3A_1/4\pi N_A \\ \Delta\alpha_0 &= 3\Delta A_1/4\pi N_A \end{aligned} \tag{11}$$

$$\begin{aligned} B &= b_R - B^* \approx A_1/4 - A_2/A_1 \\ \Delta B &\approx \Delta A_2/A_1 \end{aligned} \tag{12}$$

$$\begin{aligned} C &= c_R - [C^* + 2BB^*] \approx -[A_3/A_1 + 2(A_1/4 - A_2/A_1)(A_2/A_1)] \\ \Delta C &\approx \Delta A_3/A_1 \end{aligned} \tag{13}$$

3. RESULTS

As an example, the measured isotherms $LL^*(\rho_0)$ of C_2H_6 are shown in Fig. 1. Such isotherms were fitted to the working equation (2) by using Eqs. (3) and (4) for the determination of the coefficients A_1 to A_4 [$m = 4$ and sometimes $m = 3$ were sufficient in Eq. (2)]. These coefficients A_i are collected in Table I. As usual, standard deviations ΔA_i of the corresponding last figures are given in parentheses. From these values of A_1 (ΔA_1), A_2 (ΔA_2), and A_3 (ΔA_3), the interesting properties α_0 ($\Delta\alpha_0$), B (ΔB), and C (ΔC) in the last three columns in Table I have been calculated according to Eqs. (11), (12), and (13). The coefficient A_4 was used only for taking the rest of the infinite virial expansion into account. The maximum pressure $p_{\max}$ and the number K of pressure steps Δp_k of each isotherm are given in columns 2 and 3. For comparison, the unweighted (uw) and weighted (w) results are listed for each gas.

In general, one observes quite good agreement of corresponding data, although the uncertainties of the unweighted data are always up to 10 times larger. However, in the case of low-temperature $C(T)$ values, the reversal of the sign is remarkable [$C(T)$ has been calculated as the difference of two large numbers; see Section 4.3].

With the coefficients A_i given in Table I, the measured isotherms $LL^*(\rho_0)$ could be recalculated with a mean standard deviation $\Delta LL^*/LL^*$ of about 3×10^{-3} in the whole pressure range. This is only slightly more

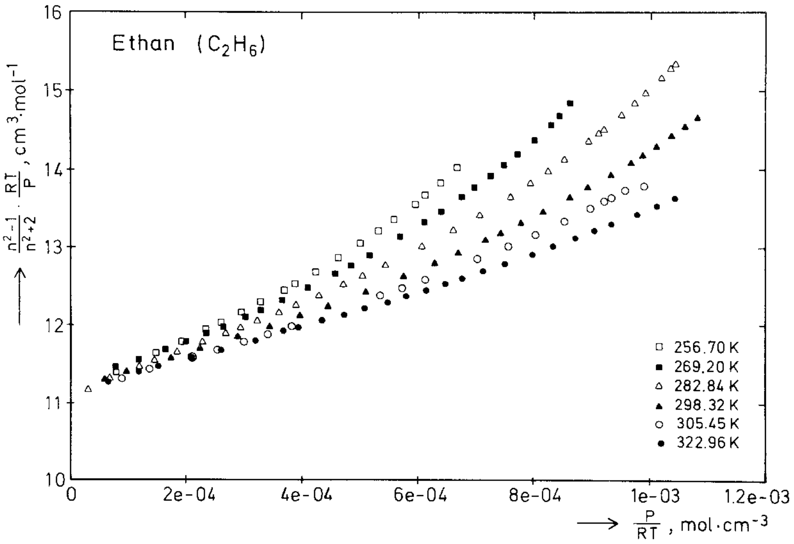

Fig. 1. Measured isotherms $LL^*(\rho_0)$ of C_2H_6.

Table I. Coefficients A_1 to A_4 of Unweighted (uw) and

T (K)	p_{max} (10^5 Pa)	K		A_1 ($cm^3 \cdot mol^{-1}$)	A_2 ($cm^6 \cdot mol^{-2}$)
C_2H_4					
256.97 (9)	20.27	26	w	10.6177 (12)	2,181.2 (4.6)
			uw	10.617 (5)	2,228 (28)
268.87 (1)	27.45	28	w	10.5301 (11)	1,987.9 (4.6)
			uw	10.529 (10)	2,003 (42)
282.60 (1)	26.98	21	w	10.5687 (10)	1,673.1 (8.5)
			uw	10.569 (12)	1,643 (32)
298.32[a] (1)	29.56	35	w	10.7576 (12)	1,531.3 (3.8)
			uw	10.753 (2)	1,558 (14)
318.04 (1)	25.21	18	w	10.5497 (17)	1,327.6 (6.1)
			uw	10.568 (9)	1,329 (28)
C_2H_6					
256.71 (14)	14.31	19	w	11.1155 (24)	2,905.7 (10.4)
			uw	11.116 (6)	2,090 (67)
269.19 (1)	19.39	26	w	11.2278 (44)	2,433.8 (3.1)
			uw	11.235 (14)	2,440 (17)
282.84 (1)	24.64	32	w	11.1944 (52)	2,255.7 (3.0)
			uw	11.201 (10)	2,282 (67)
298.35 (1)	19.00	30	w	11.1599 (34)	2,089.2 (3.4)
			uw	11.172 (11)	2,058 (23)
298.32 (1)	26.88	27	w	11.1633 (16)	2,089.7 (3.3)
			uw	11.158 (10)	2,088 (22)
305.45 (1)	25.14	20	w	11.1263 (36)	2,002.5 (2.4)
			uw	11.122 (12)	2,001 (33)
322.96 (1)	27.90	27	w	11.1260 (17)	1,757.1 (1.3)
			uw	11.136 (1)	1,760 (11)
SF_6					
257.42 (13)	7.94	12	w	10.9346 (32)	4,195.0 (7.6)
			uw	10.937 (7)	4,252 (87)
268.86 (1)	10.95	14	w	11.0101 (49)	3,877.1 (14.9)
			uw	11.018 (3)	3,809 (110)
282.61 (1)	15.11	18	w	10.9760 (10)	3,332.8 (5.7)
			uw	10.983 (3)	3,369 (33)
298.31 (1)	22.44	20	w	11.0463 (20)	3,192.6 (20)
			uw	11.028 (11)	3,272 (44)
298.32[a] (1)	17.19	13	w	10.9680 (22)	3,230.1 (11.0)
			uw	10.970 (8)	3,255 (54)
318.04 (1)	23.47	28	w	11.0089 (27)	2,606.0 (5.0)
			uw	11.009 (8)	2,584 (11)
337.73 (1)	20.85	20	w	10.8477 (76)	2,282.9 (7.1)
			uw	10.950 (40)	2,220 (219)

[a] $\lambda_0 = 546.22$ nm.

Weighted (w) Isotherms in Eq. (2) and the Quantities α_0, B, and C

A_3 ($cm^9 \cdot mol^{-3}$)	$10^{-8} A_4$ ($cm^{12} \cdot mol^{-4}$)	$10^{24} \alpha_0$ (cm^3)	$-B$ ($cm^3 \cdot mol^{-1}$)	C ($cm^6 \cdot mol^{-2}$)
924,239 (7,498)	−7.624 (51	4.20918 (48)	202.8 (4)	−3,734 (706)
871,125 (48,307)	−6.39 (49)	4.2089 (20)	207.2 (2.6)	4,912 (4,550)
669,556 (6,271)	−3.6412 (54)	4.17446 (44)	186.2 (4)	6,661 (596)
665,433 (53,171)	−3.542 (53)	4.1740 (40)	187.6 (4.0)	8,178 (5,050)
389,285 (738)	2.2011 (92)	4.18976 (40)	155.7 (8)	12,452 (70)
384,373 (6,130)	1.189 (53)	4.1899 (48)	152.8 (3.0)	11,143 (580)
335,053 (4,372)	−0.4821 (24)	4.26464 (48)	139.7 (4)	8,613 (406)
340,472 (11,613)	−0.490 (22)	4.2628 (8)	142.2 (1.3)	9,544 (1,080)
238,632 (4,914)	—	4.18223 (67)	123.2 (6)	8,389 (466)
236,427 (21,136)	—	4.1895 (36)	123.1 (2.6)	8,593 (2,000)
1,547,953 (24,609)	7.81 (25)	4.40653 (95)	258.6 (9)	−4,044 (2,214)
1,441,750 (127,834)	7.77 (3.26)	4.4067 (24)	259 (6)	5,813 (11,500)
961,776 (5,135)	3.95 (14)	4.4510 (17)	214.0 (3)	7,097 (457)
966,659 (40,671)	4.03 (1.21)	4.4539 (56)	214 (2)	7,073 (3,620)
794,701 (3,104)	6.821 (44)	4.4378 (21)	198.7 (3)	9,088 (277)
801,544 (24,082)	6.71 (35)	4.4404 (40)	201 (6)	10,312 (2,150)
634,621 (1,620)	2.929 (25)	4.4241 (13)	184.4 (3)	12,181 (145)
618,705 (12,513)	2.92 (20)	4.4289 (44)	181 (2)	11,458 (1,120)
632,889 (2,315)	1.119 (20)	4.42548 (63)	184.4 (3)	12,344 (207)
632,335 (21,423)	1.11 (20)	4.4234 (40)	184 (2)	12,321 (1,920)
563,066 (4,738)	3.280 (27)	4.4108 (14)	177.2 (2)	13,177 (426)
569,780 (30,585)	3.66 (86)	4.4091 (48)	177 (3)	12,507 (2,750)
462,787 (3,090)	1.259 (31)	4.41069 (67)	155.1 (1)	7,408 (278)
464,183 (14,375)	1.24 (31)	4.4147 (4)	155.3 (1.0)	7,394 (1,291)
3,598,763 (26,016)	—	4.3348 (13)	380.9 (7)	−36,848 (2,379)
3,204,540 (164,050)	—	4.3358 (28)	386 (8)	7,162 (15,000)
2,847,965 (42,434)	—	4.3647 (19)	349.4 (1.4)	−12,601 (3,854)
2,475,740 (60,600)	—	4.3679 (12)	343 (10)	12,423 (5,500)
1,843,677 (19,596)	−15.655 (76)	4.35122 (40)	300.9 (5)	14,760 (1,785)
1,832,010 (96,650)	−15.59 (54)	4.3540 (12)	304 (3)	19,699 (8,800)
1,509,565 (16,579)	−12.14 (57)	4.37909 (79)	286.3 (1.8)	28,811 (1,500)
1,562,910 (90,430)	−12.13 (51)	4.3718 (44)	294 (4)	32,703 (8,200)
1,515,998 (10,682)	−28.933 (66)	4.34805 (87)	291.8 (1.0)	33,628 (974)
1,534,400 (77,340)	−28.86 (3.30)	4.3488 (32)	294 (5)	34,584 (7,050)
810,247 (9,878)	6.042 (71)	4.3643 (11)	234.0 (5)	37,168 (897)
808,589 (44,040)	6.04 (1.81)	4.3643 (32)	232 (1)	35,444 (4,000)
686,391 (132,017)	—	4.3004 (30)	207.7 (7)	24,169 (12,170)
619,770 (273,750)	—	4.3409 (159)	200 (20)	24,497 (25,000)

inaccurate than the free polynomial fit given by Eq. (2) of the same order m of all data together. As mentioned above, this uncertainty is induced mainly by the pressure measurement.

4. DISCUSSION

4.1. Mean Polarizabilities α_0

Previously, an increase of $\alpha_0(T)$ or $A_1(T)$ with increasing temperature T was observed by us for some gases (e.g., Refs. 8 and 18). This result cannot be confirmed clearly by the data in Table I. The reason for this is obviously the limited accuracy of the pressure transducer in the low-pressure range (see Section 2), which leads to the observed scatter in the values of A_1 and α_0. On account of the used recursion and residual procedure, defined by Eqs. (3) and (4), this uncertainty is propagated to the determination of $B(T)$ and $C(T)$, too. Therefore, in order to get even more reliable results of α_0, B, and C, the pressure measurements have to be improved in the future. By doing this and enlarging the pressure range, it should be possible to get even higher virial coefficients of good quality with the aid of the optical method used.

In Table I, citation of footnote *a* indicates two measurements at wavelength $\lambda_0 = 546.226$ nm (green Hg spectral line). It is interesting to note the obvious anomalous dispersion of $\alpha_0(\lambda_0)$ of SF_6 in the visible wavenumber region. This can be clearly seen, because the values of α_0 and A_1 are smaller than the comparable data at $\lambda_0 = 633.0$ nm. The reality of this effect may be demonstrated by the even higher first dielectric virial coefficient A_ε (323 K) = 16.478 $\text{cm}^3 \cdot \text{mol}^{-1}$ [17], although a normal dispersion of $\alpha_0(\lambda_0)$ or $n(\lambda_0)$ of SF_6 in the visible was observed previously, too [19]. The anomalous dispersion of SF_6 has been discussed for a long time (e.g., Refs. 20 and 21) and is attributed to a large atomic contribution to the polarizability of SF_6 at flow frequencies.

The averages of A_1 (633 nm) in $\text{cm}^3 \cdot \text{mol}^{-1}$ in Table I may be compared with results from the literature:

C_2H_4—10.567 (38) (w), 10.571 (95) (uw), 10.610 (9) [22];
C_2H_6—11.159 (41) (w), 11.163 (43) (uw), 11.26 [3]; and
SF_6—10.995 (42) (w), 10.995 (36) (uw), 11.348 (21) [24].

In the case of SF_6 the obvious bad value 10.8477 in Table I at 337 K was not considered. The cited literature values are somewhat (0.02 to 0.06) smaller than the values calculated from older refractive index dispersion relations [19]. Our A_1 values are still smaller. The reason for the pronounced deviation in the case of SF_6 is not yet clear. However, this deviation cannot be attributed only to the stated impurity of 0.1 % (see Section 2).

4.2. Second Virial Coefficients $B(T)$

In the literature [5] smoothed mean values of $B(T)$ have been recommended for C_2H_4, C_2H_6, and SF_6. With respect to the observed scatter of the original literature data around the smoothed values, the agreement of the $B(T)$ values in Table I with these values can be stated to be quite good.

4.3. Third Virial Coefficients $C(T)$

The last column in Table I shows that the uncertainty ΔC of the measured $C(T)$ data is sometimes large. However, this is not amazing, because ΔC was estimated to be essentially given by $\Delta C = \Delta A_3/A_1 \approx \Delta C^*$ according to Eq. (13). Using Eq. (13), $C(T) = -[C^* + 2BB^*]$ was calculated as the difference of two large numbers ($C^* > 0$, $2BB^* < 0$, $c_R = 0$), and that explains the magnitude of $\Delta C/C$. Nevertheless, on account of the good reproducibility of the $C(298\text{ K})$ data of C_2H_6 and SF_6, we believe that the measurements, as well as the mathematical procedure used in evaluating these measurements, have given reliable $C(T)$ data. This conclusion is confirmed by the following discussion, in which only the weighted (w) $C(T)$ data in Table I are considered.

In Figs 2, 3, and 4 the weighted (w) $C(T)$ data in Table I are compared with most of the available data from the literature [5]. The drawn curves have been calculated by fitting our data together with some selected values from the literature [5] to the following empirical relation:

$$C(T) = a(T - T_0)\exp[-b(T - T_0)] \tag{14}$$

This simple function was chosen because it looks like the theoretically expected shape of $C(T)$ [e.g., by assuming a Lennard–Jones (12–6) pair interaction potential; see p. 13 of Ref. 1]. a, b, and T_0 are fitting parameters. T_0 is the zero-point temperature, defined by $C(T_0) = 0$. The maximum of Eq. (14) is given by $T_M = T_0 + 1/b$, $C(T_M) = (a/b)\exp(-1)$, and the inflection point by $T_w = T_0 + 2/b$, $C(T_w) = (2a/b)\exp(-2)$. The results of these fits [Eq. (14)] are summarized in Table II, where K is the number of points (T, C) used, and ΔC is the standard deviation of the measured from the calculated values of $C(T)$. The weighted (w) $C(T)$ data in Table I have been fitted to Eq. (14) together with the following literature values of $C(T)$ in $\text{cm}^6 \cdot \text{mol}^{-2}$:

SF_6—35,034 (333.18 K) from Ref. 11;

C_2H_6—9430 (323.15 K), 7920 (348.15 K), and 6240 (373.15 K) from Refs. 5 and 25; and

C_2H_4—9790 (298.15 K), 7050 (323.15 K), and 5980 (348.15 K) from Refs. 5 and 12 and 10,337 (271.80 K), 11,023 (283.33 K), and 9439 (293.34 K) from Refs. 5 and 26.

Although Eq. (14) was empirically chosen, the standard deviation ΔC in Table II indicates quite good fitting. In the middle of Table II some characteristic temperatures and their reduced values $T_r \equiv T/T_c$ have been collected (T_c is the critical temperature). The corresponding third virial coefficients and their reduced values have been listed is the lower part of Table II (V_c is the critical volume).

Looking at Figs. 2, 3, and 4, one can observe that some $C(T)$ measurements show only a weak dependence of $C(T)$ on temperature T

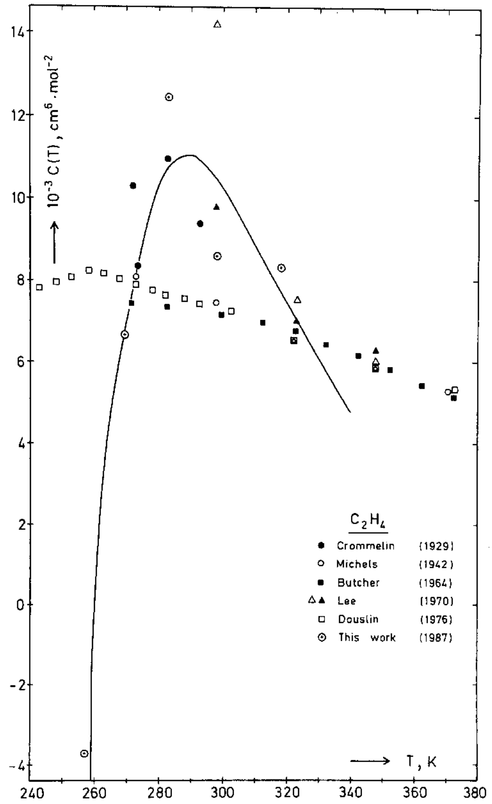

Fig. 2. Third virial coefficient $C(T)$ of C_2H_4.

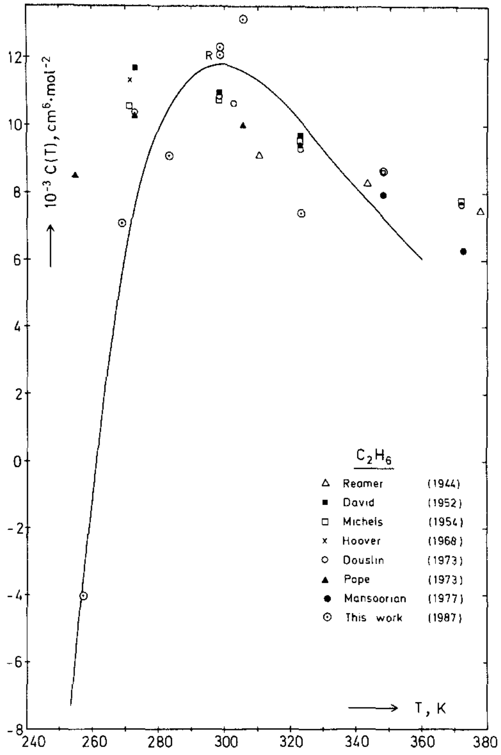

Fig. 3. Third virial coefficient $C(T)$ of C_2H_6.

without a marked maximum. On the other hand, theory (e.g., Refs. 1 and 27), as well as other measurements, including those in this work, indicates a strong dependence of $C(T)$ on T, with a marked maximum and only seldomly observed negative values of C. Assuming our results to be correct, two remarks conclude this discussion.

The first remark concerns the characteristic temperatures of Eq. (14) given in Table II. In general, quite good agreement of the corresponding reduced temperatures can be observed. Of particular interest is the position of the maximum at $T_M/T_c \approx 1.0$. Looking at the literature [5] one finds maxima of $C(T)$ in the vicinity of T_c for other substances, too. However, other scientists have not always measured $C(T_c)$ directly, as was tried in this work (see Table I). Therefore, we suppose that T_M might coincide quite generally with T_c.

The second remark results from this similar behavior of $C(T)$ of several substances in reduced representation and concerns a possible connection between C and the vapor pressure p_v. The reduced vapor

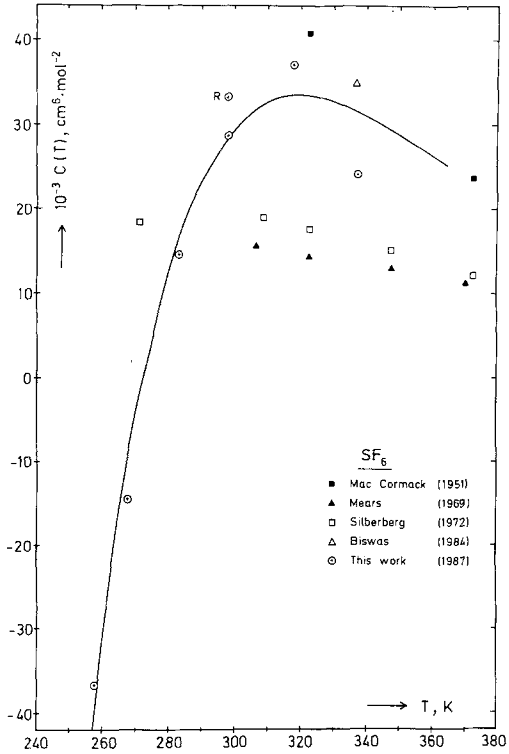

Fig. 4. Third virial coefficient $C(T)$ of SF_6.

pressure $p_r = p_v/p_c$ (p_c is the critical pressure) can be represented by the following Clausius–Clapeyron equation [28]:

$$\psi \equiv \frac{\Delta H_v}{RT_c \Delta Z_v} = -\frac{d \ln p_r}{d(1/T_r)} \tag{15}$$

ΔH_v is the molar enthalpy of vaporization and $\Delta Z_v = p_v(V_v - V_l)/RT$ is the difference of the compressibility factors of saturated vapor of volume V_v and saturated liquid of volume V_l. Differentiation of Eq. (15) yields

$$\frac{d\psi}{dT_r} = \frac{d\psi}{d(1/T_r)} \cdot \frac{d(1/T_r)}{dT_r} = \frac{1}{T_r^2} \frac{d^2 \ln p_r}{d(1/T_r)^2} \tag{16}$$

It is very interesting that available accurate vapor pressure data of different substances seem to show the following similar behavior, if ψ is drawn versus T_r (see p. 201 in Ref. 28): ψ is always positive and has a minimum at about $T_r \approx 0.85$ and derivatives $(d\psi/dT_r) < 0$ if $T_r < 0.85$ and $(d\psi/dT_r) > 0$ if

Table II. Characteristic Properties Derived from Eq. (14)

Property	C_2H_4	C_2H_6	SF_6
K	11	10	8
$a\ (\mathrm{cm^6 \cdot mol^{-2} \cdot K^{-1}})$	1,098.38	854.37	1,941.15
$10^2 b\ (\mathrm{K^{-1}})$	3.626	2.662	2.126
T_0 (K)	259.69	260.53	272.34
$\pm \Delta C\ (\mathrm{cm^6 \cdot mol^{-2}})$	1,285	1,372	4,391
T_c (K)	282.65	305.42	318.69
T_M (K)	287.27	298.10	319.38
T_w (K)	314.85	335.66	366.41
T_0/T_c	0.919	0.853	0.855
T_M/T_c	1.016	0.976	1.002
T_w/T_c	1.114	1.099	1.150
$V_c\ (\mathrm{cm^3 \cdot mol^{-1}})$	128.7	146.3	198.4
$C(T_M)\ (\mathrm{cm^6 \cdot mol^{-2}})$	11,144	11,807	33,589
$C(T_w)\ (\mathrm{cm^6 \cdot mol^{-2}})$	8,199	8,687	24,714
$C(T_M)/V_c^2$	0.673	0.552	0.853
$C(T_w)/V_c^2$	0.495	0.406	0.628

$T_r > 0.85$. On account of Eq. (15) this means a slightly S-shaped vapor pressure curve $\ln p_r$ versus $1/T_r$, with an inflection point at $T_r \approx 0.85$. Because this vapor pressure curve ends up at $T_r = 1.0$ (critical point), one may suppose the following qualitative connection between vapor pressure p_v and third virial coefficient $C(T)$:

$$\begin{array}{lll} T_r < 0.85: & d\psi/dT_r < 0, & C(T_r) < 0 \\ T_r \approx 0.85: & d\psi/dT_r = 0, & C(T_r) = 0 \\ T_r > 0.85: & d\psi/dT_r > 0, & C(T_r) > 0 \\ T_r = 1.0: & d\psi/dT_r = \max, & C(T_r) = \max(C) \end{array}$$

It should be noted that any quantitative relation between $C(T)$ and p_v does obviously not exist at present. However, we have fitted the vapor pressure data of C_2H_6 [29] and SF_6 [30] by a simple polynomial of third order in T_r and find a fair agreement between the inflection-point temperature T_{pw} of the vapor pressure curve and the zero-point temperature T_0 of $C(T)$ in Table II:

$$C_2H_6 — T_{pw} = 253.0\ \mathrm{K},\ T_0 = 260.53\ \mathrm{K};\ \text{and}$$
$$SF_6 — T_{pw} = 261.4\ \mathrm{K},\ T_0 = 272.34\ \mathrm{K}.$$

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